



ugr

**Universidad
de Granada**

DOCTORAL THESIS

**UTILIZATION OF ENERGY FROM RESIDUAL BIOMASS OF
RICE STRAW IN EGYPT**

**APROVECHAMIENTO ENERGÉTICO DE LA BIOMASA
RESIDUAL PROCEDENTE DE LA PAJA DE ARROZ EN EGIPTO**

Presented by

Noha Said El hadi

Área de Tecnologías del Medio Ambiente (Departamento de Ingeniería Civil)

Programa Oficial de Doctorado en Ingeniería Civil y Arquitectura (D19.56.1)

Universidad de Granada

Granada, 2015

Editor: Universidad de Granada. Tesis Doctorales

Autora: Noha Said Elhadi

ISBN: 978-84-9125-532-1

URI: <http://hdl.handle.net/10481/42604>

**APROVECHAMIENTO ENERGÉTICO DE LA BIOMASA
RESIDUAL PROCEDENTE DE LA PAJA DE ARROZ EN EGIPTO**

Por

Noha Said El hadi

Memoria presentada para aspirar al grado de Doctor
con mención internacional por la Universidad de
Granada

Fdo.: Noha Said El hadi

Los Directores de la Tesis:

Dr. Montserrat Zamorano Toro
Catedrática de Universidad
Área de Tecnologías del Medio Ambiente
Departamento de Ingeniería Civil
Universidad de Granada

Dr. Ángela García-Maraver
Investigadora Contratada Doctora
Área de Tecnologías del Medio Ambiente
Departamento de Ingeniería Civil
Universidad de Granada

Montserrat Zamorano Toro, Doctor Ingeniero de Caminos, Canales y Puertos Catedrática de Universidad del Departamento de Ingeniería Civil, de la ETS de Ingeniería de Caminos, Canales y Puertos de la Universidad de Granada y **Ángela García-Maraver**, Doctora en Ingeniería Química e Investigadora Contratada Doctora del Departamento de Ingeniería Civil, de la ETS de Ingeniería de Caminos, Canales y Puertos de la Universidad de Granada

CERTIFICAN QUE,

Noha Said El hadi, titulado en Ingeniería Civil, ha realizado la Tesis Doctoral **APROVECHAMIENTO ENERGÉTICO DE LA BIOMASA RESIDUAL PROCEDENTE DE LA PAJA DE ARROZ EN EGIPTO** en el Departamento de Ingeniería Civil de la Escuela Técnica Superior de Ingeniería de Caminos, Canales y Puertos de la Universidad de Granada para aspirar al grado de Doctor, reuniendo las condiciones necesarias para ser presentada y defendida ante el tribunal correspondiente.

Y para que conste a los efectos oportunos, en cumplimiento de la legislación vigente, firmamos el presente certificado en Granada, a 19 de Marzo del 2015.

Fdo.: Montserrat Zamorano Toro
Catedrática de Universidad

Fdo.: Ángela García-Maraver
Investigadora Contratada Doctora

Memoria presentado por **Dña Noha Said El hadi** para optar al grado de doctor con mención internacional por la Universidad de Granada

Fdo.: Noha Said El hadi

COMPROMISO DE RESPETO DE DERECHOS DE AUTOR

El doctorando **Noha Said El Hadi** y los directores de la tesis **APROVECHAMIENTO ENERGÉTICO DE LA BIOMASA RESIDUAL PROCEDENTE DE LA PAJA DE ARROZ EN EGIPTO** garantizamos, al firmar esta tesis doctoral, que el trabajo ha sido realizado por el doctorando bajo la dirección de los directores de la tesis y hasta donde nuestro conocimiento alcanza, en la realización del trabajo, se han respetado los derechos de otros autores a ser citados, cuando se han utilizado sus resultados o publicaciones.

Granada 19 de marzo de 2015

Directores de la tesis

Fdo.: Montserrat Zamorano Toro
Catedrática de Universidad

Fdo.: Ángela García Maraver
Investigadora Contratada Doctora

Doctorando

Fdo.: Noha Said El Hadi

TÍTULO DE DOCTOR CON MENCIÓN INTERNACIONAL

Con el fin de obtener el Título de Doctor por la Universidad de Granada con Mención Internacional, que el Real Decreto 99/2011 establece en su artículo 15, se han cumplido los siguientes requisitos:

(i) Durante el periodo de formación necesario para la obtención del Título de Doctor, el doctorando realizó una estancia mínima de tres meses fuera de España en una institución de enseñanza superior o centro de investigación de prestigio, cursando estudios o realizando trabajos de investigación. La estancia podrá realizarse una vez admitida al programa de doctorado correspondiente y será incorporada al documento de actividades del doctorando o doctoranda

(ii) Parte de la tesis doctoral se ha redactado y presentado en una de las lenguas habituales para la comunicación científica en su campo de conocimiento, distinta a cualquiera de las lenguas oficiales en España.

(iii) La tesis ha sido informada por un mínimo de dos expertos doctores pertenecientes a alguna institución de educación superior o instituto de investigación no española.

(iv) Un experto perteneciente a alguna institución de educación superior o centro de investigación no española, con el título de doctor, y distinto del responsable de la estancia mencionada en el apartado (i), forma parte del tribunal evaluador de la tesis.

TESIS COMO AGRUPACIÓN DE PUBLICACIONES

La presente tesis doctoral se presenta como reagrupamiento de los trabajos de investigación publicados por el doctorando en medios científicos relevantes en su ámbito de conocimiento. Se han cumplido los siguientes requisitos:

(i) Se ha presentado un informe de los directores de la tesis respecto a la idoneidad de la presentación de la tesis bajo esta modalidad.

(ii) Dado que las publicaciones han sido realizadas por varios autores además del doctorando, se adjunta la declaración de los restantes autores de no haber presentado dicha publicación en otra tesis doctoral o la renuncia a hacerlo.

(iii) Los artículos que configuran la tesis doctoral están publicados o aceptados con fecha posterior a la obtención del título de grado y del máster universitario, no habiendo sido utilizados en ninguna tesis anterior y haciéndose mención a la Universidad de Granada a través de la afiliación del doctorando.

FINANCIACIÓN

El trabajo desarrollado en esta Tesis Doctoral ha sido financiado por los siguientes proyectos:

- (i) Proyecto de investigación de excelencia concedido por la Consejería de Innovación Ciencia y Empresa de la Junta de Andalucía con el título “Aplicación de la biomasa procedente de los residuos generados en actividades agrícolas en Andalucía para su producción de pellets y su uso en el ámbito energético (P08-RNM-03584)”. Entidades participantes: Universidad de Granada, Empresa Energía Oriental S.L. Duración: 01/01/2009 – 31/12/2013.
- (ii) Proyecto de investigación concedido por el Ministerio de Ciencia e innovación con el título “*Optimización de la producción y logística de pellets fabricados a partir de residuos agrícolas leñosos y su aplicación térmica doméstica e industrial (CTM2009- 071999; Subprograma TECNO)*”. Entidades participantes: Universidad de Granada. Duración: 01/01/2010 – 31/12/2012.
- (iii) Beca predoctoral de la Agencia Española de Cooperación Internacional para el Desarrollo (AECID) (*Proyecto AP/045946/11*). Duración: 15/11/2011 – 15/11/2014.

DIFUSIÓN DE RESULTADOS

Los trabajos descritos en la presente memoria se encuentran recogidos en las siguientes publicaciones y comunicaciones a congresos:

PUBLICACIONES INTERNACIONALES INCLUIDAS EN EL JCR

Noha Said, Mahmoud M. Abdel daiem, Angela García-Maraver, Montserrat Zamorano, 2014. Reduction of ash sintering precursor components in rice straw by water washing. *BioResources*; 9(4): 6756-6764. Impact Factor: 1.549 (Q1 Material Science, Paper & Wood)

Noha Said, Tania Bishara, Angela García-Maraver, Montserrat Zamorano, 2013. Effect of water washing on the thermal behaviour of rice straw. *Waste Management*; 33: 2250-2256. Impact Factor: 3.157 (Q1 Environmental Engineering)

Noha Said, Sahar A. El-Shatoury, Luis F. Díaz, Montserrat Zamorano, 2013. Quantitative appraisal of biomass resources and their energy potential in Egypt. *Renewable and Sustainable Energy Reviews*; 24: 84–91. Impact Factor: 5.510 (Q1 Energy & Fuels)

Noha Said, Mahmoud M. Abdel daiem, Angela García-Maraver, Montserrat Zamorano. Modelizing densification parameters of rice straw pellets and their effect on quality properties. Submitted to *Journal of Fuel Processing Technology* (Under review). Impact Factor: 3.196 (Q1 Chemical Engineering)

Noha Said, Sahar A. El-Shatoury, Hesham M. Abdulla, Montserrat Zamorano. Effect of pelleting on hydrolysis of rice straw by a consortium of lignocellulolytic *actinomycetes*. Submitted to Journal of Biomass and Bioenergy (Under review). Impact Factor: 3.411 (Q1 Energy & Fuels)

CONGRESOS INTERNACIONALES

Noha Said, Tania Bishara, Angela García-Maraver, Montserrat Zamorano, 2012. Thermal behaviour of rice straw, 4th International Symposium on Energy from Biomass and Waste. (Venice, Italy).

Noha Said, Montserrat Zamorano, Sahar A. El-Shatoury, 2012. Renewable energy potential from biomass residues in egypt, Conference & Exhibition on Biomass of Energy, World Bioenergy. (Jonkoping, Sweden).

DEDICATION

This dissertation is dedicated to my parents and family, and to the people who dedicate their lives to seek for the truth...

ACKNOWLEDGEMENTS

Praise be to ALLAH, the Cherisher and Sustainer of the world, who with his grace this work has been done...

This thesis would have not been possible without the support of my supervisors, colleagues, family and friends who in different ways encouraged me and shared this long way. To all of you, I express my grateful acknowledgment and sincerely thanks for bringing this thesis to a successful end.

With greatest appreciation, I acknowledge the friendship, support, insight and guidance of my supervisors: Prof. Montserrat Zamorano Toro, for providing scientific consultation advices in all phases of my work and especially for her personal support always believing in my capabilities, being present at all times and giving me the needed strength to carry on when difficulties appeared and encouraging me to study earnestly and for her greatly role inside and outside the work throughout my Ph.D. years and a lot of thanks to Dr. Ángela García-Maraver for her continuous assistance and constant hard work inspired me to reach to higher aim.

My sincere thanks to Dr. Sahar A. El shatoury for her support and valuable comments on both my thesis and future research career plans and her efforts in the hydrolysis of rice straw work. I would like to express my gratitude to Dr. Nabil Nagy Atta, head of Environmental Engineering Department, Zagazig University, Egypt for his dedication, valuable advices, for being present and helping me in every ways possible, for his fatherly role through the thesis period.

Acknowledgments are also owed to my friends in Granada who have been the best friends during my stay in Granada: Tania, Mariam, Mai, Dina, Hanan, Elena, Inma, Isa, Fatin, Shadia, Wafaa, and Marwa.

I dedicate this work to my father and mother, my sister Shimaa, and my brothers Mohamed and El hadi. Without their care and support from childhood to now, I would never have made it through this process or any of the tough times in my life.

Special thanks to my husband Mahmoud for helping me throughout my life, and making me believe that I am capable of doing everything. Special thanks to his patience and his extreme efforts to complete this work.

Very special thanks to ALLAH for his great gifts, my lovely daughters Mariam and Marwa, making me happy in the tough times.

Finally, I would like to thank everybody who was important to the successful realization of my thesis, as well as expressing my apology for every one that I unfortunately forgot to mention.



INDEX

<u>RESUMEN</u>	39
<u>ABSTRACT</u>	43
<u>CAPÍTULO 1. MOTIVACIÓN, JUSTIFICACIÓN Y OBJETIVOS</u>	49
<u>CHAPTER 1. MOTIVATION, JUSTIFICATION AND OBJECTIVES</u>	59
<u>CHAPTER 2. BACKGROUND</u>	67
1. WORLDWIDE ENERGY FRAMEWORK	69
1.1. Worldwide energy supply and consumption and Environmental effects	69
1.2. Energy framework: Kyoto Protocol	72
2. RENEWABLE ENERGY IN THE NEW ENERGY FRAMEWORK	76
3. ENERGY FROM BIOMASS	78
3.1. Biomass definition and classification	78
3.2. Biomass benefits and barriers	80
3.3. Biomass energy production technologies	84
3.3.1. Thermochemical processes	84
3.3.2. Bio-chemical processes	85
3.4. Global biomass potential and consumption	86
4. QUANTITATIVE APPRAISAL OF BIOMASS RESOURCES AND THEIR ENERGY POTENTIAL IN EGYPT	89
4.1. Geography and climate	89
4.2. Energy supply and consumption	89
4.3. Energy framework in Egypt	93
4.4. Renewable energy	96
4.4.1. Renewable energy resources	99
4.4.1.1. <i>Hydropower</i>	100
4.4.1.2. <i>Wind energy</i>	101
4.4.1.3. <i>Solar energy</i>	103
4.4.1.4. <i>Biomass energy</i>	105

4.5. Biomass resources in Egypt	105
4.5.1. Agricultural residues	105
4.5.2. Animal wastes	107
4.5.3. Sewage wastes	109
4.5.4. Municipal solid wastes	110
4.6. Theoretical energy potential from biomass in Egypt	111
4.6.1. Theoretical energy from agricultural crop residues	112
4.6.1.1. <i>The potential energy content</i>	112
4.6.1.2. <i>Potential energy of some residues in different forms</i>	115
4.6.2. Theoretical energy from animal waste	116
4.6.3. Theoretical energy from sewage sludge	117
4.6.4. Theoretical energy from municipal solid waste	118
4.6.4.1. <i>Theoretical energy from thermo-chemical conversion by incineration</i>	119
4.6.4.2. <i>Theoretical energy from bio-chemical conversion through anaerobic digestion</i>	119
4.6.5. Theoretical potential energy from biomass	120
4.7. Conclusions	121
<u>CHAPTER 3. THE CHARACTERIZATION OF RICE STRAW AS A RENEWABLE FUEL</u>	123
1. INTRODUCTION	125
2. MATERIAL AND METHODS	128
2.1. Sampling	128
2.2. Analytical procedures	128
2.2.1. Chemical characteristics of rice straw	128
2.2.2. Ash composition	129
2.2.3. ESEM inspection	129
2.2.4. TGA and DSC	130
2.2.5. Melting point, sintering and slagging tendencies	131
3. RESULTS AND DISCUSSION	131
3.1. Chemical characteristics of rice straw	131
3.2. Ash composition	133
3.3. ESEM inspection	134

3.4. TGA and DSC for the straw samples	136
3.5. Melting point, sintering and slagging tendencies	138
3.5.1. Ash melting point	138
3.5.2. Sintering and slagging tendencies	138
4. CONCLUSIONS	140
<u>CHAPTER 4. EFFECT OF WATER WASHING ON THE</u>	143
<u>CHARACTERISTICS OF RICE STRAW</u>	
1. INTRODUCTION	145
2. MATERIAL AND METHODS	146
3. RESULTS AND DISCUSSION	146
3.1. Straw and ash analysis	146
3.2. ESEM inspection	149
3.3. TGA/ DSC analysis	151
3.3.1. TGA/ DSC of straw samples	151
3.3.2. TGA/ DSC of ash samples	152
3.4. Sintering and slagging tendencies	154
4. CONCLUSIONS	155
<u>CHAPTER 5. QUALITY OF PELLETS PRODUCED FROM RICE</u>	157
<u>STRAW</u>	
1. INTRODUCTION	159
2. MATERIAL AND METHOD	161
2.1. Production process of pellets	161
2.1.1. Feeding material conditions	162
2.1.1.1. <i>Binder</i>	162
2.1.1.2. <i>Feeding material moisture</i>	162
2.1.2. Operating conditions	162
2.1.2.1. <i>Temperature</i>	163
2.1.2.2. <i>Size of dies</i>	163
2.2. Analysis of pellets	163
2.2.1. Moisture content of pellets	164

2.2.2. Pellet size	164
2.2.3. Pellet density	165
2.2.4. Bulk density	165
2.2.5. Hardness	165
2.2.6. Durability	165
2.3. Experimental design and data analysis	166
3. RESULTS AND DISCUSSION	168
3.1. Quality of pellet properties	169
3.1.1. Durability	169
3.1.2. Hardness	169
3.1.3. Bulk density	170
3.1.4. Pellet density	170
3.1.5. Moisture content of pellets	174
3.1.6. Pellet size	174
3.2. Effect of feeding and operation conditions on pellet properties	175
3.2.1. Durability	176
3.2.2. Hardness	182
3.2.3. Bulk density	182
3.2.4. Pellet density	183
3.2.5. Moisture content of pellets	183
3.2.6. Pellet size	184
3.3. The best conditions for producing high quality pellets	184
4. CONCLUSIONS	187
<u>CHAPTER 6. HYDROLYSIS OF RICE STRAW</u>	189
1. INTRODUCTION	191
2. MATERIAL AND METHODS	193
2.1. Rice straw and pellets sampling	193
2.2. Characterization of the actinomycete consortium	193
2.2.1. DNA extraction and phylogenetic analysis of the strains	193
2.2.2. Enzymatic activities of the consortium	194
2.2.3. Cellulose saccharification by SAC individuals	195

2.3. Hydrolysis of rice straw by SAC	195
2.3.1. Preparation of the consortium	195
2.3.2. Hydrolysis batch experiment	196
3. RESULTS AND DISCUSSIONS	197
3.1. Characterization of the SAC consortium	197
3.2. Efficiency of SAC in straw hydrolysis	199
3.3. Influence of pelleting on the hydrolysis process	202
3.4. Actual reducing sugar yield	202
4. CONCLUSIONS	205
<u>CONCLUSIONES</u>	207
<u>CONCLUSIONS</u>	213
<u>LÍNEAS FUTURAS DE INVESTIGACIÓN</u>	219
<u>FUTURE LINES OF RESEARCH</u>	223
<u>REFERENCES</u>	227
<u>PUBLICATIONS</u>	261

INDEX OF FIGURES

Figure 1. World total primary energy supply from 1971 to 2012 by fuel (Mtoe) (IEA, 2014).	70
Figure 2. World total final consumption from 1971 to 2012 by fuel (Mtoe) (IEA, 2014).	71
Figure 3. World CO ₂ emissions from 1971 to 2012 by fuel (Mt of CO ₂) (IEA, 2014).	71
Figure 4. Map of Egypt (EL-Shimy, 2009).	89
Figure 5. Primary energy resources production and consumption in Egypt (El Saeidy, 2004).	90
Figure 6. Sectorial consumption of primary energy in Egypt (El Saeidy, 2004)	91
Figure 7. Electrical energy production and consumption a), and imports and exports by year b) (IndexMundi, 2012).	92
Figure 8. Electrical energy consumption by sector in the year 2007 (Mahmoud, 2009).	92
Figure 9. Positioning of renewable energy technologies in Egypt (Khalil, 2007; Khalil et al., 2010).	100
Figure 10. Wind regime map for Egypt (wind atlas for Egypt).	103
Figure 11. Solar radiation intensity map for Egypt (solar atlas for Egypt).	104
Figure 12. ESEM inspection and spots chemical analysis for Egypt straw.	135
Figure 13. ESEM inspection for ash of Egypt straw sample.	136
Figure 14. TGA and DSC thermograms of the different straw samples.	137
Figure 15. DSC thermograms for the different straw ash samples.	138
Figure 16. Rice straw: a) before combustion; b) ash at 550 °C; and c) ash at 1000 °C.	139
Figure 17. ESEM inspection for washed Egypt straw.	150
Figure 18. ESEM inspection for ash of the washed sample.	150
Figure 19. TGA and DSC thermograms of washed (W) and unwashed (U) Egypt straw.	151
Figure 20. TGA and DSC for ash of washed (W) and unwashed (U) Egypt straw.	152

- Figure 21.** Ash photos of washed straw samples: a) at 550 °C; and b) at 1000 °C. 155
- Figure 22.** Pellets photos for the different dies a) D1, b) D2, and c) D3 at M3 and S2. 175
- Figure 23.** Variable effects on pellet properties a) durability, b) hardness, c) bulk density, d) pellet density, e) M_p and f) L_p/D_p ratio. 180
- Figure 24.** Relations between pellet properties a) durability/hardness, b) bulk density/pellet density, c) pellet density/hardness, d) durability/ M_p , e) pellet density/ M_p , f) bulk density/ M_p . 181
- Figure 25.** Phylogenetic tree of 16S rDNA sequences from the SAC and their most similar GenBank sequences. Only bootstrap values above 50% were displayed. 198
- Figure 26.** Total saccharification of pelleted (P) / shredded straw (S), samples 1 without starch (a) and samples 2 with starch addition (b), using SAC at different experimental settings compared to corresponding uninoculated control samples denoted by C. 201
- Figure 27.** Actual RS yield of pelleted and shredded straw during straw hydrolysis by the *actinomyce* consortium SAC. 203
- Figure 28.** Scanning electron micrograph of rice straw pellets after 7 days of the hydrolysis experiment. a) un-inoculated; b) inoculated with the SAC consortium. 204

INDEX OF TABLES

Table 1. Key meetings and events for negotiating a new agreement replacing the Kyoto Protocol (Prescott, 2013).	75
Table 2. Types of biomass feedstocks used for energy purposes (Tumuluru et al., 2011).	83
Table 3. Estimated GHG inventory in Egypt in million tons CO ₂ (EEAA, 2012).	94
Table 4. Potential share of local manufacturers of renewable energy equipment (Khalil, 2007).	98
Table 5. Estimated crop residue generation and utilization in Egypt during the year 2004 (GTZ, 2006).	106
Table 6. Major uses of crop residues in Egypt (GTZ, 2006).	107
Table 7. Total production of animal wastes in Egypt (El-Mashad et al., 2003; Hamdy, 1998).	108
Table 8. Typical composition of municipal solid wastes in Egyptian cities (Badran and El-Haggar, 2006; Bushra, 2000).	111
Table 9. Theoretical agricultural crop production, dry biomass, and potential energy in Egypt calculated according to estimated crop production in 2007.	114
Table 10. Ethanol production and its energy content from lignocellulosic biomass in Egypt.	116
Table 11. Theoretical potential energy from biomass residues in Egypt.	121
Table 12. Analysis data of different straw samples.	133
Table 13. Ash composition of the different straw samples (% ash).	134
Table 14. The variation in the parameters due to straw washing.	148
Table 15. Percentage of inorganic elements in ash and removal ratio due to washing.	149
Table 16. Parameters and guidelines published in UNE-EN ISO 17225-6 (2014), including specifications of non-woody pellets.	164
Table 17. Full factorial design of experiments.	167
Table 18. Pellet properties (response) according to design of experiments.	171

Table 19. Regression coefficients of the variables for durability, hardness, and bulk density of pellets produced.	178
Table 20. Regression coefficients of the variables for pellet density, M_p , and L_p/D_p of pellets produced.	179
Table 21. The best conditions for producing high quality pellets of rice straw.	186
Table 22. Feeding and operation conditions to produce pellet samples	193
Table 23. The 16S rDNA sequences of SAC isolates and the similar sequences from NCBI BLAST.	197
Table 24. Extracellular lignocellulytic enzymes activity and degree of cellulose saccharification (DCS) of individual strains of the <i>actinomycete</i> consortium SAC.	199



RESUMEN

RESUMEN

La utilización de la biomasa como fuente de energía renovable es muy importante desde el punto de vista energético y ambiental. Egipto produce una importante cantidad de biomasa a partir de residuos agrícolas, residuos sólidos municipales, desechos animales, y los lodos de depuradora, con un contenido total de energía teórico de 416.9×10^{15} J. La cantidad de biomasa seca producida a partir de los residuos agrícolas se ha estimado en 12.33 millones de toneladas/año, de las cuales el 63.75% se producen a partir del cultivo del arroz. En consecuencia, la paja de arroz podría ser considerada como un combustible renovable aplicable en la generación de calor y electricidad, lo que permitiría: (i) reducir la dependencia de Egipto de los combustibles fósiles; (ii) reducir las emisiones de CO₂ en el marco de las políticas de potenciación del uso de energías renovables puestas en marcha en el país; y (iii) reducir las emisiones generadas por la quema incontrolada de este residuo en el campo.

En relación del proceso de conversión térmica de la paja de arroz, el análisis termogravimétrico (TGA) y la calorimetría diferencial de barrido (DSC) han mostrado que el uso de esta biomasa podría ocasionar problemas operativos debido a la presencia de altos contenidos en potasio, cloro y silicio en la materia prima. Esta composición da lugar a una alta cantidad de ceniza con elevada tendencia a la sinterización y escorificación, lo que afectaría negativamente a los sistemas de conversión térmica. Para reducir estos problemas y mejorar su comportamiento de combustión, es necesario aplicar pretratamientos tales como el lavado con agua, que permitió obtener una reducción no solo de la cantidad de cenizas sino también de los compuestos inorgánicos relacionados con el riesgo de sinterización.

El uso de la paja de arroz para producir energía conlleva un elevado coste ligado a su manejo, almacenamiento y transporte, ya que la materia prima presenta una baja densidad aparente. El proceso de pelletización reduce estos problemas, ya que consiste en una densificación de materia que además permite aumentar la baja eficiencia térmica de la biomasa y proporcionar un tamaño homogéneo que facilite un tratamiento automático o semi-automático. En general, la calidad de los pellets depende de las propiedades de la materia prima y de las condiciones en las que se lleva a cabo el proceso de fabricación. Por lo tanto, para determinar las condiciones óptimas de operación que permiten la producción de pellets de paja de arroz con la mayor calidad, se ha procedido a densificar esta biomasa bajo diferentes condiciones en lo relativo a: (i) contenido de humedad de la materia prima (12, 15, y 17%); (ii) uso de almidón como aditivo en diferentes porcentajes (1% y 2 %); (iii) temperatura de densificación (menor y mayor de 50 °C); y (iv) uso de matrices planas con valores diferentes en cuanto a diámetro y longitudes de compresión (6/20, 6/24 y 8/32 valores en mm). La calidad de los pellets fabricados se determinó de acuerdo a la norma *UNE-EN ISO 17225-6:2014 sobre Biocombustibles sólidos. Especificaciones y clases de combustibles. Parte 6: Clases de pellets de origen no leñoso* desde el punto de vista de su durabilidad, dureza, contenido de humedad, dimensiones, densidad de pelet y densidad aparente. Los resultados han mostrado que el contenido de humedad del material de alimentación, el diámetro de la matriz, el porcentaje de uso de almidón como aditivo y la temperatura de funcionamiento son factores importantes para optimizar la calidad del pellet. La durabilidad del pellet y la densidad aparente fueron los parámetros que se vieron más afectados por las condiciones de producción.

Por otra parte, el uso de paja de arroz para producir biocombustibles líquidos (especialmente etanol) es una opción factible si se consiguen aplicar tecnologías de fermentación a bajo coste. En este sentido el proceso de densificación de la biomasa podría reducir los costes relacionados con la manipulación, almacenamiento y transporte, aunque también podría afectar al proceso de fermentación. Por ello se ha estudiado el efecto de la densificación de la paja de arroz en la hidrólisis y sacarificación como un paso preliminar para la producción de bioetanol, utilizando para ello el consorcio *Streptomyces* en la hidrólisis microbiana. Los resultados han mostrado que el consorcio aplicado es eficiente y tiene la capacidad de penetrar y desintegrar las capas interiores de la paja de arroz. Asimismo, la tasa de sacarificación alcanzó el 40% y se observó un incremento del 55% de la eficiencia de la sacarificación del consorcio *Streptomyces* en el caso del uso de pellets fabricados con aditivo de almidón.



ABSTRACT

ABSTRACT

The utilization of biomass as a renewable source of energy is important from the energetic as well as from the environmental point of view. Egypt produces a considerable amount of biomass from agricultural residues, municipal solid wastes, animal wastes, and sewage sludge, with a total theoretical energy content of 416.9×10^{15} J. The amount of dry biomass produced from agricultural crop residues is about 12.33 million tons/year, and 63.75% of this amount is produced from rice straw. In consequence, rice straw could be used as a renewable fuel for heat and power generation, contributing to: (i) the replacement of fossil fuels; (ii) the reduction of CO₂ emissions according to the renewable energy framework in Egypt; and (iii) the prevention of the pollution caused by open burning of straw.

In relation to the thermal conversion process of rice straw, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have showed that it could cause some operating problems such as those caused by the presence of high contents of potassium, chlorine and silicon in the raw material. This composition produces high quantity of ashes with important sintering and slagging tendencies that negatively affect to thermal conversion systems. In order to reduce these problems and improve the combustion behavior, samples of rice straw were washed with water as a pretreatment, which resulted in a reduction of undesirable inorganic compounds related to ash problems.

The use of rice straw as a fuel implies high costs associated with handling, storage and transportation because of the low value of its bulk density. Pelletisation process consists of a mass densification that reduces these problems, increases the traditionally low

thermal efficiency of biomass, and provides homogeneous size, which facilitates an automatic or semi-automatic treatment. In general, the quality of the pellets depends on the properties of the feedstock and quality management of the manufacturing process. Therefore, in order to determine the best conditions to produce high-quality pellets, the pelleting of rice straw was performed under different operating conditions related to: (i) the moisture content of feeding material (12, 15, and 17%); (ii) the use of starch as an additive with percentages of 1% and 2%; (iii) the operating temperature (<50°C and >50°C); and (iv) three flat dies with different diameter/compression length (6/20, 6/24 and 8/32 values in mm). The quality properties of the pellets manufactured such as durability, hardness, moisture content, dimensions, and pellet and bulk density were determined according to the norm *UNE-EN ISO 17225-6:2014 about Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets*. The results showed that the moisture content of the feeding material, the die hole size, the starch additive content, and the operating temperature, represented important factors for the improvement of pellet qualities in the majority of the cases. The pellet durability and bulk density were the most indicative parameters for pellet quality and were significantly affected by most of the different factors.

Finally, in relation to the use of rice straw to produce liquid biofuels (especially ethanol) it can be considered as a highly feasible option if there is access to proper low-cost conversion and fermentation technologies. In consequence, the pelleting process could reduce the costs related to handling, storage and transportation, but it could also affect the fermentation process. The effect of pelleting on hydrolysis and saccharification of rice straw as preliminary steps for bioethanol production was studied by using *Streptomyces* consortium in microbial hydrolysis. Results have showed that the

saccharification rate reached up to 40% and the *Streptomyces* consortium increased the efficiency of saccharification by 55% in the case of pellets with starch additive. Moreover, the applied consortium was efficient and had the ability of penetrating and disintegrating the interior layers of rice straw.



CAPÍTULO 1

MOTIVACIÓN, JUSTIFICACIÓN Y OBJETIVOS

La energía es esencial para el desarrollo económico de la sociedad, además de proporcionar una mejor calidad de vida. Su consumo ha variado a lo largo del tiempo, y depende, entre otros factores, del nivel económico, las condiciones climáticas y su coste (Bilgen et al., 2008).

El consumo general y masivo de combustibles fósiles ha traído consigo un rápido crecimiento económico en las sociedades industriales avanzadas, pero también ha puesto el incremento de emisiones de dióxido de carbono a la atmósfera, con graves consecuencias en el calentamiento global y el cambio climático (Bilgen et al., 2008). El uso de fuentes de energía alternativas supone una oportunidad para reemplazar y/o reducir el consumo de combustibles fósiles y obtener energía de forma más segura, económica y eficiente. En este sentido las fuentes de energía renovable son aquellas que provienen de recursos capaces de regenerarse de forma natural en una escala temporal humana; entre ellas se encuentran el sol, viento, agua, biomasa, mareas, olas y el calor interior de la tierra (Bilgen et al, 2008; Franki et al, 2013). Este tipo de fuentes de energía puede proporcionar electricidad, agua caliente, calefacción, carburantes, etc., reduciendo sus los efectos negativos al medio ambiente.

Desde 1990 hasta hoy, las energías renovables han madurado y su uso se ha ampliado considerablemente, lo que ha hecho que jueguen en la actualidad un papel importante en el panorama energético mundial (Vojdani, 2010; Youssef et al., 2009). En este sentido, tanto los países en vías de desarrollo como los ya desarrollados prestan cada vez más atención a los beneficios que ofrecen las energías renovables, entre ellos: mayor seguridad energética, reducción de las emisiones de gases de efecto invernadero y de impactos ambientales locales, un mayor desarrollo económico e industrial, y más

opciones para acceso a la energía confiable y moderno (Franki et al., 2013). Actualmente la energía renovable suministra el 17% de la energía primaria del mundo, contando la biomasa tradicional, las grandes hidroeléctricas y nuevas energías renovables como la minihidráulica, la biomasa moderna, la eólica, la solar, la geotérmica y los biocombustibles. Sin embargo, se proyecta duplicar la cuota de las energías renovables en el consumo global de energía final en 2030 (Franki et al., 2013). La biomasa tradicional, principalmente para cocinar y calentarse, representa alrededor del 9% (Demirbas et al., 2009); la energía hidroeléctrica participa en un porcentaje inferior al 6% y crece lentamente, sobre todo en los países en desarrollo; y las nuevas energías renovables suponen el 2% y crecen muy rápidamente en los países desarrollados y en algunos países en desarrollo (Bilgen et al., 2008). Las más elevadas tasas de participación de la biomasa en el consumo final de energía se encuentran en diferentes regiones del mundo tales como África, Asia meridional, Asia oriental, China y América Latina, con tasas de 60.00, 56.30, 25.10, 23.50 y 18.20%, respectivamente. La cuota de la biomasa de Europa, América del Norte y Oriente Medio es de 3.50, 2.70 y 0.30%, respectivamente (Demirbas, 2005; Saidur et al., 2011).

El término *biomasa* se refiere a la materia orgánica que ha almacenado energía a través del proceso de fotosíntesis. La luz del sol es la responsable del crecimiento de las plantas, y la energía almacenada en ellas es conocida como energía de la biomasa. Esta energía procede de la energía solar que los seres vivos han almacenado y de forma general se puede decir que la biomasa comprende las materias hidrocarbonadas, no fósiles, en las que se ha producido la reducción y fijación de CO₂ mediante el proceso de fotosíntesis y que es liberado de nuevo a la atmósfera cuando la biomasa vegetal o animal se pudre (McKendry, 2002a). Su utilización como fuente de energía es

importante desde el punto de vista energético, así como desde el punto de vista medioambiental (El-Mashad et al., 2003; Sun et al., 2008). A diferencia de los combustibles fósiles, las emisiones de CO₂ procedentes de la biomasa son neutras debido a que se libera el carbono fijado en el proceso de fotosíntesis, lo que resulta en un impacto neto nulo sobre el medio ambiente (Murphy, 2001; Ren et al., 2008). Además, el uso de la biomasa reduce la tasa de agotamiento de los combustibles fósiles y tiene un potencial teórico capaz de suministrar el 100% de las necesidades energéticas del mundo (Baird y Eng, 1993; Youssef et al., 2009).

Aunque la biomasa más usada en la producción de energía para la calefacción y cocción es la madera procedente de los árboles (Ladanai y Vinterbäck, 2009), este término abarca una gran variedad de materiales con diferentes composiciones químicas y características. Así, en la actualidad, la biomasa utilizada como combustible procede no sólo de madera, sino también de vegetación seca, plantas acuáticas y residuos agrícolas, entre otras fuentes. En el caso de los residuos agrícolas, éstos suponen una producción anual de 140 mil millones de toneladas métricas anuales, que serían susceptibles de ser convertidas en energía (PNUMA, 2009); concretamente, la energía contenida en esta biomasa equivaldría, aproximadamente a 50 mil millones de toneladas de petróleo. Esta energía podría desplazar sustancialmente el uso de combustibles fósiles y proporcionar energía renovable a casi 1.6 millones de personas en los países en desarrollo que todavía no tienen acceso a la electricidad (PNUMA, 2009). Los residuos agrícolas que se podrían utilizar para producir energía son diversos, variando desde hojas de remolacha de azúcar y paja de maíz hasta cereales y arroz (Tumuluru et al., 2011).

El arroz es uno de los cultivos más importantes en países de África y del sur y sudeste de Asia, tales como Egipto, Tailandia, China o Japón (Delivand et al., 2011; Gadde et al., 2009; Liu et al., 2011; Matsumura et al., 2005; Said et al., 2013a). La producción de este cultivo genera grandes cantidades de paja; por cada tonelada de granos cosechados se producen alrededor de 1.35 toneladas de paja de arroz (Kadam et al., 2000). Estas cifras suponen aproximadamente el 50% del peso seco de las plantas de arroz, con una variación significativa del 40 al 60%, dependiendo del cultivo y el método usado. En consecuencia, la producción anual de la paja de arroz podría estimarse en unos 731 millones de toneladas, que se distribuyen en África, Asia, Europa, América y Oceanía, con los siguientes valores, respectivamente: 20.9, 667.6, 3.9, 37.2 y 1.7 millones de toneladas (Balat et al., 2008; Sarkar et al., 2012).

La paja de arroz está caracterizada por su baja densidad aparente, su lenta degradación en el suelo, el riesgo de transmisión de enfermedades, y el alto contenido de minerales (Karimi et al, 2006a; Kargbo et al, 2010; Mani et al, 2006), por lo que una vez recolectado el arroz, la paja suele dejarse en el campo, lo que supone la producción de una gran cantidad de residuos (Abou-Sekkina et al., 2010; Said et al., 2013a; Werther et al., 2000). Con la finalidad de eliminarla, es práctica habitual su quema en el campo, lo que implica un gran impacto ambiental debido a la emisión de gases contaminantes que afecta la efecto invernadero y a la salud pública (Mussatto y Roberto, 2004; Wongjewboot et al., 2010). Sin embargo, la paja de arroz tiene una alta energía potencial que podría ser utilizada para producir energía térmica y/o eléctrica, por lo que podría ser una fuente alternativa de combustibles fósiles (Lee et al., 2005), además de reducir los problemas ambientales derivados de su quema a cielo abierto y suponer un ingreso para los agricultores debido al valor añadido que implicaría el uso de este

subproducto (Ewida et al., 2006; Peng et al., 2009; Said et al., 2013b; Suramaythangkoor y Gheewala, 2008; Zhaosheng et al., 2008).

La energía contenida en la paja de arroz se puede recuperar directamente mediante procesos de combustión, o bien mediante técnicas indirectas, como la gasificación, pirólisis, digestión anaerobia o la conversión bioquímica (Aly y Megeed, 2008; Ewida et al., 2006; Jung et al., 2008; Liang et al., 2009; Said et al., 2012; Summers, 2001). La composición química, abundancia y bajo precio de la paja de arroz, así como su carácter renovable, hace que en los últimos años se considere la paja de arroz como un buen material que puede ser utilizado en la producción de bioetanol mediante un proceso de conversión bioquímica, (Sánchez y Cardona, 2008). Este material está caracterizado por un alto contenido en celulosa (25-45%), hemicelulosa (20-30%) y lignina (10-25%) lo que hace posible que se pueda hidrolizar fácilmente en azúcar fermentable (Aly y Megeed, 2008; Binod et al., 2010; Jung et al., 2008; Lequerica et al., 1984; Sharma et al., 2001; Sun y Cheng, 2002; Vlesenko et al., 1997). La paja de arroz podría generar 205 mil millones de litros de bioetanol por año, aproximadamente el 5% del total del consumo, la mayor cantidad generada por una fuente de biomasa (Yoswathana et al., 2010).

A pesar de las ventajas indicadas, el uso de la paja de arroz como fuente de energía renovable supone una serie de limitaciones para su uso. En primer lugar su alto contenido de cenizas, el riesgo de generación de procesos de sinterización, formación de escoria, y problemas de corrosión puede provocar problemas de funcionamiento en los sistemas de conversión térmica (Baxter et al., 1998; Jenkins et al., 1996; Peng et al., 2009; Said et al., 2013b; Werther et al., 2000; Zygarlicke et al., 2000). Otros obstáculos

importantes son los asociados al coste y la logística para su recogida, transporte, manipulación y almacenamiento, derivados de su baja densidad aparente, con valores aproximados entre 40 kg/m^3 y 75 kg/m^3 (Kargbo et al., 2010; Mani et al., 2006). Estos aspectos hacen que hoy día no existan incentivos o beneficios a los agricultores para recoger la paja de arroz en lugar de quemar de campo, por lo que la paja de arroz no se suele utilizar comercialmente como materia prima para el calor y la energía (Kargbo et al., 2009).

La aplicación de pretratamientos a la paja de arroz, como el uso de caolín o su mezcla con otros combustibles como el carbón, pueden ser soluciones que permitan mejorar la eficiencia de calderas y controlar así la formación de escorias y procesos de sinterización (Picco et al., 2010). Otros estudios han concluido que el lavado de paja de arroz con agua podría reducir el contenido de los compuestos indeseables que provocan el ensuciamiento y la formación de escoria (Bakker et al., 2002; Jenkins et al., 1996). Finalmente, el aumento de la demanda de combustibles sólidos de biomasa, ha dado lugar a que el mercado de combustibles densificados, como los pellets, se haya incrementado durante los últimos años para diferentes materias primas. Así los pellets, elaborados a partir de residuos agrícolas, se están convirtiendo rápidamente en una importante fuente de producción de energía renovable con fines industriales y domésticos, que podría hacerse extensivo al caso de la paja de arroz (Larsson et al., 2008; Lehtikangas, 2001; Liu et al., 2013; Obernberger y Thek, 2004).

La pelletización de la paja de arroz permitiría aumentar su densidad aparente hasta valores entre 600 y 800 kg/m^3 (Obernberger y Thek, 2004), incrementar su densidad energética y conseguir una mayor uniformidad en su forma y tamaño, lo que reduce los

costes de transporte, facilita su dosificación y manipulación, reduciendo la formación de polvo, además de facilitar el almacenamiento para su utilización fuera de la temporada en la que se produce este residuo (Gilbert et al., 2009); por este motivo los pellets de paja de arroz presentarían grandes ventajas a la hora de ser utilizados en diferentes sistemas de conversión de energía (Gilbert et al, 2009; Kaliyan y Vance Morey, 2009; Vinterback, 2004).

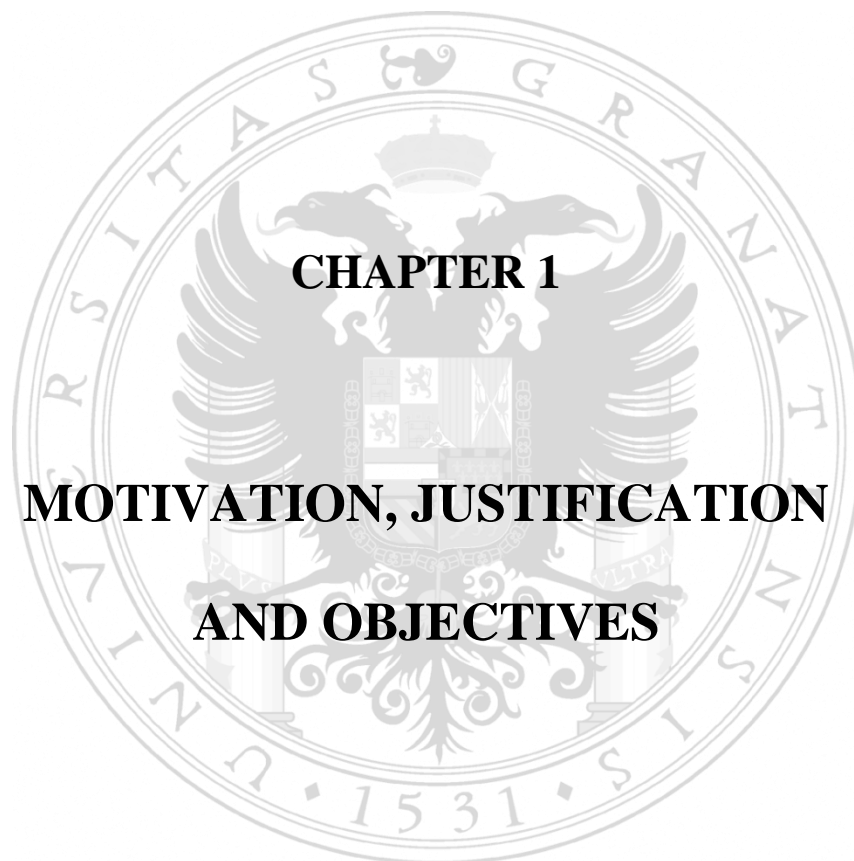
Egipto es un país con limitados recursos energéticos procedentes de combustibles fósiles, sin embargo, la demanda de energía en este país está aumentando en proporción directa con el aumento de la población y el desarrollo industrial, todo ello para satisfacer las necesidades tecnológicas y el desarrollo socioeconómico del país; por ello la demanda de energía primaria ha crecido con una tasa media anual del 4.64% durante los últimos años (Maiga et al., 2008). En consecuencia, el desarrollo sostenido de Egipto precisa de una garantía en el suministro de energía de forma continua; por este motivo el país ha centrado su atención en la diversificación de fuentes de energía, que incluyen el uso de recursos energéticos renovables propios (El-Khayat y Ameen, 2010). Así en los últimos diez años Egipto ha sido uno de los países en desarrollo que ha implantado, con éxito, programas para la potenciación del uso de recursos energéticos renovables (Zannoun, 2009).

En este sentido, Egipto produce millones de toneladas de residuos de biomasa al año, cuya inadecuada gestión hoy día produce importantes problemas de contaminación y de salud (Youssef et al., 2009); sin embargo estos residuos podrían contribuir con más de 151 PJ (petajulios) de energía primaria (de contabilidad ambiental, 2002). De acuerdo con la implementación de medidas para fortalecer el uso de las energías renovables, el

uso de biomasa para producir energía debe ser considerado como una opción viable. En este sentido Egipto es una de los mayores productores de arroz en el mundo (Abo-State et al., 2014; Arafat et al., 2010; Nakhla et al., 2013), con una producción anual que supera los 3 millones de toneladas, que se incrementa con el aumento del crecimiento de la población y del rendimiento de los cultivos de arroz (Nakhla et al., 2013). La aplicación de tecnologías adecuadas que permitiesen utilizar la energía procedente de los residuos de la paja de arroz favorecería la reducción de dependencia energética, además de reducir los problemas ambientales relacionados con la gestión de residuos.(Stahl y el Ramadán, 2007).

En consecuencia, el objetivo principal de esta investigación es el estudio de la utilización de la energía procedente de la biomasa residual de la paja de arroz en Egipto. Con el fin de lograr este objetivo, se definieron los siguientes objetivos secundarios:

- a) Evaluación de la cantidad de biomasa producida en Egipto y estudio de su potencial energético.
- b) Caracterización de la paja de arroz para la producción energética como fuente de energía renovable.
- c) Estudio del efecto del pre-tratamiento por lavado con agua en las características y el comportamiento térmico de la paja de arroz.
- d) La influencia de los parámetros de densificación de las propiedades de calidad de los pellets de paja de arroz.
- e) Análisis del efecto del proceso de densificación en la hidrólisis y sacarificación de pellets fabricados con paja de arroz.



CHAPTER 1

MOTIVATION, JUSTIFICATION AND OBJECTIVES

Energy is essential to economic and social development and improved quality of life in all countries. Its use has varied over time with the level of economic growth, weather conditions, and energy prices, among many other factors. Nowadays, almost every human activities require energy that we each use in many forms every day: heating, cooking, lighting, TV, commuting, working, shopping, etc. (Bilgen et al., 2008).

Widespread and massive consumption of fossil fuels has led to rapid economic growth in advanced industrial societies, but has also increased carbon dioxide in the atmosphere and consequently caused global warming and climate change (Bilgen et al., 2008). In consequence alternative energy sources are an opportunity to replace and/or subsidize fossil fuels and obtain safest, most cost-efficient, and most practical energy. In this sense renewable energy is generally defined as energy that comes from resources that are naturally replenished on a human timescale such as sunlight, wind, rain, tides, waves, biomass and geothermal heat (Bilgen et al., 2008; Franki et al., 2013); this type of energy sources can provide electricity, hot water/space, motor fuels, and rural (off-grid) energy services reducing negative environmental effects.

Since 1990 to present, renewable energy technologies have matured and become more widely adopted, receiving worldwide attention and playing an important role in meeting the future needs of the world (Vojdani, 2010; Youssef et al., 2009). Both developed and developing countries are increasingly motivated by the social benefits offered by renewable energy, including enhanced energy security, reduced greenhouse gas emissions and local environmental impacts, increased economic and industrial development, and more options for reliable and modern energy access (Franki et al., 2013). Currently renewable energy supplies 17% of the world's primary energy

counting traditional biomass, large hydropower and new renewables such as small hydro, modern biomass, wind, solar, geothermal, and biofuels. Nevertheless it is projected to double the share of renewable energy in the global final energy consumption by 2030 (Franki et al., 2013). Traditional biomass represents about 9%; large hydropower is slightly less than 6% and is growing slowly, primarily in developing countries; finally new renewables are 2% and are growing rapidly in developed countries and in some developing countries (Bilgen et al., 2008). The high share of biomass in final energy consumption was found in different developing regions of the world such as Africa, South Asia, East Asia, China and Latin America with ratios 60.00, 56.30, 25.10, 23.50 and 18.20 %, respectively; these values could be explained because of the use of biomass for cooking and heating (Demirbas et al., 2009). However lower biomass share was found in the case of developed countries; the percentages of use of biomass in Europe, North America and Middle East were 3.50, 2.70 and 0.30 % respectively (Demirbas, 2005; Saidur et al., 2011).

The term *biomass* refers to organic matter that has stored energy through the process of photosynthesis. It exists as plants and also transfers through the food chain to animals' bodies and their wastes, all of which can be converted for everyday human use through processes such as combustion, which releases the carbon dioxide stored in the plant material (McKendry, 2002a). The utilization of biomass as a source of energy is important from an energetic as well as an environmental viewpoint (El-Mashad et al., 2003; Sun et al., 2008). Unlike coal, CO₂ emissions from biomass are negated by the photosynthetic contribution during the growth cycle of biomass, resulting in a net zero impact on the environment (Murphy, 2001; Ren et al., 2008); moreover, biomass

reduces the rate of fossil fuel depletion and has the theoretical potential to supply 100% of the world's energy needs (Baird and Eng, 1993; Youssef et al., 2009).

The most common biomass used for energy is wood from trees used for heating and cooking for a very long time (Ladanai and Vinterbäck, 2009); nevertheless biomass includes a large variety of fuels with different chemical compositions and combustion characteristics. Many of the biomass fuels used today comes also in the form of dried vegetation, aquatic plants, and agricultural residues. Focusing on agricultural activities, globally, it produces 140 billion metric tons of biomass every year, for example sugar beet leaves and straw of maize, cereal, and rice (Tumuluru et al., 2011), that could be converted on energy (UNEP, 2009). Equivalent to approximately 50 billion tons of oil, agricultural biomass waste converted to energy can substantially displace fossil fuel and provide renewable energy to some 1.6 billion people in developing countries, which still do not have access to electricity (UNEP, 2009).

Rice is a widely grown crop in Africa and South and South-East Asia such as Egypt, Thailand, China, or Japan (Delivand et al., 2011; Gadde et al., 2009; Liu et al., 2011; Matsumura et al., 2005; Said et al., 2013a). The rice collection harvest generates large amounts of straw; for each ton of grain harvested, about 1.35 tons of rice straw remain in the field (Kadam et al., 2000) making up approximately 50% of the dry weight of rice plants, with a significant variation of 40–60% depending on the crop and agricultural method. In consequence, the annual production of rice straw is about 731 million tons which is distributed in Africa, Asia, Europe, America and Oceania as 20.9, 667.6, 3.9, 37.2 and 1.7 million tons, respectively (Balat et al., 2008; Sarkar et al., 2012).

Rice straw is usually left in the field so represents one of the largest amount of unused agricultural residue (Abou-Sekkina et al., 2010; Said et al., 2013a; Werther et al., 2000). The options for the disposal of rice straw are limited by its low bulk density, slow degradation in the soil, harboring of rice stem diseases, and high mineral content (Karimi et al., 2006a; Kargbo et al., 2010; Mani et al., 2006). In consequence, nowadays, field burning is the major practice for removing rice straw, but it results in the great impact on the greenhouse aspect as gas emissions as well as air pollution and consequently affects public health (Mussatto and Roberto, 2004; Wongjiewboot et al., 2010). However, rice straw has a high energy potential and thus can become a source of alternative energy that substitutes fossil energy (Lee et al., 2005) for reducing greenhouse gas emissions as well as avoids the local pollution problems from open burning (Said et al., 2013b; Suramaythangkoor and Gheewala, 2008). Consequently the use of rice straw is a potential source of energy, because it could produce thermal or electric energy directly; but it could be also a value-added by-product (Peng et al., 2009) because it would protect the environment, reduce field-burning pollution, and also increase the income of farmers (Ewida et al., 2006; Zhaosheng et al., 2008).

Energy from rice straw can be recovered directly in form of gas through combustion process or can be converted to a valuable energy product through indirect techniques such as gasification, pyrolysis, anaerobic digestion, biochemical conversion, where the products can then be burned (Aly and Megeed, 2008; Ewida et al., 2006; Jung et al., 2008; Liang et al., 2009; Said et al., 2012; Summers, 2001). Recently, rice straw is also regarded as a promising starting material for 2nd generation bioethanol production through biochemical conversion process, because it is abundant, inexpensive and renewable (Sánchez and Cardona, 2008). A distinctive character that makes it a

potential feedstock for fuel ethanol production is the high cellulose and hemicelluloses content that can be readily hydrolysed into fermentable sugar (Aly and Megeed, 2008; Binod et al., 2010); it contains between (25 – 45%) of cellulose, (20 – 30%) hemicellulose and (10 – 25%) lignin (Jung et al., 2008; Lequerica et al., 1984; Sharma et al., 2001; Sun and Cheng, 2002; Vlesenko et al., 1997). Globally, rice straw could potentially produce 205 billion liters bioethanol per year, which it would be about 5% of total of consumption. It is the largest amount from a single biomass feedstock (Yoswathana et al., 2010).

Nevertheless, and despite its advantages, technical limitations related to rice straw composition causes operating problems in thermal conversion systems. These problems include high ash content, sintering, slag formation, and corrosion problems (Baxter et al., 1998; Jenkins et al., 1996; Peng et al., 2009; Said et al., 2013b; Werther et al., 2000; Zygarlicke et al., 2000). Another major hurdle with respect to the utilization of rice straw for energy production are the associated costs and logistics of collecting, transport, handling and storage due to its low density; its bulk density is around 75 kg/m³ (Kargbo et al., 2010) and 40 kg/m³ in the case of loose straw (Mani et al., 2006). In consequence rice straw has not yet been commercially used as a feedstock for heat and energy because of insufficient incentives or benefit for farmers to collect rice straw instead of field burning (Kargbo et al., 2009).

Pretreatment process of rice straw, such as the use of kaolin and blending rice straw with other fuels such as coal, may be suggested solutions to enhance combustion efficiency of boilers and to control fouling and slag formation (Picco et al., 2010). Another studies have concluded that washing rice straw with water could be a possible

way of reducing the content of the undesirable compounds which cause fouling and slag formation (Bakker et al., 2002; Jenkins et al., 1996). Finally, the pellets' market has increased during recent years for different raw materials. In the case of the pellets made from agricultural residues, they are rapidly becoming an important renewable source of energy production for industrial and domestic purposes; particularly there has recently been a revival of interest in producing pellets using rice straw (Larsson et al., 2008; Lehtikangas, 2001; Liu et al., 2013; Obernberger and Thek, 2004).

Pelletization process of rice straw would increase the bulk density from an initial bulk density of 40-200 kg/m³ to a final bulk density of 600-800 kg/m³ (Obernberger and Thek, 2004). Moreover, the process also provides potential storage for off-season utilization in the case of raw materials that are harvested only for few weeks of a year, such as rice straw (Gilbert et al., 2009). Finally, because of uniform shape and sizes, high energy and bulk density, pellets can be easily handled using the standard handling and storage equipment with less dust formation, and can be easily adopted in different energy conversion systems (Gilbert et al., 2009; Kaliyan and Vance Morey 2009; Vinterback, 2004).

Egypt is a country of limited fossil fuel resources and, due to the vital role played by the energy sector, energy demand is increasing in direct proportion to the increase in population and industrial development to satisfy technological needs and the development of lifestyles in Egypt. Primary energy demand has grown at an average annual rate of 4.64% during the last years (Maiga et al., 2008). In consequence securing energy supply on a continuous basis is a vital element for sustained development plans; therefore Egypt has given due consideration to the diversification of its energy portfolio

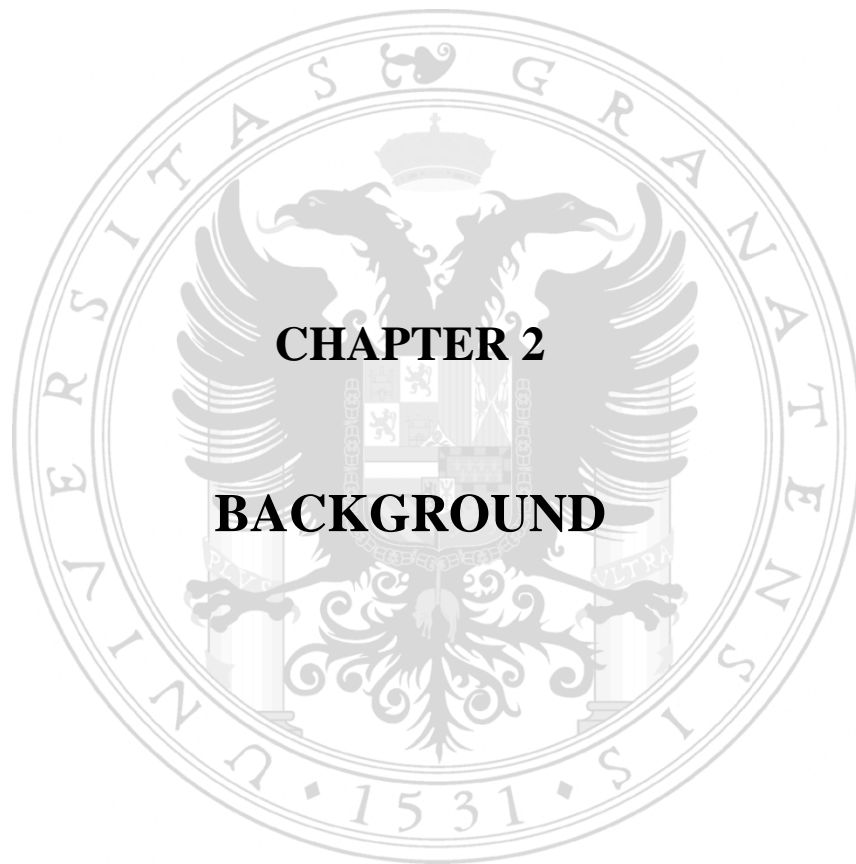
by utilization of its renewable energy resources (El-Khayat and Ameen, 2010). In this sense, during the last decade, Egypt has been one of the developing countries following successful programs for the development of renewable energy resources (Zannoun, 2009).

Egypt produces millions of tons of biomass waste every year, which could contribute more than 151 PJ (petajoules) of primary energy (NREA, 2002), but nowadays these wastes are causing pollution and health problems (Youssef et al., 2009). According to the implementation of measures to strengthen the use of renewable energy, the use of biomass from waste to produce energy should be considered as a viable option. In this sense it is one of the largest rice producer in the world (Abo-State et al., 2014; Arafat et al., 2010; Nakhla et al., 2013) so the quantity of rice straw generated annually exceeds 3 million tons and this amount increases with increasing population growth and rice cultivation yield (Nakhla et al., 2013). A suitable technology to use the renewable energy of rice straw would help to reduce Egypt's dependency on fissile fuels and give a significant contribution to reduce environmental pollution (Stahl and Ramadan, 2007).

In consequence the main objective of this research is to study the utilization of energy from residual biomass of rice straw in Egypt. In order to achieve this objective, the following secondary objectives were defined:

- a) The development of a quantitative appraisal of biomass resources and their energy potential in Egypt.
- b) Characterization of rice straw as a renewable energy source.

- c) Effect of the water washing pretreatment in the characteristics and thermal behavior of rice straw
- d) The influence of densification parameters on the quality properties of rice straw pellets.
- e) Analysis of the effect of densification process on hydrolysis and saccharification of pellets produced from rice straw.



CHAPTER 2

BACKGROUND

1. WORLDWIDE ENERGY FRAMEWORK

1.1. Worldwide energy supply and consumption and environmental effects

Historically, energy use has varied over time with the level of economic growth, weather conditions, and energy prices, among many other factors. Starting in the late 1980s and lasting through 2000, energy consumption generally increased with declining energy prices and strong economic growth. Recently, as energy prices have risen, the potential for more energy conservation has received increased attention. It can be concluded that with the high demand on oil, the prices will be raised subject to the rapid growth rate in energy consumption and the depletion in fossil oil resources (Mubarak et al., 2006).

Figure 1 and 2 illustrate the progress of energy supply and consumption by fuel, in million tons oil equivalent (Mtoe), all over the world between 1971 and 2012, respectively. It is possible to conclude that the energy supply for the different fuels increases with the time (Figure 1) and, in consequence since 1971, the total energy supply is higher than the energy consumption (Figure 2); however, much of the world's energy is currently produced and consumed in ways that could not be sustained, moreover, the current predictions estimate that the energy demand for 2030 will be 50 to 80% higher in comparison with that required in 1990 (IEA, 2014). Finally, the use of electricity, gas and renewable fuels has increased with time, while the increase of the use of coal has maintained nearly constant (Figure 2).

Fossil fuels such as coal, oil and gas are ubiquitous and provide about three quarters of the world's energy (Bilgen et al., 2008); its energy has fuelled industrial development, and continues to fuel the global economy. However, when these same fossil fuels are

burned, they emit greenhouse gases that are now recognized as being responsible for climate change (Lee, 2002; Wolfson and Schneider, 2002). The primary greenhouse gases emitted through fuel combustion is carbon dioxide (CO_2) (Ravindranath and Sathaye, 2002), which travel up into the upper atmosphere (the troposphere) where they act as a screen to sunlight. They allow the sunrays in but stop the heat radiation from re-emerging, much as happens with the glass in greenhouse (Bilgen et al., 2008).

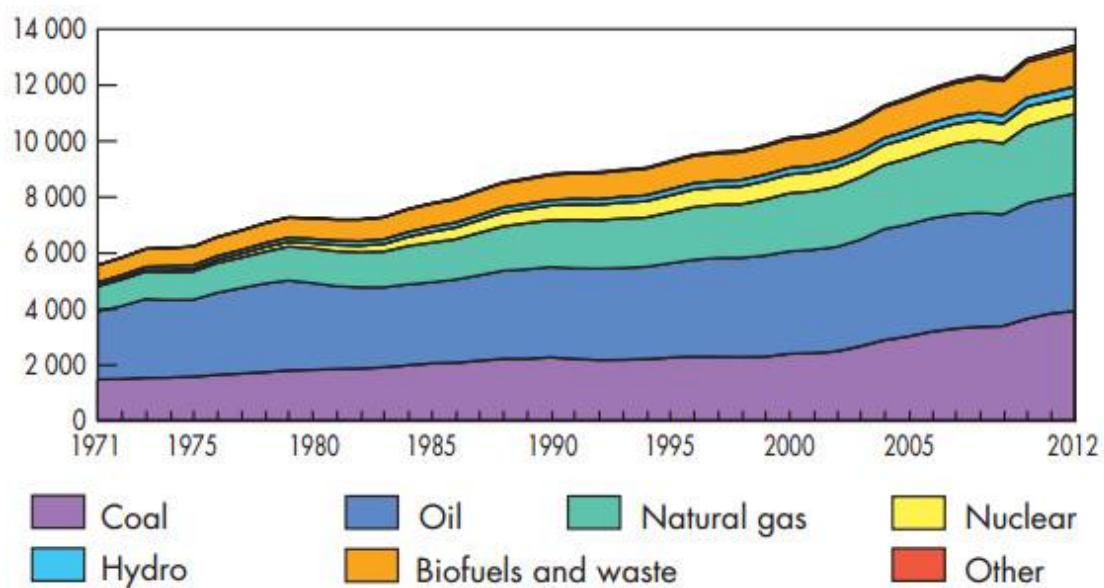


Figure 1. World total primary energy supply from 1971 to 2012 by fuel (Mtoe) (IEA, 2014)

The vast tonnage of CO_2 gas we have released into the atmosphere seems likely to upset the natural balance. Figure 3 shows the significant increase in CO_2 emitted from the combustion of fossil fuels. The result is that the greenhouse, in this case the whole world, heats up causing icecaps melting and sea levels rise (Bilgen et al., 2008). On the other hand, global warming could also lead to the disruption of crop growing as climate patterns change. It would not be simply a matter of increased temperatures such as the climate system would become erratic, with more storms and more droughts (Lee, 2002;

Wolfson and Schneider, 2002). In fact, the greenhouse effect has already increased the average temperature in the Earth by 0.7 °C, and it is estimated that this temperature will increase by 4 to 6 °C in 2050 (IEA, 2012). In consequence, the need to control atmospheric emissions of greenhouse and other gases and substances will increasingly need to be based on efficiency in energy production, transmission, distribution and consumption in the countries (Elliot, 1997; Field and Raupach, 2004; Jaccard et al., 2002).

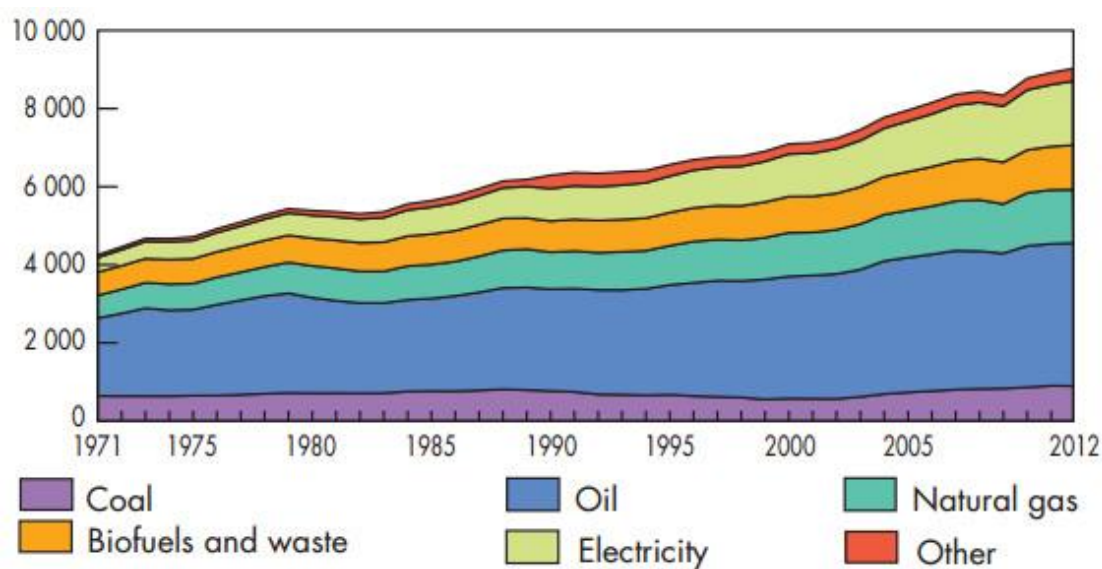


Figure 2. World total final consumption from 1971 to 2012 by fuel (Mtoe) (IEA, 2014)

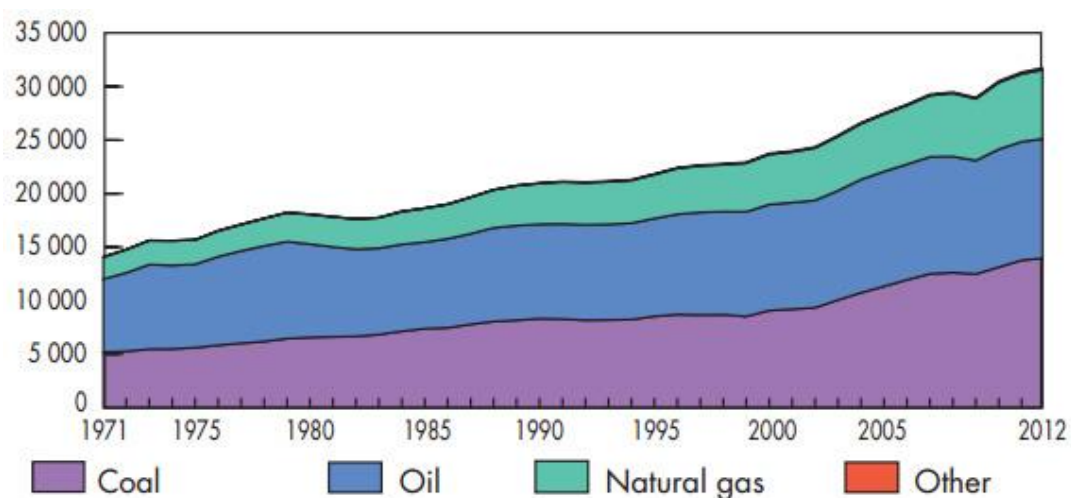


Figure 3. World CO₂ emissions from 1971 to 2012 by fuel (Mt of CO₂) (IEA, 2014)

1.2. Energy framework: Kyoto Protocol

Reducing climate change will necessitate profound changes in the way we produce, distribute and consume energy. In this sense, in 1972, the Stockholm Conference adopted a declaration that set out principles and an action plan for the preservation and enhancement of the human environment. It also raised the issue of climate change for the first time, warning governments to be mindful of activities that could affect the climate. In 1988, the United Nations Environment Program organized an internal seminar to identify environmental sectors that might be sensitive to climate change.

The Intergovernmental Panel on Climate Change (IPCC), a forum for the investigation of the potential causes and scale of climate change, was established. Since its foundation, the IPCC has published four reports (in 1990, 1995, 2001 and 2007) collecting scientific data about climate change, its causes and impact. The first IPCC report awakened world leaders, policymakers and the public, alerting them to the potential dangers of global warming and leading to a United Nations conference in Rio de Janeiro in 1992. During that conference the United Nations Framework Convention on Climate Change was adopted. This nonbinding treaty, with no mandatory limits of greenhouse gas and no enforcement mechanisms, was meant to commit signatory nations to voluntary action to stabilize greenhouse gas concentrations in the atmosphere (Prescott, 2013).

In 1995, at the first conference of the parties in Berlin (Germany), as it became apparent that major nations such as the United States and Japan would not meet the voluntary stabilization target by 2000, parties to the treaty decided, to enter into negotiations on a protocol to establish legally binding limitations or reductions in greenhouse gas

emissions (Fletcher, 2004). During negotiations, the third Conference of Parties (COP) took place in December 1997 in Kyoto (Japan), and entered into force on 16 February 2005; after intensive negotiations, the Parties adopted the Kyoto Protocol. This document outlined specific greenhouse gas emissions targets for industrialized developed countries, following the principle of “common but differentiated responsibilities”. The countries agreed to legally binding reductions in greenhouse gas emissions of an average of 5% below 1990 levels in the first emissions reduction period: between 2008 and 2012. The Kyoto Protocol was underpinned by five key concepts:

- Legally binding targets for the industrialized countries;
- Implementation: the countries were required to prepare policies and measures for the reduction of emissions, to increase the absorption of greenhouse gases and to adopt “flexible mechanisms”;
- Minimizing impacts on developing countries by establishing an adaptation fund for climate change;
- Transparent accounting, reporting and review;
- Establishing a Compliance Committee to enforce the implementation of commitments under the Protocol.

The Kyoto Protocol adopted “flexible mechanisms” to assist in delivering emissions reductions. These are:

- Emissions trading, allowing countries to sell permitted but non-“used” emissions units to countries exceeding their targets;
- The clean development mechanism that allows the countries to implement emissions reduction projects in developing countries. Such projects can earn

saleable certified emission reduction units, which can be counted towards the Kyoto Protocol targets;

- Joint Implementation, allowing the countries to earn emission reduction units from an emissions removal or reduction project in another country, which can be counted towards meeting its target.

Resolving specific issues that were not resolved in Kyoto and planning for implementation and ratification took up the four years following the signature of the Kyoto Protocol. COP 4 (1998, Buenos Aires), COP 5 (1999, Bonn), COP 6 (2000, Hague and Bonn) and COP 7 (2001, Marrakech) 26 held expert discussions about Kyoto mechanisms, plans for ratification and the withdrawal, in 2001, of the United States – by far the largest greenhouse gas emitter among the countries – from active participation in the Kyoto process. The Kyoto Protocol came into force in February 2005 after its ratification by Russia, while Australia and the United States kept refusing to ratify it. Since 2005, efforts to negotiate a successor regime were done. The key meetings and events for negotiating a new agreement replacing the Kyoto Protocol are summarized in Table 1.

Table 1. Key meetings and events for negotiating a new agreement replacing the Kyoto Protocol (Prescott, 2013)

Date and name of event	Main outcomes
2005, Montreal: COP 11/ MOP 1	The first Meeting of the Parties (MOP) of the Kyoto Protocol initiated discussions on commitments for industrialized countries in the period beyond 2012.
2007, Washington Declaration	A non-binding agreement between governments from the G8 countries and Brazil, China, India, Mexico and South Africa on the outline of a successor to the Kyoto Protocol. It envisaged a global emissions trading system for both industrialized and developing countries.
2007, IPCC Fourth Assessment Report	The IPCC warned policymakers that the pace of climate change was faster than previously believed and that its effects on the planet were worse than previously thought. The report further estimated that to keep warming at 2 °C, greenhouse gas emissions would need to be cut from their 2000 levels by 25% to 40% by 2020 and by 50% to 85% by 2050.
2007, Bali: COP 13/MOP 3	An agreement on a timeline and structured negotiation on the post-2012 framework (“Bali Action Plan” or “Kyoto II Road Map”). Establishing Ad Hoc Working Group on Long-Term Co-operative Action under the Convention (AWG-LCA) – a new subsidiary body to conduct negotiations. Australia finally ratified the Kyoto Protocol.
June 2009, G8 meeting in Italy	G8 nations committed to the 2 °C target and a successor regime to the Kyoto Protocol.
2009, Copenhagen: COP 15/ MOP 5	No legally binding agreement was adopted due to the lack of political consensus on how to share the burden to achieve the necessary 50% to 80% reduction in greenhouse gas emissions by 2050 and even less consensus on how to set mid-term quantitative emissions targets for 2020. Instead, a modest 13-paragraph non-binding “political accord” was negotiated outside the COP framework and then “noted” by COP 15.
2010, Cancun: COP 16/MOP 6	No progress towards negotiating a successor to Kyoto.
2011, Durban: COP 17/MOP 7	Concluded that talks on a legally binding agreement should be completed no later than 2015 and come into force by 2020. Parties agreed that a new instrument should be “applicable to all Parties”. Establishment of a Green Climate Fund to help developing countries reduce their emissions. The Fund is to be endowed with US\$100 billion from 2020, but it is unclear where the money would come from.
2012, Rio de Janeiro: Rio+20 Conference	The UN Conference on Sustainable Development focused on securing renewed political commitment to a green economy and the institutional framework for sustainable development. The outcome document “The future we want” underscored the need for urgent and ambitious action to combat climate change.
2012, Doha: COP 18/MOP 8	Agreement on a timetable for developing a new international agreement by May 2015. 38 industrialized countries agreed a second commitment period of the Kyoto Protocol to start in January 2013 and to last eight years. It was also agreed that the Kyoto Protocol’s “flexible mechanisms” can continue as of 2013. Developed countries reiterated their commitment to deliver on promises to continue long-term climate financial support to developing nations. Germany, the United Kingdom, France, Denmark, Sweden and the European Commission announced financial pledges for the period up to 2015, totaling about US\$6 billion.

2. RENEWABLE ENERGY IN THE NEW ENERGY FRAMEWORK

The fight against climate change and the continued trend of the rising prices of the fossil energy products in the international market have focused on the need to develop renewable energy sources worldwide. For many developed and developing countries, renewable energy offers promise as a means of improving energy security, reducing the environmental impact of energy use, and promoting economic development. Renewable energy sources like wind, solar, geothermal, hydrogen and biomass play an important role in the world future and they are used for heating, electricity, and transport (Khalil et al., 2010).

Renewables for heating (cooking, space, and water heating) accounted for 75 % of all renewable energy use in 2010, with biomass contributing 96 % of this share (Franki et al., 2013). In 2011, around 50 countries installed wind power capacity, and solar photovoltaic (PV) capacity is moving rapidly into new regions and countries. More than 200 million households, as well as in many public and commercial buildings around the world, use solar hot water collectors. Interest in geothermal heating and cooling is also on the rise globally. By the end of 2011, renewable energy sources accounted for more than 20 % of global power generated, 25 % of global installed power generation capacity, and half of newly installed power generation capacity added that year (Franki et al., 2013; IEA, 2012).

The contribution of renewable energy to global final consumption in commercial heat, mainly combined heat and power, and transport reached 3.9 and 2.4%, respectively, in 2010. Renewable energy is used in the transport sector in the form of gaseous and liquid biofuels; liquid biofuels provided about 3.3 % of global road transport, more than any

other renewable energy source in the transport sector. Electricity powers trains, subways, and a small but growing number of passenger cars and motorized cycles, and there are limited but increasing initiatives that link electric transport with renewable energy (Franki et al., 2013; IEA, 2012).

The share of renewable energy in electricity production fluctuated between 1990 and 2010, decreasing from 19.5 % in 1990 to a low of 17.5 % in 2003, and then rebounding to 19.4 % in 2010. The reason for the decline between 1990 and 2000 is that electricity demand grew at a faster pace than renewable energy. Hydropower contributed 83 % to this global share, followed by wind-based generation, which accounted for a little more than 8%. All other sources combined accounted for about 10 % of total renewable-source-based electricity supply in 2010. While the historic share of renewable energy in electricity production was relatively flat through 2010, more recent trends suggest that it may be increasing. Renewables accounted for almost half of the estimated 208 (GW) of new electric capacity added globally during 2011. Wind and solar photovoltaic (PV) accounted for almost 40 % and 30 % of new renewable capacity, respectively, followed by hydropower (nearly 25 %) (Franki et al., 2013; IEA, 2012).

The share of renewable energy in the total final energy consumption remained relatively stable, growing from 16.6 % in 1990 to 18.0 % in 2010. This share will have to double from an estimated starting point of at most 18 % in 2010, implying an objective of up to 36 % by 2030 (Franki et al., 2013). Biomass is currently the largest renewable energy source and has very specific properties comparing to the other renewable technologies, (Ladanai and Vinterbäck, 2009; Saidur et al., 2011). It is a versatile energy source generating electricity, heat and biofuels, moreover, converting it into energy can

revalorize waste materials, mitigate the environmental impacts of waste disposal, and reduce the mass and volume of the waste (Kalt and Kranzl, 2011). Consequently, it can play an important role in the future fuel supply trends.

3. ENERGY FROM BIOMASS

3.1. Biomass definition and classification

The world's energy markets rely heavily on the fossil fuels coal, petroleum crude oil, and natural gas as sources of thermal energy, gaseous, liquid, and solid fuels, as well as chemicals fuels. Since millions of years are required to form fossil fuels in the earth, their reserves are finite and subject to depletion as they are consumed. The only natural, renewable carbon resource known that is large enough to be used as a substitute for fossil fuels is biomass. Unlike fossil fuel deposits, biomass is renewable in the sense that only a short period of time is needed to replace what is used as an energy resource (Klass, 2004). As a renewable energy source, biomass is one of the options to secure energy supply and to reduce greenhouse gas emissions from fossil fuels in response to the climate change threat (Black and Richter, 2010).

Biomass was the oldest form of fuel used in history. It is the first-ever fuel used by humankind and is also a fuel that was the mainstay of the global fuel economy till the middle of the 18th century (Abbasi, 2010; Balat and Ayar, 2003). It is used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities (Zheng et al., 2010).

The European Technical Specification UNE-EN 14588 (2011) defines biomass as “all biological materials excluding those that were included in geological formations

suffering a mineralization process”. This is the case of coal, petroleum and natural gas, which formation and composition millions of years ago is not comparable with the “carbon neutral balance” of biomass. Carbon dioxide from the atmosphere and water absorbed by the plants roots are combined in the photosynthetic process to produce carbohydrates that form the biomass. The solar energy that drives photosynthesis is stored in the chemical bonds of the biomass structural components. During biomass combustion, oxygen from the atmosphere combines with the carbon in biomass to produce CO₂ and water. The process is therefore cyclic because the carbon dioxide is then available to produce new biomass. When this cycle is in balance, it has a net zero impact on atmospheric carbon, which is why biomass carbon is often called “carbon neutral balance (McKendry, 2002a; Miner, 2010).

Thus, biomass is a carbon-based material derived from living organisms or organisms that recently lived and covers organic materials that include plant materials, animal and human wastes. There are many different types of biomass, but the main biomass resources are: wood and forest residues, agricultural crops, agricultural residue, sugarcane bagasse, sewage, municipal solid wastes and algae (Potgieter, 2011).

Biomass, once processed, is referred to “feedstock” that is available for energy purposes. Types of biomass feedstock available for energy purposes include: agricultural residues, dedicated energy crops, forestry, industry, parks and gardens, waste and other (Table 2). The product derived from a particular feedstock is dependent on which part of the plant and the conversion process used. The possible products that can be derived from biomass include solid biofuel, biodiesel, ethanol, methane,

hydrocarbons, and natural oils, which can be further processed into any number of desirable fuels (Tumuluru et al., 2011).

Concerning to solid biofuels, the classification in UNE-EN ISO 17225-1 (2014) is based on the origin and source. The solid biofuels are divided to woody, herbaceous, fruit, and blends and mixtures biomass. Woody biomass includes trees, bushes, and shrubs while herbaceous biomass includes plants that have non-woody stem and which die back at the end of the growing season. Fruit biomass from parts of a plant that hold the seeds and blends refer to intentional mixing of biomass and mixtures refer to the unintentional mixed biomass (Tumuluru et al., 2011).

3.2. Biomass benefits and barriers

Besides the advantages of biomass as a renewable energy resource of energy, there are also some downsides to use it. Consequently, it is important to know the biomass benefits and barriers to optimize the use of this technology.

The most important biomass benefits are summarized as following (Dael et al., 2013; Demirbas, 2001a; Kalt and Kranzl, 2011; Rosie et al., 2008):

- Biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy. It is a versatile energy source generating electricity, heat and biofuels.
- If it is grown and utilized on a sustainable basis, biomass is carbon dioxide neutral. Thus, the substitution of fossil fuels for energy production using biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-

renewable energy source. Many large power producers in industrialized countries are looking for biomass as a means of meeting greenhouse gas reduction targets.

- The natural decomposition of biomass produces methane, which is about twenty times more active as a greenhouse gas than carbon dioxide. On the other hand, biomass fuels have negligible sulfur content and therefore, do not contribute to sulfur dioxide emissions, which cause acid rain. Furthermore, the combustion of biomass produces less ash than coal combustion, and the ash produced can be used as a soil additive on farm targets.
- Biomass is a domestic resource, which is not subject to world price fluctuations or the supply uncertainties of imported fuels. In developing countries in particular, the use of liquid biofuels, such as biodiesel and ethanol, reduces the economic pressures of importing petroleum products.

By contrast, the barriers and constraint to biomass use are considered as following (Demirbas, 2001b, Rentizelas et al., 2009; Yan and Lin, 2009):

- Biomass is not concentrated and has a low bulk density, which makes transportation and handling difficult and costly.
- The incomplete combustion of biomass produces organic particulate matter, carbon monoxide and other organic gases. If high temperature combustion is use, oxides of nitrogen will be produced. The health impact of air pollution inside buildings is a significant problem in developing countries, where biomass is burnt inefficiently in open fires for domestic cooking and space heating.
- There is the potential for widespread use of natural forests to cause deforestation and localized fuel wood scarcity with serious ecological and social ramifications.

- There is a potential conflict over the use of land and water resources for biomass energy and other uses, such as food production.
- Some biomass applications are not fully competitive at this stage. In electricity production, for example, there is strong competition from new, highly efficient natural gas fired combined cycle plants.
- The production and processing of biomass can involve significant energy input, such as fuel for agriculture vehicles and fertilizers, resulting in a poor energy balance for the biomass application. Biomass processes need to minimize the use of energy intensive and fossil fuel based inputs and maximize waste and energy recovery.
- There are often political and institutional constraints to biomass use, such as policies, taxes and subsidies that encourage the use of fossil fuels. Energy prices often do not reflect the environmental benefits of biomass and other renewable energy resources.

Table 2. Types of biomass feedstocks used for energy purposes (Tumuluru et al., 2011)

Supply sector	Type	Example
Agricultural Residues	Dry lignocellulosic agricultural residues	Straw (maize, cereal, rice), sugar beet leaves, and residue flows from bulb sector
	Livestock waste	Solid manure (chicken manure) Liquid manure (cattle, pigs, sheep manure)
Dedicated energy crops	Dry lignocellulosic woody energy crops	SRW – willow; SRC – poplar; Eucalyptus
	Dry lignocellulosic herbaceous energy crops	Miscanthus; Switch grass; Common reed; Reed canary grass; Giant reed; Cynara cardu; Indian shrub
	Oil energy crops	Sugar beet; Cane beet; Sweet sorghum; Jerusalem Artichoke; Sugar millet
	Starch energy crops	Wheat; Potatoes; Maize; Barley; Triticale; Corn (cob); Amaranth
	Others	Flax (Linum); Hemp (Cannabis); Tobacco stems; Aquatic plants (lipids from algae); Cotton stalks; Kenaf
Forestry	Forestry by-products	Bark; Wood blocks; Wood chips from tops and branches; Wood chips from thinning; Logs from thinning
Industry Residues	Wood industry	Industrial waste wood from sawmills and Industrial waste wood from timber mills (bark, sawdust, wood chips, slabs, off-cuts)
	Food industry Residues	Fibrous vegetable waste from virgin pulp production and from production of paper from pulp, including black liquor Wet cellulosic material (beet root tails); Fats (used cooking oils); Tallow, yellow grease; Proteins (slaughter house waste)
	Industrial products	Pellets from sawdust and shavings; Briquettes from sawdust and shavings; Bio-oil (pyrolysis oil); Ethanol; Bio-diesel
Parks and Gardens	Herbaceous	Grass
	Woody	Pruning
Waste	Contaminated waste	Demolition wood; Biodegradable; municipal waste; Sewage sludge; Landfill gas; Sewage gas
Others	Roadside hay	Grass/hay
	Husks/Shells	Almond; Olive; Walnut; Palm pit ; Cacao

3.3. Biomass energy production technologies

Conversion of waste biomass and organic substrates into energy encompasses a wide range of different types and sources of biomass, conversion options, end uses applications and infrastructure requirements (Karagiannidis et al., 2009). Many of the processes are suitable for either the direct conversion of biomass or the conversion of intermediate types of biomass (Iakovou et al., 2010). Factors that influence the choice of a conversion process include the type and quantity of biomass feedstock and the desired form of the produced energy, i.e. end-use requirements, environmental standards, economic conditions and other project-specific factors (Hulteberg and Karlsson, 2009).

Biomass can be converted into useful products or exploitable energy via two main process categories: thermochemical and bio-chemical processes. Thermochemical conversion processes convert biomass into a solid, liquid or gaseous fuel, such as gasification and pyrolysis (Balat et al., 2009). Bio-chemical conversion is based on biological processes; in this case the most significant options are: alcohol production from biomass containing sugar, starch and/or celluloses, and biogas production from crops or organic waste material (e.g. animal manure) (Iakovou et al., 2010).

3.3.1. Thermochemical processes

Thermo-chemical processing of biomass and wastes offers a number of ways to produce energy and if this is applicable, a potential attractive method is provided to avoid waste accumulation. In addition to obtain heat from biomass, wastes can be converted into a mixture of gases, liquids and carbon chars (Rosie et al. 2008). Thermochemical conversion processes have been briefly described below.

- Combustion is used over a wide range of outputs to convert the chemical energy stored in biomass into heat, mechanical power or electricity (De Kam et al., 2009). Combustion of biomass produces hot gases at temperatures around 800–1000 °C. It is possible to burn any type of biomass but in practice, combustion is feasible only for biomass with inherent moisture content less than 50%, above which pre-drying is feasible; biomass with high moisture content is better suited for biochemical conversion processes (Velis et al., 2009).
- Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation at high temperatures, typically in the range 800–900 °C (Cao et al., 2006). The low calorific value gas produced can be burnt directly or it can be used as a fuel for gas engines and gas turbines, as well as feedstock in the production of chemicals.
- Pyrolysis is the conversion of biomass into liquid, solid and gaseous fractions. It can be used to produce predominantly a liquid fraction enabling the conversion with an efficiency of up to 80%, if flash pyrolysis is used (McKendry, 2002b). This fraction can be used in engines and turbines and its use as a feedstock for refineries is also being considered (Iakovou et al., 2010).
- Liquefaction is the conversion of biomass into a stable liquid hydrocarbon (Xu and Etcheverry, 2008). There are several liquefaction methods under research, such as acid hydrolysis, enzyme hydrolysis, steam explosion and supercritical water for the production of bio-ethanol or polylactic acid (Kobayashi et al., 2008).

3.3.2. Bio-chemical processes

Biochemical conversion is the process by which biomass is converted into gas (CO₂/CH₄), waste (compost or fertilizer) and water (water or C₂H₅OH) by using

microorganisms. These systems are among the most promising, environmentally sustainable alternatives for reducing atmospheric carbon dioxide levels (Rosie et al. 2008). Biochemical conversion processes have been briefly described below.

- Fermentation is used commercially on a large scale to produce ethanol from sugar (e.g. sugar cane, sugar beet) and starch crops (e.g. maize, wheat) (Kopsahelis et al., 2007). The biomass is ground down and the starch converted by enzymes to sugars, with yeast then converting the sugars to ethanol. The conversion of lignocellulosic biomass (such as wood and grasses) is more complex, due to the existence of longer-chain polysaccharide molecules and requires acid or enzymatic hydrolysis before the resulting sugars can be fermented to ethanol (Iakovou et al., 2010).
- Anaerobic digestion is the conversion of organic material directly into biogas, a mixture of mainly methane and carbon dioxide, with an energy content of about 20–40% of the lower heating value of the feedstock (Sosnowski et al., 2003). It is a commercially proven technology and is widely used for treating organic wastes with high (i.e. over 80–90%) moisture contents (Igoni et al., 2008).

3.4. Global biomass potential and consumption

Since the beginning of civilization, biomass has been a major source of energy throughout the world. Biomass is the primary source of energy for nearly 50% of the world's population (Karekezi and Kithyoma, 2006) and wood biomass is a major renewable energy source in the developing world, representing a significant proportion of the rural energy supply (Hashiramoto, 2007). In the past decade, the number of countries exploiting biomass opportunities for the provision of energy has increased rapidly, and has helped make biomass an attractive and promising option in comparison

to other renewable energy sources; in consequence the global use of biomass for energy increases continuously and has doubled in the last 40 years (World Bank, 2009).

Nowadays, biomass is the fourth largest energy resource after coal, oil, and natural gas and is currently the largest renewable energy source comparing to the other renewables (Ladanai and Vinterbäck, 2009). The contribution of biomass to the global energy demand of 532 EJ in 2010 was 10% (IEA, 2012) and according to Tumuluru et al. (2011), biomass accounts for about 14% of world energy consumption. For many developing countries, such as China, India, Thailand and Brazil, biomass has been used over centuries as the main energy carrier to provide for domestic energy requirements, it accounts for 35% of primary energy consumption in developing countries (Demirbas et al., 2009). In many cases, biomass fulfills the most basic needs for heating and cooking but there is a need to develop energy for the provision of light, transport and industrial uses (Black and Richter, 2010).

The global primary energy demand was 302 EJ in 1980, 420 EJ in 2000, and 532 EJ in 2010 (IEA, 2012), and is expected to increase to 826 EJ (as averaged for different scenarios) by 2050 (Smeets et al., 2004). In this scenario, the future potential for energy from biomass depends to a great extent on land availability. Currently, the amount of land devoted to growing biofuels is only 0.025 billion hectares or 0.19% of the world's total land area of 13.2 billion hectares and 0.5 - 1.7% of global agricultural land (Faaij, 2008; Smeets et al., 2004). Different scenarios predicted future potential of biomass, also, many studies during the past decades attempt to estimate the future demand and supply of bioenergy (Fischer and Schrattenholzer, 2001; Fujino et al., 1999; Hall et al., 1993; Hoogwijk, 2004; IPCC, 2000; Lashof and Tirpak, 1990; Rogner, 2000; WEC,

1994). However, differences between the various scenarios and studies about the estimated amount has been found due to large differences in demand and energy mix as a result of variations in population dynamics, economic and technological development: differences in the type of biomass included; differences in the theoretical, technical, economic, or ecologic limitations related to the supply of woody biomass for energy use; differences in data on key parameters, such as the consumption of wood fuel, the annual growth of forests, and the efficiency of conversion (Ladanai and Vinterbäck, 2009). Consequently the estimation of the total global bioenergy production potential in 2050 ranged from 33 to 1,135 EJ annually, from which 0 to 358 EJ annually came from woody biomass (Hoogwijk et al., 2003; Ladanai and Vinterbäck, 2009); energy crops from surplus agricultural land have the largest potential contribution of 0-988 EJ/year (Hoogwijk et al., 2003).

Because the highest share of biomass in final energy consumption was found in Africa (60 %) (Amigun et al., 2008; Demirbas, 2005; Saidur et al., 2011), it is projected that Africa has the largest potential for bioenergy production by 2050 in the world: 317 exajoules (EJ) per year, which could constitute a quarter of the projected total world potential (1272 EJ per year) (Smeets et al., 2007). In this sense, during the last decade, Egypt has been one of the developing countries following successful programs for the development of renewable energy resources (Zannoun, 2009). There is a good potential for the utilization of biomass energy resources in Egypt; so, the incorporation of biomass with other renewable energy sources will increase the potential for solving energy and environmental problems. As a consequence, a quantitative appraisal of biomass resources and their energy potential in Egypt will be analyzed and discussed in the section presented below.

4. QUANTITATIVE APPRAISAL OF BIOMASS RESOURCES AND THEIR ENERGY POTENTIAL IN EGYPT

4.1. Geography and climate

Egypt forms the northeast corner of Africa and covers a total area of almost one million Km² (Figure 4) (EL-Shimy, 2009). It has hot and dry weather in summer and a warm winter with average rainfall of 50 mm/year. The inhabited part of Egypt is the 1,000 km valley from Aswan to Alexandria, flanked by desert (Bushra, 2000). According to the Central Agency for Public Mobilization and Statistics (CAPMS, 2013), Egypt has an estimated population of about 83 million in 2013.



Figure 4. Map of Egypt (EL-Shimy, 2009)

4.2. Energy supply and consumption

The energy sector plays a major role in Egypt's economic development. The primary energy resources and production in Egypt are shown in Figure 5. It is clear that crude oil is the most important, representing 53.11% of the total resources. Electricity from the High Dam in Aswan accounts for a share of about 5% and natural gas accounts for

41.89 % of the total resources. On the other hand, primary production of coal accounts for only 1.6 PJ, and Egypt has to import coal. The sectorial energy consumption in Egypt is summarized in Figure 6. The industrial sector accounts for about 46% of consumption, representing the highest value of energy consumption among the sectors (El Saeidy, 2004).

Production of crude oil continues to decline despite new discoveries and improvements in oil recovery techniques at mature fields. Its production had fallen from 740 thousand barrels per day (bbl/day) in 2004 to 680 thousand bbl/day in 2009. On the other hand, its consumption increased from 590 thousand to 683 thousand bbl/day over the same years, making the country a net importer of oil. In contrast, natural gas production continued to rise from 32.56 billion m³ in 2004 to 62.69 billion m³ in 2009 while its consumption increased from 31.46 to 44.37 billion m³ over the same years, and the country became a major exporter, with its natural gas exports being estimated at 18.3 billion m³ in 2009. The proven reserves of natural gas in 2011 were 2.2 trillion m³ and there is growing concern among some experts that Egypt's gas reserves could be depleted as early as 2020, after which the country could face a deficit between consumption and production (IndexMundi, 2012).

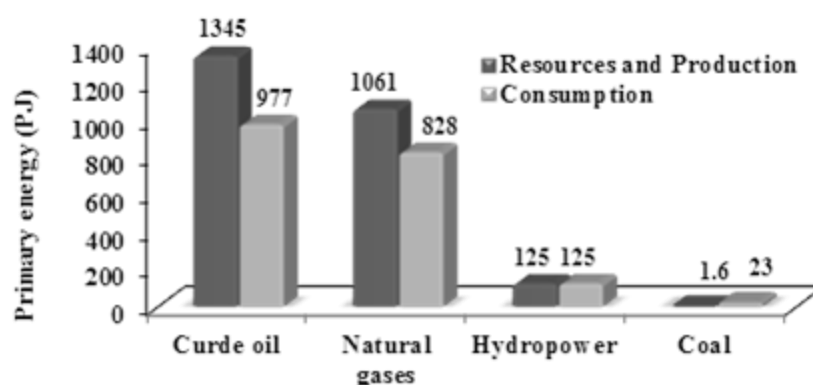


Figure 5. Primary energy resources production and consumption in Egypt (El Saeidy, 2004)

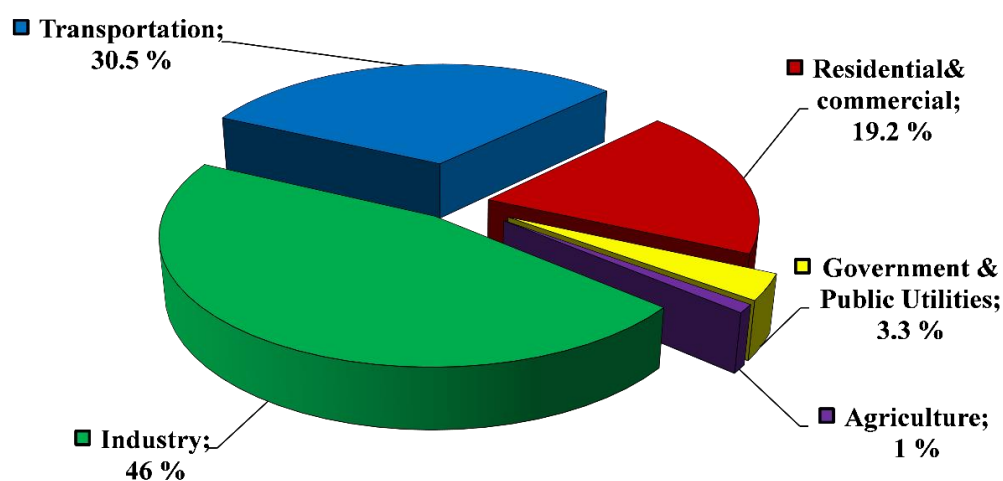
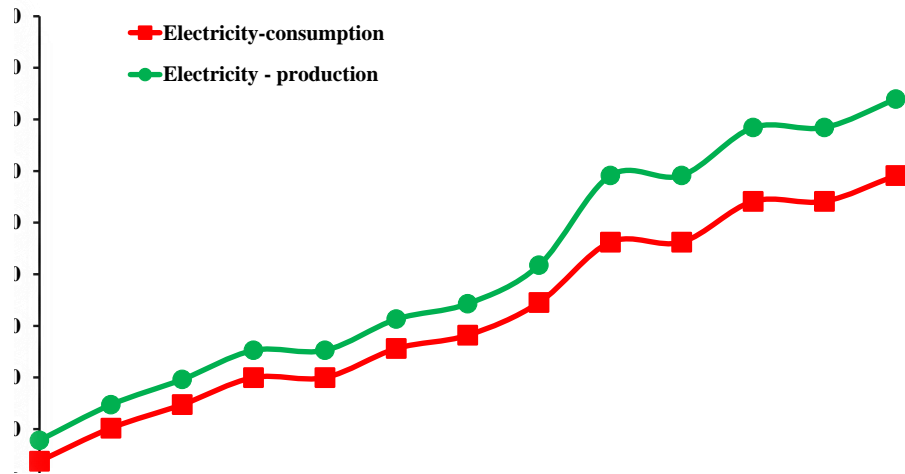


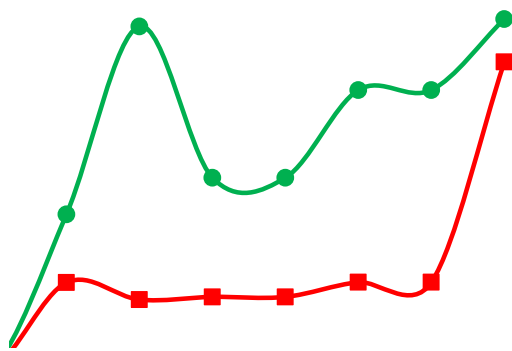
Figure 6. Sectoral consumption of primary energy in Egypt (El Saeidy, 2004)

Electrical demand and consumption are growing rapidly in Egypt. As new industrial/residential cities and tourist complexes are built and the standard of living improves, demand for electricity is increasing at a faster rate than overall economic growth (Elmassry, 2006). Figure 7a shows electrical energy production and consumption from 2000 to 2012, while imports and exports of electrical energy are shown in Figure 7b. The rapidly increasing rates of electrical energy consumption and production, whose values doubled over the last decade, can be clearly observed. The large increase in demand across all sectors is leading to high electricity generation growth rates. It has been forecast that electricity consumption will reach 250 TWh by 2020 (GTZ, 2010).

Figure 8 presents the electrical energy consumption by sector for the year 2007 as a percentage of the total electrical energy consumption in Egypt (Mahmoud, 2009). The data in the Figure show that the residential and industrial sectors account for the major parts of electrical energy consumption in Egypt: about 36.9% and 35.1% of electrical energy consumption, respectively. Together, the rest of the sectors account for only about 28% of total electrical energy consumption.



a)



b)

Figure 7. Electrical energy production and consumption a), and imports and exports by year b) (IndexMundi, 2012)

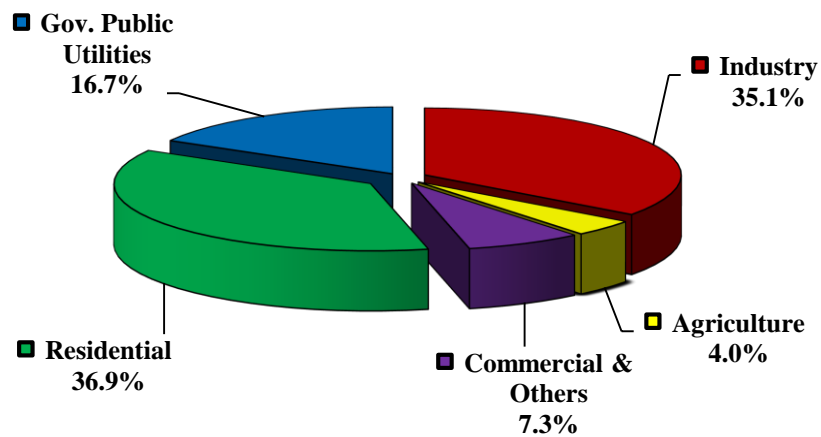


Figure 8. Electrical energy consumption by sector in the year 2007 (Mahmoud, 2009)

4.3. Energy framework in Egypt

Egypt is one of the countries expecting to face damaging effects due to climate change, although its contribution to the global greenhouse gas emissions is 0.57% (Selim, 2009) and despite that fact that it is considered a non-annex I country not requiring any specific emission reduction or limitation targets under the Kyoto protocol (UNFCCC, 2010). Nevertheless, Egypt has included in its National plans mitigation measures to reduce greenhouse gases with regards to the main sectors contributing to climate change which are energy, industry, agriculture and waste (UNFCCC, 2010). Table 3 shows the trend in GHG emissions in Egypt in the different sectors as calculated by Climate Change Central Department of the Egyptian Environmental Affairs Agency (EEAA) from year 2000 until year 2010. These calculations were based on emission increase rate of 5.1% and population increase rate of 1.7% - 2.3% (EEAA, 2012). The agricultural sector represented the highest share of GHG emissions after the energy sector.

Emissions from the energy sector are attributed to fuel combustion in the different sectors (industry, transportation, agriculture, residential and commercial, electricity generation and petroleum production and industries) and fugitive fuel emissions. Industrial emissions are associated with heavy industries such as cement and iron and steel production. Agricultural emissions are mainly those from enteric fermentation of livestock, manure management, rice cultivation, agricultural soils and field burning of agricultural residues. Finally, GHG emissions associated with waste include those from solid waste disposal sites and wastewater handling and waste incineration (UNFCCC, 2010).

Egypt has shown efforts to contribute to global greenhouse gas emissions reductions through the Kyoto Protocol's Clean Development Mechanism (CDM) (Nakhla et al., 2013). In 1992, Egypt established a climate change unit in the Egyptian Environmental Affairs Agency as the focal point of the United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol with the aim of coordinating and integrating all national and international activities relevant to climate change (EEAA and UNFCCC 2010). The unit became the Central Department for Climate Change. Then in 1997, Egypt established a National Committee of Climate Change to supervise the climate change policies. Moreover, the Egyptian Environmental Affairs Agency has assigned the Egypt Council for the CDM as the Designated National Authority to manage the CDM activities and approve suitable projects (EEAA and UNFCCC 2010).

Table 3. Estimated GHG inventory in Egypt in million tons CO₂ (EEAA, 2012).

Indicators, GHG Emission	2000	2002	2004	2006	2008	2010
Total	193.30	208.03	212.60	219.30	288.40	318.20
Energy Sector	88.91	95.69	97.79	100.87	132.66	146.37
Transport Sector	27.44	29.54	30.18	31.14	40.95	45.18
Industrial Sector	27.83	29.95	30.61	31.57	41.50	45.82
Agricultural Sector	31.70	34.11	35.45	35.96	47.29	52.18
Waste Sector	17.39	18.72	19.13	19.73	25.95	28.63

On the sectorial level, two committees in Ministry Water Resources and Irrigation were established. In addition, a climate change information Centre was formulated for Agriculture Sector and an adaptation program in Agriculture Sustainable Development Strategy up to 2030 was conducted (UNFCCC, 2010).

The Ministry of Environment along with the relevant ministries had established efforts to mitigate GHGs in the different sectors as follows (EEAA and UNFCCC 2010):

- The energy sector; Egypt's Strategy for Energy Supply and Use integrated the main policies and measure that could meet the longer term challenges including security of energy supplies; sustainability of current energy usage; and the abatement of GHG emissions. It was proposed that reductions of GHG emissions from the energy sector could be achieved through including renewable energy; energy efficiency; lower carbon fuels; nuclear power; and improved transportation fleets;
- The industrial sector; a number of policies and measures have been adapted to decrease GHG emissions per unit of product in industrial processes and product use (excluding those related to energy). However, barriers such as need of information about GHG emissions reduction opportunities; long payback periods on investments; and lack of access to investment capital and/ or high interest rate on investments, hinder the achievement of considerable GHG emissions reduction;
- The transport sector; The Ministry of Transport adopted a strategy to improve public transport; improve energy efficiency; switching of fuel; the development and use of new technologies; the development of rail transport and new methods for freight transport; the development of power train technologies; shifting from diesel to electrified railways; and the development and use of fuel cells technology;
- The agricultural sector; national efforts for GHG emission reduction included paddy rice cultivation, live- stock production, soil management, improvement of feeding patterns and technologies to enhance veterinary care, and development

of breeding programs for livestock production; an sustaining rice cultivated areas under 1.47 million acres, then reducing these to 1.26 million acres by 2017 while switching from conventional cultivars to short duration cultivar and applying intermittent irrigation;

- The waste sector; several plans and programs have been developed to improve the process of collection, reuse and recycling of waste.

4.4. Renewable energy

The Egyptian oil reserves are depleting and there are high and justifiable expectations that in the coming few years Egypt traditionally a net exporter, will be a net oil importer country. This depleting oil reserves situation has converted natural gas on the main energy source feeding growing local needs and the role of the main exported fuel that guarantees for Egypt an indispensable flow of hard currency. However, the local demand for energy and electricity has been rapidly growing at the same time where the two major energy sources of the country, namely oil and natural gas, are in a precarious situation. This double role can in fact cause a faster depletion of the rich natural gas reserves that Egypt currently enjoys (Ibrahim, 2012) so, in consequence the future of energy in Egypt is challenging.

Securing energy supply on a continuous basis is a vital element for sustained development plans, and Egypt, as a country of limited fossil fuel resources as well as growing demand for electrical energy, has given due consideration to the diversification of its energy portfolio by utilization of its renewable energy resources (El-Khayat and Ameen, 2010). Moreover, it is important that the development of Egypt is realized with the most efficient and modern energy technology as much as possible in order to reduce

the environmental impact of the improvement of the population's well-being (Patlitzianas, 2011).

Acknowledging this critical energy situation and in order to face this challenge, the Supreme Council of Energy has approved in 2008 a strategy to diversify the energy sources in the electricity sector and reduce the dependency on fossil fuel by considering a larger contribution from renewable energy sources. Accordingly, the share of renewable energy in the electricity generation should reach 20% by the year 2020 (Abdel Halim et al., 2003). This target is expected to be met largely by scaling-up of wind power as solar is still very costly and the hydro potential is largely utilized. The share of wind power is expected to reach 12%, while the remaining 8% would come from hydro and solar. This translates into a wind power capacity of about 7200 MW by 2020 (Ibrahim, 2012).

The Egypt's New and Renewable Energy Authority (NREA) was set up in 1986, with the establishment of testing and certification laboratories and personnel training. The practical work of NREA began with assessing renewable energy resources and investigating the choices of different technologies through studies and pilot projects, as well as introducing some of these technologies to the Egyptian market and supporting the initiatives of local industry. In pursuit of its reform agenda, the Egyptian government has set an ambitious renewable energy program to generate 500 MW of solar energy, more than 600 MW of wind power, and 600 MW of hydroelectric power by 2017 (Ahmed and Abouzeid, 2001). Egypt has large deserts and abundant land mass, only 7% of which is heavily populated. These areas are well suited to host renewable

energy projects to increase the country's share of renewable energy as well as to export excess energy to Europe.

The Egyptian national grid is extensive, providing over 99% of the population with modern electric energy services. Currently, grid connected renewable energy projects in Egypt enjoy the right of access and priority in dispatching. Through the current world concern with searching about new energy resources; supporting renewable energy technologies already in use, increasing the efficiency of current systems and promoting renewable energy technology worldwide, the United Nations and other international organizations are supporting a lot of projects and programmers especially in developing countries (Ibrahim, 2012).

Increasing penetration of renewable energy sources within the energy sector in Egypt is essential. For that reason, different stakeholders must join together to develop renewable energy technologies. The anticipated local market share for manufacturing different renewable energy technologies is presented in Table 4.

Table 4. Potential share of local manufacturers of renewable energy equipment (Khalil, 2007).

Technology	Share of local manufacturers (%)	
	Reactive policy	Proactive policy
Wind energy	40	60
Solar water heaters	70	95
Photovoltaic systems	20	30
Biomass	50	95
Concentrated solar power	30	50

This table shows that the local share of renewable energy equipment manufacture could range from 30% to 95% depending on the technology. The estimated share is totally dependent on the establishment, development and monitoring of an appropriate renewable energy strategy (Khalil et al., 2010).

4.4.1. Renewable energy resources

Different renewable energy resources have been applied in Egypt. For example hydropower has played a role in electricity generation for decades and solar and wind energy are substantial in the country and represent the greatest potential for widespread application, offering significant potentials for the energy problem solving in Egypt (Ibrahim, 2012). Recently, biomass has also begun to contribute in electricity production (Ghazy et al., 2009). The present share of hydropower and wind energy is 12% and 1.8% of electricity generation, respectively (Hamouda, 2012; Ibrahim, 2012), meanwhile, the share of solar and biomass energy is still limited and in progress.

Each renewable energy technology is positioned in relation to each other in line with the strategic goals and objectives including long-term market vision. Potential market attractiveness factors include: average annual growth rate and size, value added for industry, competition strength, technology requirements, technology maturity and expected future environmental impacts, technology provisions, implementation satisfaction (Khalil et al., 2010). The five selected renewable energy technologies are positioned for Egypt based on these factors in Figure 9. This figure shows that wind energy (WE) technology is leading all other technologies in power generation (Khalil, 2007) followed by solar water heating (SWH). Concentrating solar power (CSP) technology is in last position. PV technology is located in the medium range of

positioning, considered a harvesting domain, followed by biomass technology (Khalil et al., 2010).

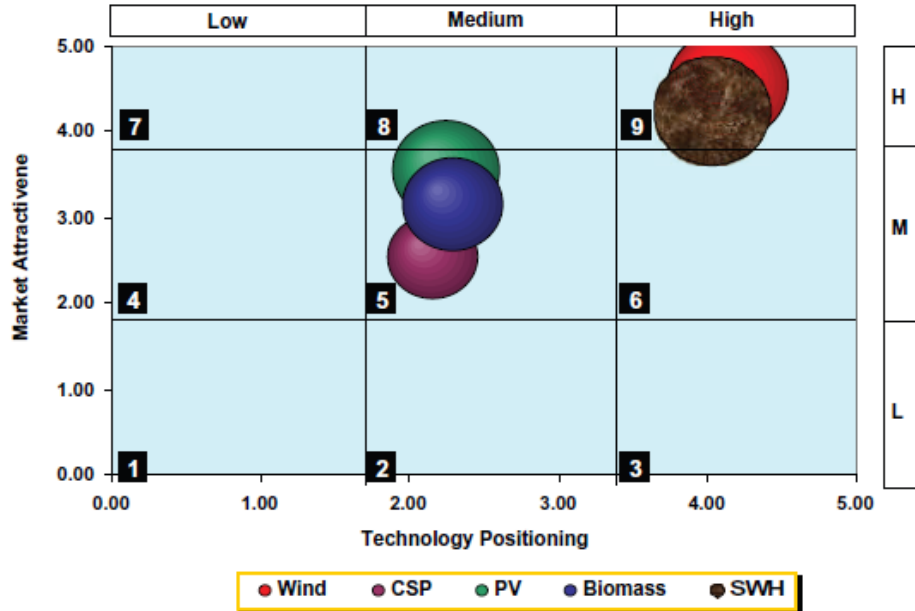


Figure 9. Positioning of renewable energy technologies in Egypt (Khalil, 2007; Khalil et al., 2010).

A brief revision of renewable energy sources have been included bellow.

4.4.1.1. Hydropower

In 2009, renewable energy, mainly hydropower, accounted for 12% of Egypt's electricity generation. Government policy has consistently emphasized hydropower, but there is a view that most potential hydro resources have been already developed. Nowadays Egypt's hydropower potential is about 3664 MW with an estimated energy of 15,300 GWh/annum. There are currently five main hydropower generation locations, all of which located on the River Nile. Almost all the electricity generation comes from the Aswan High Dam and the Aswan Reservoir Dams. The Aswan High Dam power project has a theoretical generating capacity of 2.1 GW, although low water levels often

prevent it from operating anywhere near design capacity. An ongoing refurbishment program is expected to extend the operational life of the turbines by about 40 years and increase generating capacity at the dam to 2.4 GW. The remaining hydropower sites are considered very modest when compared to the Aswan sites (Ibrahim, 2012).

4.4.1.2. Wind energy

Egypt is endowed with an abundance of wind energy resources especially in Suez Gulf area which considered one of the best sites in the world due to high and stable wind speeds. The West of Suez Gulf Zone is the most promising sites to construct large wind farms due to high wind speeds which ranges between 8 and 10 m/s in average, proximity to load centers and transmission infrastructure, and availability of large uninhabited desert area. There are also other promising sites having wind speed of 7–8 m/s in the east and west of River Nile near Beni Suef and Menia Governorates and El Kharga Oasis in the New Valley Governorate. Nonetheless, the geographic concentration of large wind farms is expected to be one of the main challenges that need to be adequately studied and addressed before large scale development takes place (Ibrahim, 2012).

The first phase of the Wind Atlas for Egypt was finalized in March 2003 with the publication of the detailed Wind Atlas for the Gulf of Suez (Mahammad, 2007). This atlas includes wind data for 13 sites covering the decade from 1991 to 2001. The second phase of the project, the Wind Atlas for Egypt: Measurements and Modeling 1991–2005, was released in 2006, covering Egypt's entire land area based on a comprehensive eight-year wind-resource assessment. The purpose of the Wind Atlas was to establish a meteorological basis for assessing Egypt's wind energy resources in six designated

regions: the northwest coast, the northeast coast, the Gulf of Aqaba, the Gulf of Suez, the Red Sea, and the western desert. According to the Wind Atlas, the western part of the Gulf of Suez is home to some of Egypt's best wind resources. Here, average yearly wind speeds surpass 7 m/s, and there is potential for some 20,000 MW of wind capacity. The Gulf of Suez is the region where both short- and medium-term plans for Egypt's wind energy developments are focused.

Figure 10 illustrates the distribution of wind-generation potential in Egypt at a height of 50 m. 36 Pink, red, and purple areas indicate areas with economic potential for wind energy generation, while yellow areas represent marginal ones. Already, Egypt has a plethora of wind farms in the Zafarana region along the Red Sea, with a total installed capacity of 430 MW. Meanwhile, a solid plan for an additional 280 MW of installed capacity in this region is under way. Plans for two plants of 120 MW each, and one 200 MW plant, are also being pursued in Zafarana and Gulf El-Zayt with assistance from Germany, Japan, and Spain, respectively. A long-term plan for increasing national wind-farm capacity to 7500 MW by 2020 exists and has been approved by Egypt's Supreme Council of Energy (Salama, 2006).

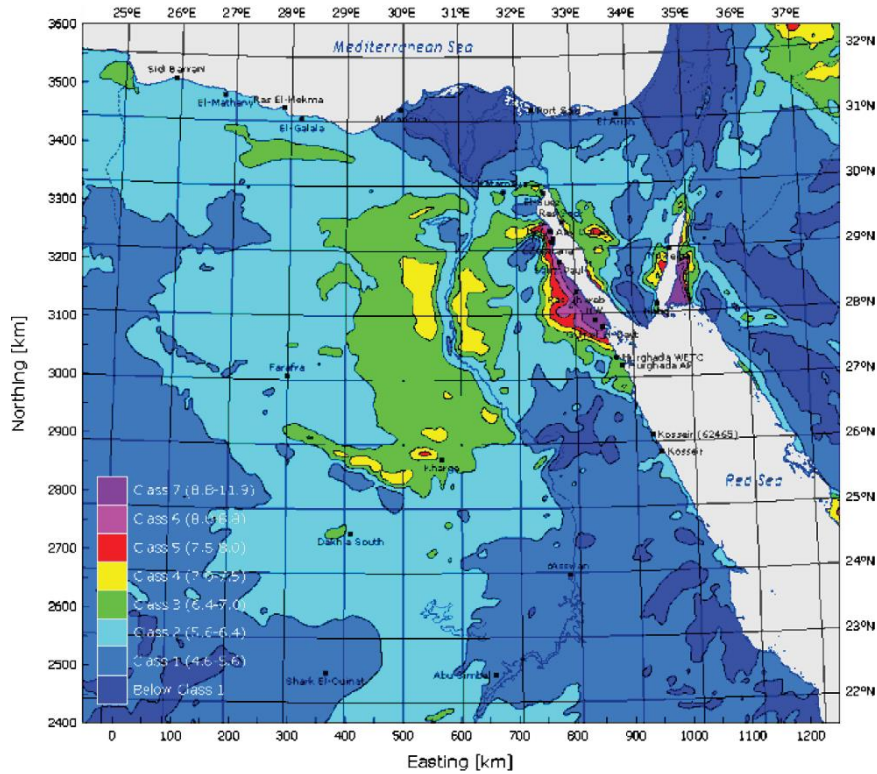


Figure 10. Wind regime map for Egypt (wind atlas for Egypt).

4.4.1.3. Solar energy

According to the 1991 Egyptian solar radiation Atlas, the country averages between 5.4 and more than 7.1 (kWh/m^2) of annual daily direct solar radiation, from north to south (Elsobki, 2009). The annual direct normal solar irradiance ranges from 2000 kWh/m^2 to 3200 kWh/m^2 , rising from north to south, with a relatively steady daily profile and only small variations in resource (Figure 11). Such conditions are supported by 9–11 h of sunlight/day, with few cloudy days throughout the year. Thus, Egypt has very favorable solar resources for a variety of solar energy technologies and applications. Both the solar radiation Atlas and the German Aerospace Center estimate Egypt's economically viable solar potential in the range of 74 billion MWh/year, or many times Egypt's current electricity production (Mortensen et al., 2005). The Energy Research Center at Cairo University's Faculty of Engineering estimates that 6 MW of solar PV are

currently installed in Egypt. In addition, a 150 MW integrated-solar combined-cycle power plant is under construction in Kureimat, with a solar component of 30 MW.

In the South Countries, enjoying more than 250 uninterrupted sunshine days, the development potentials of solar energy appears very obvious, despite the relatively higher cost of this energy (in kW/h) compared to other renewable energy technologies such as wind energy. Patlitzianas (2011) studied the business opportunities for solar energy development in Egypt and found that they are really significant and Egypt is an interesting example to show the practical possibilities of the development of Solar Energy in Southern Mediterranean countries. Significant business opportunities in Egypt will come out through the Mediterranean solar plan that is expected to cover numerous projects based on various technologies involving the countries of the Southern and Eastern regions of the Mediterranean. The general objective of the Mediterranean solar plan is the creation of a total of 20 GW of new generation capacity from solar and other renewable energy sources around the Mediterranean Sea by 2020.

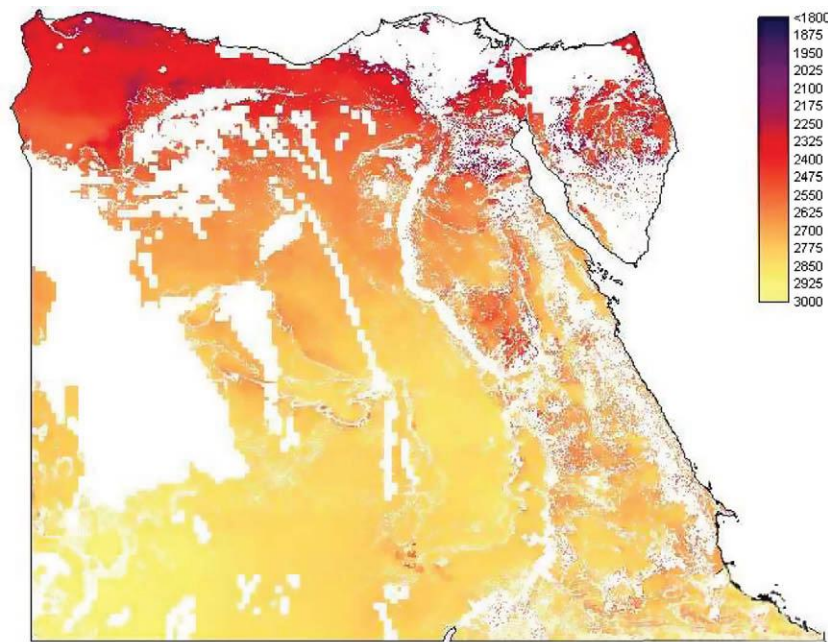


Figure 11. Solar radiation intensity map for Egypt (solar atlas for Egypt).

4.4.1.4. Biomass energy

Egypt produces millions of tons of biomass waste every year, which could contribute more than 151 PJ (petajoules) of primary energy (NREA, 2002). Biomass resources are currently used inefficiently, particularly agricultural residues, which are combusted in open fire stoves in villages (Zannoun, 2009). However, real environmental benefits of biomass utilization can be achieved through large-scale application of biomass-based fuel to generate energy (Mat, 2003). Furthermore, there have been insufficient investigations regarding the production of biomass in Egypt and an analysis of existing and potential biomass sources will be required well before the start-up of large-scale production of bioenergy from this renewable fuel. As a consequence, biomass resources and their energy potential in Egypt will be analyzed and discussed in the sections presented below, where, biomass resources have been estimated based on agricultural residues, animal wastes, sewage wastes, and solid wastes.

4.5. Biomass resources in Egypt

4.5.1. Agricultural residues

Agricultural residues are the amount of crop that remains after the collection of the main product. Residues depend upon a wide range of local conditions and the primary factors influencing the amount of crop residue are the type and variety of crops planted and their yields (Karaj et al., 2010). The effective total cultivated area is around 6.09 million ha annually (EQI, 2005) and approximately 3.44 million ha of land are cultivated in Egypt, yielding crops two or three times a year. Therefore, Egypt produces millions of tons of agricultural wastes every year (Aref, 1995; Shehata, 2002; Youssef et al., 2009), contributing to about 50% of the total biomass potential (NREA, 2000).

Over 27 million tons of crop residues were generated in 2003 (GTZ, 2006). Types of crop residues and their estimated quantities and percentages in relation to the total residue generation are listed in Table 5. Wheat straw is the most abundant residue, followed by maize, rice straw, and sugar cane residues, respectively. Actual crop residue generation may vary by 10 to 15% or more in any given year. Table 5 lists the quantity and percentage of each crop residue produced during the year 2004. At least 77.8% of the crop residues are reutilized for various purposes other than for energy generation, as shown in Table 6.

Table 5. Estimated crop residue generation and utilization in Egypt during the year 2004 (GTZ, 2006).

Types of residues	Residue generation (per year)		Total utilization (per year)	
	(1000 tons)	Percentage (%)	(1000 tons)	Percentage (%)
Wheat straw	8212	30	8130	99
Rice straw	4968	18.2	1900	38.2
Maize residue	6655	24.3	5657 to 6322	85.0 to 95.0
Sorghum stalks	1272	4.6	1208	95.0
Barley straw	212	0.8	196	92.5
Cotton stalks	1252	4.6	626	50.0
Sugar cane residue	4793	17.5	3830	80.0
Total	27364	100	21284 to 21949	77.8 to 80.2

Nationally, unutilized crop residues are estimated to amount to between 4.422 and 5.684 million tons. The largest amount of unused crop residue is rice straw, by a wide margin (GTZ, 2006), followed by cotton stalks. Hamdy (1998) mentioned that about 52% of

agricultural residues are burnt directly on the fields or in inefficient burners (with less than 10% efficiency) in small villages. Both methods result in loss of energy as well as negative impacts on the environment. Moreover, traditional storage in farms and on roofs provides a large opportunity for insects and other disease carriers to grow and attack humans, animals, or new crops (El-Mashad et al., 2003). The burning of crop residues is, however, practiced by farmers, despite legal requirements (GTZ, 2006).

Table 6. Major uses of crop residues in Egypt (GTZ, 2006).

Crop residue	Use
Wheat straw	Animal feed
Rice straw	Composting, animal bedding, vegetable storage, animal feed following treatment with urea or ammonia, and manufacture of construction products
Maize residues	Animal feed and fuel
Sorghum stalks	Animal feed and fuel
Barley straw	Animal feed
Cotton stalks	Fuel
Sugar cane residues	Animal feed , building material, industrial fuel, and paper manufacture

4.5.2. Animal wastes

Animal wastes are another form of biomass used for energy generation. The amount of animal waste residue depends on the animal's type, size, and population density for each location (Karaj et al., 2010).

Large amounts of animal wastes are produced in Egypt. The total cattle herd (including domesticated buffalo) in 2009 was estimated at about 6.248 million head (Maldonado and Sherif, 2010). Table 7 shows that the total amount of cattle (buffalo and cow) manure is about 10.5 million tons/year (El-Mashad et al., 2003; Hamdy, 1998), representing the majority of animal waste.

Table 7. Total production of animal wastes in Egypt (El-Mashad et al., 2003; Hamdy, 1998).

Animal	Total waste (1000 tons/year)
Cows	5403
Buffaloes	5097
Horses, asses, mules, and camels	2348
Sheep and goats	729
Chickens, ducks, and turkeys	< 1
Total	13578

The uncontrolled handling and storage of manure causes loss of organic matter and also pollution problems. Hamdy (1998) mentioned that about 60% of cattle waste is used as fuel by direct burning in low efficiency burners (less than 10%); another 20% of the animal waste is used as organic fertilizer, and the rest is lost in handling. From the overview given in Table 7, it can be concluded that cattle manure has the greatest potential to be used as a source of clean energy and organic fertilizer. It can also be concluded that sustainable treatment of such resources is of vital concern for Egypt.

4.5.3. Sewage waste

The sludge waste from urban and industrial sewage treatment plants comprises residuals that have serious effects on the environment. Due to the increasing population density and the currently low capacity for wastewater treatment prevailing in Egypt, a future increase in the number and capacity of wastewater treatment plants (WWTPs) can be expected. As a consequence, the amount of sewage sludge produced is also expected to increase.

Based on population studies and rates of water consumption, the total wastewater flows generated by all governorates in Egypt, assuming full coverage by wastewater facilities, were estimated by Lasheen and Ammar (2009) at about 3.5 billion m³/year. Approximately 1.6 billion m³/year is treated, and additional treatment plant capacity equivalent to 1.7 billion m³ is planned by the year 2017. Depending on the currently applied treatment technology, the amount of sewage sludge produced in Egypt was estimated at around 2 million tons/year of dry sludge in 2008 (Ghazy et al., 2009).

For many years, the methods and technologies implemented for sewage sludge treatment in Egypt were very limited. Recently, the application of anaerobic digestion technology for sludge stabilization and power generation was applied in Al Gabel Asfer WWTP. Windrow composting of dried sewage sludge is another type of sludge treatment that has been recently applied in Egypt, having been already applied in the Al Berka WWTP in Cairo and the (9N) site in Alexandria. These WWTPs are the largest centralized wastewater treatment plants in Egypt and produce more than 50% of the total dry sewage sludge produced in all of Egypt's WWTPs. The dried sludge from these plants is mainly reused in agriculture. About 0.66 million tons of the dried sewage

sludge were sold to farmers in 2007, representing more than 85% of the total sewage sludge produced by all WWTPs in Egypt (Ghazy et al., 2009).

4.5.4. Municipal solid wastes

Municipal solid wastes, which comprise garbage, originate from residential, commercial, and institutional sources as well as construction, demolition, and municipal services (Tchobanoglous et al., 1993). In general, the more urbanized the area is, the higher the amount of waste generation per capita (Tchobanoglous et al., 1993). A positive correlation exists between increased welfare and generation of municipal waste (Karaj et al., 2010).

Egypt generated an estimated 15.3 million tons of municipal solid waste in 2001, of which approximately 75% was generated in urban centers (CEA, 2002). According to the Central Agency for Public Mobilization and Statistics, the estimated municipal solid waste generated in Egypt reached about 34.6 million tons in 2007.

The typical composition of municipal solid waste in Egyptian cities is shown in Table 8, where organic waste is the main component, representing 60% of the waste produced (Badran and El-Hagggar, 2006; Bushra, 2000; EQI, 2005). Eleven percent of the material is denoted as “other” and mainly includes construction and demolition debris and hazardous waste.

Between 30% and 50% of the municipal solid waste generated in developing countries is usually left unattended on the streets or vacant land plots (Abdrabo, 2008; UNEP, 2003). In this sense the quantity of uncollected solid wastes in different governorates in

Egypt reached a total of 25 million m³ by 2004 (EEAA, 2005). Landfilling and incineration have recently been introduced in Egypt as more environmentally sound solid waste treatment techniques (EQI, 2005). Sanitary landfilling is usually the lowest-cost option, as long as the required landfill area is available. There are no landfill regulations or standards that provide a basis for compliance and monitoring; however national guidelines for these standards are being prepared by the EEAA. The practice of sanitary landfilling is still in its infancy in Egypt (Bushra, 2000).

Table 8. Typical composition of municipal solid wastes in Egyptian cities (Badran and El-Haggar, 2006; Bushra, 2000).

Waste composition	Percentage (%)
Organic waste	60
Paper	10
Plastic	12
Glass	3
Metals	2
Textiles	2
Other	11

4.6. Theoretical energy potential from biomass in Egypt

The information presented in the previous section has shown the high biomass production in Egypt, based on agricultural residues, animal waste, sewage waste, and solid waste. These could be used to produce bioenergy, reducing fossil fuel consumption and also improving the environment as a safe method of waste disposal.

The theoretical energy potential from biomass in Egypt has been analyzed in this study. The results are summarized in the subsections below.

4.6.1. Theoretical energy from agricultural crop residues

To estimate the theoretical energy potential of crop residues, according to Klass (1998), several parameters are necessary: theoretical annual crop production, annual theoretical residue production, availability, and dry weight. The collectible dry residue or dry biomass (D_b) is the theoretical biomass production in terms of weight. It is determined by Equation (1) for a given crop. In this mathematical expression, A_{cp} is the theoretical annual crop production in tons, r is the residual factor that gives the total mass of residue when multiplied by the total country yield for that crop generated, a is the availability factor or availability of collectible crop residues as waste biomass, and w is the dry weight factor expressed as a percentage.

$$D_b = A_{cp} \times r \times a \times w \quad (1)$$

Table 5 shows agricultural crop production and dry biomass according to Equation (1) based on agricultural crop production in Egypt for the year 2007 according to CAPMS (2013). The residue factor (r) and availability factor (a) have been considered following Klass (1998). The highest theoretical dry biomass production corresponded to rice (7.86 million tons/year).

4.6.1.1. The potential energy content

The potential energy content of the collectible dry residue (P_e) has been calculated using Equation (2) (Klass, 1998), where D_b is the amount of residue, O_c its organic content expressed as a percentage, and HHV the higher heating value of the organic material.

$$P_e = D_b \times O_c \times \text{HHV} \quad (2)$$

Table 9 also shows the potential energy from biomass according to Equation (2); the organic content (%) and HHV (18.6 GJ/ dry tons) have been determined according to Klass (1998).

Although wheat straw represents the highest amount among the crop residues and has considerable biomass and energy content, it was excluded from the mathematical analysis because 99% of it is used as animal feed. Barley straw was also excluded from the analysis because it is generated in low quantities and is mainly used as animal feed (Tables 5 and 6). So in this study, wheat and barley straw have not been included as suitable candidates for crop energy production in Egypt.

The analysis indicates that a total of 12.33 million tons/year of dry biomass could produce a theoretical energy of 185.75 PJ/year. The biomass that could give the highest theoretical energy production is rice (113.99 PJ/year). The rest of the crops include biomass with considerably lower potential energy content.

Table 9. Theoretical agricultural crop production, dry biomass, and potential energy in Egypt calculated according to estimated crop production in 2007.

Crop	Production (A_{cp}) (1000 tons/year)	Residue factor (r)	Available factor (a)	Dry weight % (w)	Dry biomass (D_b) (million tons/year)	Organic content (O_c)%	Energy content (P_e) (PJ/year)
Sugar cane	16656	0.52	1.00	20	1.73	84	27.06
Rice	6868	1.43	1.00	80	7.86	78	113.99
Maize	5572	1.10	0.60	53	1.95	90	32.63
Sorghum	827	1.57	0.64	40	0.33	84	5.19
Cotton	621	2.45	0.60	50	0.46	81	6.88
Total					12.33		185.75

4.6.1.2. Potential energy of some residues in different forms

Considering the important role of biomass for energy production and its increasing importance in the transport sector, studies on biomass utilization and the production of bioenergy and biofuels should be undertaken. In Egypt, transportation fuels represent around 30.5% of the total fuel energy consumption. The availability of high energy materials in Egypt suggests that biofuel (especially ethanol) is highly feasible if there is access to proper low-cost conversion and fermentation technologies (Aly and Megeed, 2008). The use of lignocellulosic biomass residues as feedstocks (i.e. starting material) allows a substantial increase in the fuel ethanol production capacity and a reduction in the cost of ethanol production to a competitive level (Reith and Uil, 2002). Rice straw, maize residues and sugar cane residues are the most abundant lignocellulosic agriculture wastes produced in Egypt and the most suitable candidates for biofuel production (Aly and Megeed, 2008).

Table 10 shows the theoretical ethanol yield and energy content from rice straw, maize residues, and sugar cane residues; the theoretical ethanol yield and the energy content of bioethanol (19.6 MJ/L) have been calculated according to Aly and Megeed (2008). The total theoretical energy content of ethanol from these residues is about 94.8 PJ/year. Rice straw represents the highest value among these residues, accounting for about 67.5% of the total energy content. So, it is considered the most important of such residues and can be used as a clean fuel to decrease the dependence on crude oil in the transportation sector and to provide an environmentally safe technology for the straw disposal. Not only ethanol but also other different forms of bioenergy can be recovered by biochemical conversion of rice straw through different available techniques, such as

biogas from anaerobic digestion, syngas through gasification, or bio-oil from pyrolysis (Jung et al., 2008; Liang et al., 2009).

The potential energy based on the estimated amount of rice straw biomass has been estimated in the forms of bio-oil, syngas, and biogas. The bio-oil yield (68% of straw weight) and its heating value (19.00 MJ/kg oil) have been taken from Jung et al. (2008), while the syngas yield (1.84 m³/kg straw) and its heating value (6.01 MJ/m³ gas) have been found according to Liang et al. (2009). The heating value for biogas (6.81 MJ/kg straws) was estimated according to Summers (2001). The estimated values of potential energy from bio-oil, syngas, and biogas were 101.55, 86.92, and 53.53 PJ/year, respectively. So, pyrolysis is the best technique for recovering energy from rice straw, followed by gasification, biochemical conversion, and finally anaerobic digestion.

Table 10. Ethanol production and its energy content from lignocellulosic biomass in Egypt.

Lignocellulosic biomass waste	Dry biomass (10⁶ ton /year)	Ethanol yield (L/dry ton)	Ethanol production (10⁶ L/year)	Energy content (PJ/year)
Rice straw	7.86	416	3269.76	64.0
Sugar cane residues	1.73	424	733.52	14.4
Maize residues	1.95	428	834.60	16.4
Total	11.54		4837.88	94.8

4.6.2. Theoretical energy from animal waste

Animal waste has been mainly used as fertilizer (Basso and Ritchie, 2005; Kuligowski et al., 2010; Schröder, 2005); however the anaerobic digestion of manure is known to

have the potential to produce energy (Wilkie et al., 2004). This technology has the potential to solve waste-handling problems while producing renewable gas, electricity, heat, and also fertilizer (Oregon, 2009).

Using Xuereb's conversion factor of 130 MJ/gal (Xuereb, 1997), Cooper and Laing (2007) estimated that the energy (biogas) produced annually from a single head of cattle is equal to 50 gallons of gasoline. Taking into account the total cattle population in Egypt as indicated above (6.248 million head of cattle), the theoretical total potential is 40.61 PJ of energy, which equals approximately half the amount of bioethanol energy that would be produced from lignocellulosic residues in Egypt.

4.6.3. Theoretical energy from sewage sludge

With improved control and treatment of industrial wastewater, sewage sludge can be utilized as a valuable fertilizer and soil conditioner as well as for energy production by collecting methane from sludge digestion, which can generate electricity in a secondary step (EIB, 1999; Lasheen and Ammar, 2009).

In this study, theoretical electrical generation from 1 kg of dry sewage sludge has been calculated as 0.78 kWh/kg of dry sludge, assuming that the quantity of digested gas obtained during the anaerobic digestion is 1 m³/kg of volatile solids destroyed and the lower heating value of the digested gas is approximately 6.22 kWh/m³ (Ghazy et al., 2009).

Considering the theoretical sewage sludge production explained in Section 3.3 (2.0 million tons of dry sludge), the estimated annual theoretical electrical energy generated

from 0.78 KWh/kg of dry sludge is about 1560 GWh. The average calorific value used in the energy calculation for sewage sludge is 2000 kcal/ kg dry matter (NREA, 2002). The potential energy from sewage sludge in Egypt can be estimated as about 16.74 PJ based on the indicated amount of sewage sludge and its average calorific value. Despite its minor energy content, it may contribute to the observed amount of the energy used to operate the WWTP that produces this sludge.

Energy production from sewage sludge is fairly well developed in Egypt. For example Al-Gabel Al-Asfer WWTP is the biggest wastewater treatment plant in Egypt, having a current sewage treatment capacity of 1.8 million m³/day, which will be increased to 3.0 million m³/day in 2020. The application of anaerobic digestion technology for sludge stabilization and power generation in Al-Gabel Al-Asfer WWTP has achieved good results and considerable experience of operation and maintenance has been gained. A large portion of the biogas produced is currently used for the operation of hot water boilers, which are used to heat the raw sewage sludge in the primary digesters. Dual fuel generators use the excess digested gas to generate electricity, representing about 37–68% of the power consumed by the WWTP. The digested sludge is dewatered, dried, and then reused in agriculture. Thus, there is an interest in using such technology on a large scale in Egypt, especially in big wastewater treatment plants in major cities (Ghazy et al., 2009).

4.6.4. Theoretical energy from municipal solid waste

Energy can be recovered from the organic fraction of waste through two methods: (i) thermo-chemical conversion by incineration and (ii) bio-chemical conversion by

anaerobic digestion in which only the biodegradable fraction of the organic matter can contribute to the energy output.

4.6.4.1. Theoretical energy from thermo-chemical conversion by incineration

In thermo-chemical conversion all of the organic matter, biodegradable as well as non-biodegradable, contributes to the energy output. The power generation potential (P_{gp}) and the net power generation potential (NP_{gp}) from waste, both expressed in kilowatt hours, have been estimated using Equations 3 and 4 (CPH and EEOC, 2000), where W is the total quantity of waste (tons), NCV is the net calorific value (k-cal/kg), and CE is the conversion efficiency.

$$P_{gp} = \left(\frac{1000}{860} \right) \times W \times NCV \quad (3)$$

$$NP_{gp} = P_{gp} \times CE \quad (4)$$

In this study NCV has been considered as 1200 k-cal/kg when CE is 25% (CPH and EEOC, 2000). Taking into account the estimated amount of solid waste available in Egypt in 2007, the power generation potential becomes 48279 GWh (173.8 PJ) and net power generation potential becomes 12069.8 GWh.

4.6.4.2. Theoretical energy from bio-chemical conversion through anaerobic digestion

In bio-chemical conversion, only the biodegradable fraction of the organic matter can contribute to the energy output. In this case P_{gp} and NP_{gp} from waste, both expressed in kilowatt hours, can be estimated by Equations 4 and 5 (CPH and EEOC, 2000), where W is the total quantity of waste (tons), VS is the total organic/volatile solids (say 50%), OBF is the organic bio-degradable fraction (approx. 66% of VS), DE is the typical

digestion efficiency (60%), BY is the bio-gas yield ($0.80 \text{ m}^3/\text{kg}$ of VS destroyed), CV is the typical calorific value of bio-gas (5000 kcal/m^3), and CE is the typical conversion efficiency (30%).

$$P_{gp} = \left(\frac{1000}{860} \right) \times W \times VS \times OBF \times DE \times BY \times CV \quad (5)$$

For 34.6 million tons of solid waste, the power generation potential is equal to 31864.2 GWh (114.7PJ) and net power generation potential is 9559.3 GWh.

From the previous results it can be noticed that the power generation potential value obtained from solid waste using thermo-chemical conversion is greater than that obtained using biochemical conversion. This is because all of the organic matter, biodegradable as well as non-biodegradable, contributes to the energy output in thermo-chemical conversion. Meanwhile, in bio-chemical conversion only the biodegradable fraction of the organic matter can contribute to the energy output.

4.6.5. Theoretical potential energy from biomass

Table 11 summarizes the maximum theoretical potential energy that could be obtained from biomass wastes in Egypt, considering biomass from agricultural crops, sewage sludge, municipal solids, and animal waste. It is possible to conclude that the total theoretical energy production from biomass is 416.9 PJ, representing 92.6% of the total production in all installed power plants in Egypt nowadays.

Because of the large amount of residual biomass from agricultural crops and its considerable energy content, it represents the major part of the total theoretical energy

(44.6%), followed by municipal solid waste (41.7%); on the other hand, animal waste accounts for about 9.7% and sewage sludge for only 4.0% of the total amount. Due to the increase in crude oil consumption and decrease in its production over the years, the potential energy of agricultural crop residues and solid waste may contribute to decreasing the consumption of crude oil by approximately 19% and 17.8%, respectively, based on its consumption amount, which is indicated in Figure 5.

Finally, rice straw represents the most important agricultural biomass residue due to its large amount and high energy potential, accounting for about 61.5% of the potential energy of crop residues, and its energy can be recovered in different forms such as bioethanol, bio-oil, biogas, and syngas.

Table 11. Theoretical potential energy from biomass residues in Egypt.

Biomass type	Theoretical potential energy (PJ)	Percentage of total energy (%)
Agricultural crop residues	185.75	44.60
Animal wastes (cows and buffalo)	40.61	9.70
Sewage waste (sewage sludge)	16.74	4.00
Municipal solid waste	173.80	41.70
Total	416.90	100.00

4.7. Conclusions

The main sources of biomass waste in Egypt are agricultural waste (crop residues), followed by sewage waste, municipal solid waste, and animal waste. The amount of dry biomass produced from agricultural crop residues is about 12.33 million tons/year, and 63.75% of this amount is produced from rice straw.

According to the quantity of biomass waste calculated in this study and its energy content, agricultural crop residues represent the highest value of theoretical potential energy from the main biomass sources in Egypt; this source could produce 44.6% of the total theoretical energy potential. Agricultural crop residues are followed by municipal solid waste, which could produce 41.7% of the total theoretical energy potential from an annual amount of 34.6 million tons. Ethanol production from agricultural crop residues is a feasible option for second generation biofuel production in Egypt. Lignocellulosic agricultural wastes are cheap renewable resources and allow a substantial increase in fuel ethanol production capacity. Rice straw, maize residues and sugar cane residues are the most abundant lignocellulosic agricultural biomasses produced in Egypt, and represent the most suitable candidates for ethanol production. In this study, the total theoretical ethanol yield from these wastes is estimated at about 4837.88 million L/year, with an energy content of 94.8 PJ/year, of which 67.5% of the energy is represented by rice straw. As a consequence, crop residues, especially rice straw, would represent a good candidate as a renewable energy source in Egypt which could be used as a clean fuel and would decrease the dependence on fossil fuel; its energy can be recovered in other different forms such as bio-oil, biogas, and syngas.

Finally, buffalo and cow manure represent the major part of animal waste in Egypt. About 6.248 million head of buffalo and cows could produce 9.7% of the total theoretical energy. On the other hand, 2 million tons/year of dry sewage sludge accounts for only 4.0% of total theoretical energy production.



CHAPTER 3

**CHARACTERIZATION OF RICE STRAW AS
A RENEWABLE FUEL**

Based on the analysis of biomass resources and their potential energy in Egypt, the rice straw residues represented the most important among the different biomass residues due to the high unutilized amount and potential energy, and the possibility of use it as a renewable fuel for heat and power generation, replacing fossil fuels and preventing pollution caused by open burning. In consequence, studying the characterization of residue biomass from rice straw for recovering its energy is the first step and it was the main objective of this chapter.

1. INTRODUCTION

Rice straw is considered to be the most important of agriculture residues and represents one of the major by-products from rice production process in most rice producing countries (Abou-Sekkina et al., 2010; Said et al., 2013a). The rice collection harvest generates large amounts of straw, for each ton of grain harvested, about 1.35 tons of rice straw remain in the field (Kadam et al., 2000) making up approximately 50% of the dry weight of rice plants, with a significant variation of 40–60% depending on the crop and agricultural method. The annual production of rice straw is about 731 million tons which is distributed in Africa, Asia, Europe, America and Oceania as 20.9, 667.6, 3.9, 37.2 and 1.7 million tons, respectively (Balat et al., 2008; Sarkar et al., 2012).

During the rice harvest, the elimination of rice straw is frequently carried out by farmers by burning it in the fields because of the difficulty and high cost of removing it and because of its null use (Abril et al., 2009); the justification for this practice is the reincorporation of part of the necessary nutrients for the crop (N, P, K and amorphous silica) (Datnoff et al., 1997). However, open burning after grain harvest results in emissions to air that have a deleterious effect on air quality and human health

(Suramaythangkoor and Gheewala, 2010); these emissions show high concentrations of pollutants in form of particles (PM_{2.5} and PM₁₀), CO_x, hydrocarbons, NO_x, SO₂, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorated compounds, dioxins and furans, with the corresponding affectation to the environment and to human health (Abril et al., 2009; EEA, 2007). There are other elimination options such as crushing and mixing it with the soil, or removing it for its use. Since the alternative of burying the straw generates between 2.5 and 4.5 times more methane than burning it, this practice is not recommendable either (Fitzgerald, 2000); moreover, the abandoned rice straws in the field sometimes may flow into the drainage during the rainy season, causing an obstruction of the drainage, or providing the place for the propagation of the bacteria (Chou et al., 2009).

Rice straw as agricultural waste biomass could be a source of alternative energy that therefore substitutes fossil energy for reducing greenhouse gas emissions as well as avoids the local pollution problems from open burning (Suramaythangkoor and Gheewala, 2008). Because of the high price of crude oil, attention has been focused on rice straw as a potential renewable energy source (Lee et al., 2005); however it has not yet been commercially used as a feedstock for heat and energy because of insufficient incentives or benefit for farmers to collect rice straw instead of field burning (Kargbo et al., 2009).

The energy of rice straw can be recovered via thermal conversion process such as direct combustion, where generating electricity by combustion straw directly not only saves energy, protects the environment, and reduces field-burning pollution, but also increases the income of farmers (Ewida et al., 2006; Zhaosheng et al., 2008). The rice straw can

also be converted to a valuable energy product through indirect techniques such as bioethanol through biochemical conversion process, where a distinctive character that makes it a potential feedstock for bioethanol production is the high cellulosic content (20–50 % cellulose and 20–35 % hemicelluloses) that can be readily hydrolysed into fermentable sugar (Aly and Megeed, 2008; Binod et al., 2010; Sánchez and Cardona, 2008). Direct combustion of rice straw has the advantage of high energy conversion efficiency compared with indirect techniques but it suffers from some technical limitations and causes operating problems in thermal conversion systems such as high ash content, sintering, fouling, slag formation, and corrosion problems (Baxter et al., 1998; Fu et al., 2009; Jenkins et al., 1996).

The characteristics of agricultural biomass residues in general terms and those of rice straw in particular vary depending on the type of plant, the growing location, season, and harvesting methods (Kadam et al., 2000; Shawky et al., 2011). For example, the characteristics of sugar cane bagasse differ than wheat and rice straw; in addition the characteristics differs for the same type of straw according to harvesting time, soil, cultivation and storage conditions such as rain washing, solar drying, and soil contamination (Bakker et al., 2002; Jenkins et al., 1996; Jenkins et al., 1998; Pronobis, 2005).

In consequence, the characterization of rice straw as a solid fuel is the initial and most important step during the investigation and application of this fuel. The thermal characteristics, physical and chemical compositions are a unique fundamental code that characterizes and determines the properties, quality, potential applications and environmental problems related to this fuel (Saidur et al., 2011).

The main objective of this chapter was to investigate and compare the characteristics of rice straw collected from different regions in Spain (Andalusia, Murcia and Valencia) and Egypt (El Sharkia province). The physical and chemical compositions were determined using analysis such as X-Ray fluorescence (XRF) and Environmental Scanning Electron Microscope (ESEM) inspection. The thermal characteristics of the straw was studied using thermogravimetric analysis (TGA and DSC) as complimentary methods that provide useful and valuable information about the nature and composition of the organic wastes, moreover, it is widely used to study the mechanisms of the thermal decomposition and combustion of biomass (Fernández et al., 2012; Zhaosheng et al., 2008).

2. MATERIAL AND METHODS

2.1. Sampling

The rice straw samples were collected from different provinces in Spain (Andalusia, Murcia, and Valencia), and Egypt (El Sharkia province). Characteristics for the grinded straw samples and also for their ashes obtained at 550 °C were performed according to the procedures in the section below.

2.2. Analytical procedures

2.2.1. Chemical characteristics of rice straw

Chemical characterization of rice straw has included ultimate analysis, ash and volatile matter (VM) content, heating value and lignocellulose analysis. Analytical procedures used have been explained bellow.

Ultimate analysis for the straw samples was performed according to UNE-EN 15104,

2011. Ash contents of rice straw samples were determined by igniting grinded straw samples in muffle furnace at 550 °C according to UNE-EN 14775, 2010 and VM was determined at 900 °C according to UNE-EN 15148, 2010. Three measurement series per sample were obtained and the average value was calculated.

Higher heating value (HHV) at constant volume was determined by adiabatic bomb calorimeter according to UNE-EN 14918, 2011. Three measurement series per sample were obtained and the average value was calculated.

Finally the lignin content was determined by acid hydrolysis according to Sluiter et al. (2012) and was measured by UV-Spectrophotometry ($\epsilon_{205} = 110 \text{ L/g cm}$). Glucose was quantified with the Glucose-TR kit (Spinreact) and the Reducing Sugars (RS) were determined with the Somogyi-Nelson method (Somogyi, 1945). Finally the cellulose content was calculated from the glucose and the difference between total reducing sugar (TRS) and glucose corresponded to the sugars from hemicellulose, using an anhydrous correction of 0.90 and 0.89 for calculating cellulose and hemicellulose, respectively. All analyses were carried out based on dry weight in triplicate and the average values were taken.

2.2.2. Ash composition

The major elements of the ash obtained at 550 °C, according to UNE-EN 14775, 2010, were analyzed through X-Ray Fluorescence according to UNE-EN 15290, 2011.

2.2.3. ESEM inspection

Straw and ash samples were inspected using ESEM, FEI model Quanta 400, to obtain

the image, size of particles, and composition of the straw and ash analyzed in the selected spots.

2.2.4. TGA and DSC

The TGA and DSC of the samples were performed using a SHIMADZU TGA-50H thermo analyzer in an oxidative atmosphere. Before the application of these experimental methods, the particle size was reduced to less than 0.5 mm to ensure the heat transfer rate within the kinetic regime of decomposition (Rath et al., 2002). Moreover, the initial mass of the sample was between 2-5 mg for the ash and between 6-8 mg for the rice straw to avoid any possible effect on mass and heat transfer during the process of biomass decomposition (Blasi et al., 2001; Calvo et al., 2004).

The samples are heated from 30 to 1000 °C at heating rate of 5 °C/min for the ash and 10 °C/min for the rice straw, to maintain an oxidative atmosphere for thermal decomposition of the particles and this heating rate is generally considered capable of ensuring that there is no temperature gap between the sample and its surroundings, moreover, the low heating rate makes the chemical kinetic properties of the biomass sample clearer (Bilbao et al., 1997; Deng et al., 2013; Liu et al., 2002). According to Calvo et al. (2004) and Saddawi et al. (2012), an air atmosphere was passed continuously at a flow rate of 100 mL/min for the rice straw and 50 mL/min for the ash; moreover, higher flow rate was applied and did not give uniform and expressed relation for the thermograms. The oxygen in the air atmosphere enhances the decomposition of the material at low temperatures, and when the temperature becomes sufficiently high, oxygen is likely to cause the combustion of the char residue generated in the early stages of solid decomposition (Liu et al., 2002). The analysis for each sample was

repeated to ensure that it follows the same trace for the same conditions.

2.2.5. Melting point, sintering and slagging tendencies

Melting points were detected from DSC thermograms of the different rice straw ash samples. The sintering of the rice straw samples was detected by combusting the samples in a muffle furnace and observing the appearance at different temperatures (550-1000 °C) (Bakker et al., 2002; Jenkins et al., 1996). The prediction of slagging or fouling tendencies of the straw samples has been determined using the alkali index that expresses the quantity of alkali oxide in the biomass per unit of fuel energy. It has been computed according to Equation 6 where I is the alkali index, expressed as kg alkali/GJ or lb alkali MMBtu⁻¹, Q is the heating value (GJ/kg), Y_f is the mass fraction (dimensionless) of ash, Y_{K_2O} and Y_{Na_2O} are the mass fractions (dimensionless) of K₂O and Na₂O in the ash (Jenkins et al., 1998; Skrifvars et al., 2005). Miles et al. (1995) suggested that above 0.17 kg alkali/GJ (0.4 lb alkali MMBtu⁻¹) fouling is probable, and above 0.34 kg/GJ (0.8 lb MMBtu⁻¹), fouling is virtually certain to occur.

$$I = (1/Q) Y_f (Y_{K_2O} + Y_{Na_2O}) \quad (6)$$

3. RESULTS AND DISCUSSION

3.1. Chemical characteristics of rice straw

The composition of different straw samples is shown in Table 12 and some differences have been detected. Carbon contents in the different samples ranged between 39.01 % and 41.24%, hydrogen content were between 6.49% and 6.99% and nitrogen content in the range of 0.40% and 1.23 %. Ash contents of the straw samples varied between 13.25% and 18.66%. Valencia straw recorded the highest ash content followed by

Egypt, Murcia and Andalusia straw, in contrast with VM contents that ranged between 81.93% and 89.04%. The HHV of the straw reached values between 14.06 and 14.96 MJ/kg, similar to other studies (Bakker et al., 2002; Calvo et al., 2004; Deng et al., 2013; Jenkins et al., 1998; Jung et al., 2008; Skrifvars et al., 2005), and differences between the samples has not been detected.

Table 12. Analysis data the different straw samples

Parameter	Egypt	Murcia	Valencia	Andalusia
C (%)	39.01	40.64	37.74	41.24
H (%)	6.59	6.80	6.49	6.99
N (%)	0.64	0.40	1.23	0.63
Ash content (%)	16.81	15.52	18.66	13.25
VM (%)	85.19	86.19	81.93	89.04
HHV (MJ/kg)	14.17	14.67	14.06	14.96
Lignin (%)	21.89	20.80	22.06	20.69
Cellulose (%)	31.01	32.23	30.80	33.65
Hemicellulose (%)	26.47	25.26	24.79	26.68
Alkali index				
(kg alkali/GJ)	1.91	1.75	2.09	1.85

As shown in Table 12, cellulose represented the largest component of lignocellulose materials of rice straw, followed by hemicellulose and lignin with values ranged between (30.80 to 33.65 %), (24.79 to 26.68 %) and (20.69 to 22.06 %), respectively. Similar results were found in other studies (Aly and Megeed, 2008; Badger, 2002; Binod et al., 2010; Knauf and Moniruzzaman, 2004; Mielenz, 2001; Sánchez and Cardona, 2008). Whereas cellulose and hemicellulose are macromolecules constructed from different sugars; making rice straw potential feedstock for liquid fuel production

such as bioethanol (Aly and Megeed, 2008; Binod et al., 2010; Saidur et al., 2011; Sánchez and Cardona, 2008).

It could possible to conclude that the most important difference between samples analyzed is related to the ash content and the differences may be attributed to the variation of growing location, harvesting time, soil, cultivation and storage conditions such as its exposure to rain washing and soil contamination (Bakker et al., 2002; Jenkins et al., 1996; Pronobis, 2005; Shawky et al., 2011).

3.2. Ash composition

The results of ash composition for the straw samples are shown in Table 13. It was observed that for all the samples the highest ash component was the silica, although its content has varied depending on the sample; it ranged from 49.99 %, in the case of the rice straw from Andalusia, to 65.43 %, in the case of the sample from Egypt. Most of the silica in rice straw appears to be in the plant cell wall and its level is highly dependent upon soil type (Soest, 2006), so differences could be explained because of the different origin of the sample. The second highest ash component was potassium oxide ranges from 13.01 %, in the case of samples from Egypt, to 18.14 %, for samples from Andalusia; its high content is attributed to the use of fertilizers in the agricultural (Bapat et al., 1997; Grubor et al., 1995). The third highest ash component was chlorine, its content in the ash ranged between 4.18 %, in the case of samples from Murcia and 7.54 %, for samples from, where its level in the straw depends on soil conditions and result in a significant amount in the ash (Pronobis, 2005).

Table 13. Ash composition of the different straw samples (% ash)

Component	Egypt	Murcia	Valencia	Andalusia
Na₂O	3.11	0.98	2.17	2.72
MgO	2.24	2.25	4.85	3.37
Al₂O₃	0.19	0.17	0.46	0.36
SiO₂	65.43	61.83	59.80	49.99
P₂O₅	0.68	0.97	1.79	1.04
SO₃	1.26	1.73	3.58	2.05
Cl	5.40	4.18	4.70	7.54
K₂O	13.01	15.57	13.55	18.14
CaO	2.13	3.66	5.37	6.44
TiO₂	0.02	--	0.03	--
MnO	0.21	0.16	0.11	0.24
Fe₂O₃	0.15	0.10	0.25	0.22
NiO (×10⁻³)	5.30	9.10	-	12.30
CuO (×10⁻³)	1.70	6.30	3.90	6.50
ZnO (×10⁻³)	16.70	20.10	23.60	19.30
Rb₂O (×10⁻³)	10.50	5.10	7.40	6.20
SrO (×10⁻³)	16.00	37.30	52.00	16.70
ZrO₂ (×10⁻³)	1.80	5.40	2.50	--
Cr₂O₃ (×10⁻³)	--	--	--	--
Br (×10⁻³)	--	--	--	--
Total *	93.88	91.68	96.75	92.17

-- No detected

* Total is not 100 % because there is other elements have not been detected.

3.3. ESEM inspection

Samples of rice straw were inspected by ESEM combined with chemical analysis at various selected spots. As one example of the different rice straws, Figure 12 shows ESEM inspection of Egypt rice straw. The chemical analysis at the selected spots showed that the straw is consisting primarily of C, Si and O. Also, high amounts of Cl,

K and observed amounts of other elements such as Na and Mg have been detected. It has been observed that the dark layers rich with C, indicated by spot 1 and 3, meanwhile, the dense layer with light appearance rich with Si, indicated by spot 4, while some randomly dispersed particles like inclusions that have more light appearance rich with Cl and K indicated by spot 2.

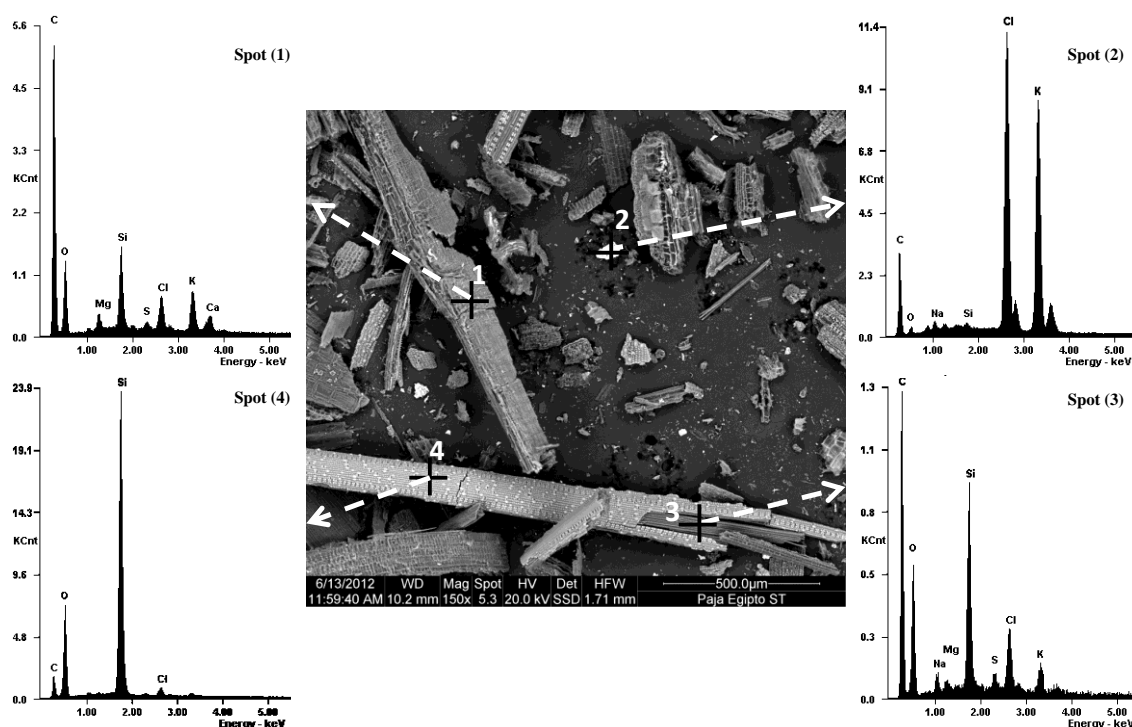


Figure 12. ESEM inspection and spots chemical analysis for Egypt straw

In the conversion of rice straw to ash, the combustion process removes the organic matter and leave silica rich residue and the ash maintained some of structure of the original straw, see Figure 13. Supporting the results expounded in the previous section, high amounts of Cl and K were detected by ESEM addition to elements such as Na and Mg were detected at spot 1, and similarly for spot 3, signed on zones with a lighter appearance. Si was the predominating component at spot 2, though similar constituents were observed at spot 4. These findings are in line with the results reported by Skrifvars

et al. (2005) for rice straw samples.

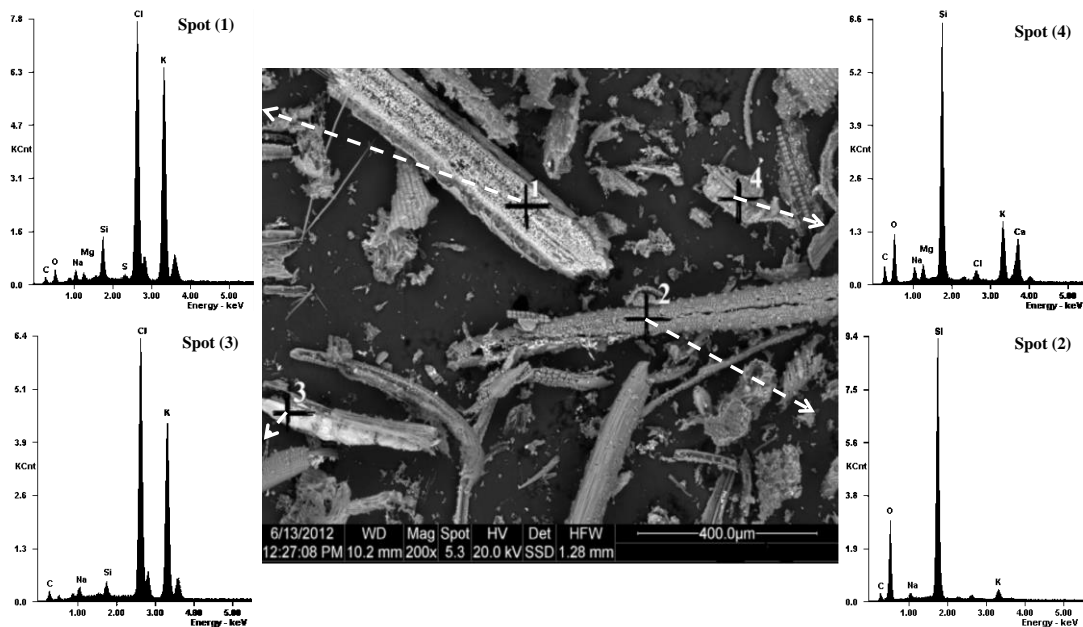


Figure 13. ESEM inspection for ash of Egypt straw sample.

3.4. TGA and DSC for the straw samples

TGA and DSC thermograms in an air atmosphere for the different straw samples have been detected to determine the thermal nature as shown in Figure 14. These thermograms showed slight difference for the different straw samples. TGA curve indicated the mass loss of the sample. It initially decreases below 100° C because of drying and loss of the moisture that the samples contained owing to the hygroscopic nature of rice straw and there may be also loss of very light volatiles (Calvo et al., 2004; Singh, 1996). After 200° C, straw devolatilization begins and high loss in the weight occurs due to decomposition and the emission of volatiles from cellulose and hemicelluloses, also small amounts of volatiles from the lignin component may also give off (Calvo et al., 2004; Koufopoulos et al., 1989; Sun et al., 2002). After 300 °C, the weight loss is corresponding to lignin decomposition and the decomposition rate becomes very low after 460 °C and becomes negligible at around 600 °C, similar results

found by Jung et al. (2008). The maximum mass loss has been occurred in the range between 200 and 500 °C for the different straw samples. DSC thermograms show that the overall thermal degradation of rice straw is an exothermic process and the large exothermic peaks were observed at around 300 °C, which is attributed to the decomposition of hemicelluloses and cellulose (Chakraverty et al., 1987; Sun et al., 2002). Andalusia straw recorded the highest mass loss rate and lowest char residue in TGA profile and the highest exothermic peak in DSC profile compared to the others. It may be related to its lowest ash content and highest volatiles among the different straw samples, see Table 12. In the other hand, Valencia straw recorded the lowest mass loss rate, highest char residue and the lowest exothermic peak, meanwhile, the TGA and DSC curves for Egypt and Murcia straw are nearly close.

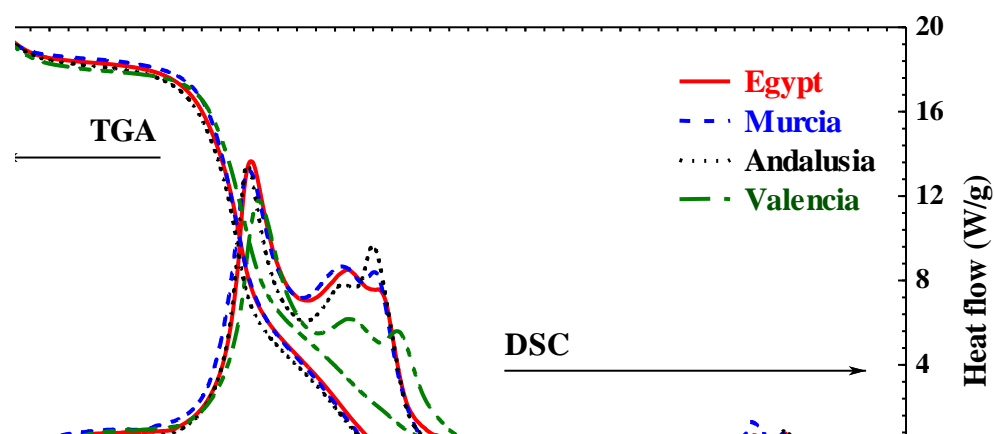


Figure 14. TGA and DSC thermograms of the different straw samples.

3.5. Melting point, sintering and slagging tendencies

3.5.1. Ash melting point

Since the fuel ash consists of a mixture of different inorganic compounds, the ash has

no well-defined melting point and the melting process takes place over a wide temperature range starting with the initial deformation temperature (where sintering begins), continuing with the hemisphere temperature and ending with the flow temperature (Picco, 2010; Saddawi et al., 2012). The DSC curves for the different unwashed rice straw ashes were detected in order to ascertain the melting point. Figure 15 shows the DSC curves for the different rice straw ash samples. It was possible to represent the melting points as maximum of the endothermic peaks of the DSC traces (Buzarovska et al., 2008). The maximum endothermic peaks for the different samples were in the range between 700 and 800 °C.

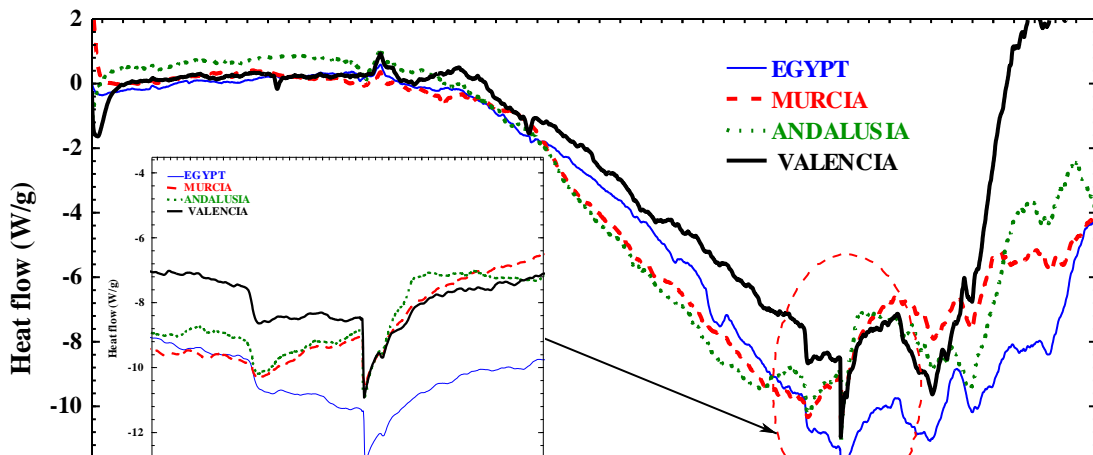


Figure 15. DSC thermograms for the different straw ash samples.

3.5.2. Sintering and slagging tendencies

The appearance and behavior of the straw samples were observed by combustion at different temperature (550-1000 °C) in muffle furnace. The straw ash obtained at 550 °C had a dark grey coloring (Figure 16b); this color could result from residual carbon compounds that require a higher temperature or longer time for completely burning the

straw samples (Wattanasiriwech et al., 2010). The combustion of ashes at 700 °C resulted in a grey color, and they were easy to remove. Nevertheless, when the combustion temperature increased to 800 °C, light ash sintering was observed and the sintering increased with increasing combustion temperature, up to 900 °C. Severe sintering and slag formation with dark brown color was observed when the combustion temperature increased to 1000 °C, making it impossible to remove the ash from the crucibles (Figure 16c). Similar results were found by Bakker et al. (2002) and Jenkins et al. (1996). This may be due to the fact that silica in combination with alkali and alkaline earth metals, especially potassium, can lead to the formation of compounds which readily slag and foul at normal furnace temperatures (Miles et al., 1995; Skrifvars et al., 2005). Moreover, chlorine could be an important facilitator in fouling and in the vaporization of alkali species, leading to the formation of more severe deposits (Miles et al., 1995).

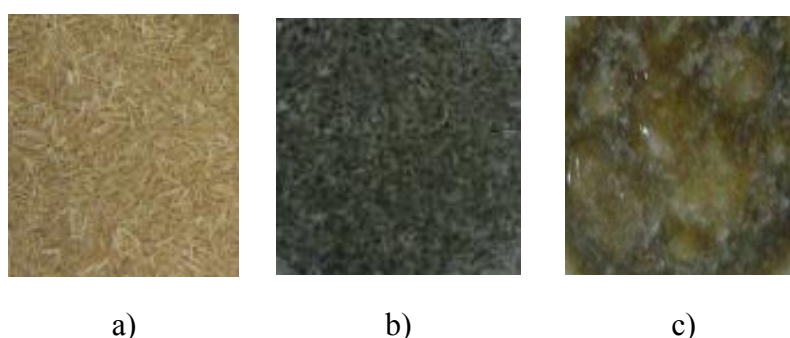


Figure 16. Rice straw: a) before combustion; b) ash at 550 °C; and c) ash at 1000 °C.

Table 12 lists the alkali index values for the different straw samples which are computed according to Equation (6). The alkali index value for all samples exceeded the probable value of 0.17 kg alkali/GJ as well as the critical value of 0.34 kg/GJ, which indicates that the samples will slag or foul. Sinters and slags of rice straw ash are related to the

presence of potassium, chlorine, and silicon in the straw and mainly related to the high relative content of alkaline compounds in straw ashes (Baxter et al., 1998; Peng et al., 2009; Picco, 2010; Werther et al., 2000).

4. CONCLUSIONS

The characterization of rice straw samples collected from different regions has shown that, because of the high content of C (39.01 - 41.24%), VM (81.93 - 89.04%), and HHV (14.06 - 14.96 MJ/kg), rice straw energy can be recovered directly via thermal conversion process such as direct combustion or can be converted to a valuable energy product such as bioethanol through biochemical conversion due to its high content of cellulose (30.80 - 33.65%) and hemicellulose (24.79 - 26.68%).

On the other hand, it has been concluded that the characteristics of rice straw depend on the variation of growing location, harvesting time, soil, cultivation and storage conditions such as its exposure to rain washing and soil contamination. The most important difference detected between samples analyzed is related to the ash content and its composition, however the thermal behavior and composition has not showed important differences.

Finally, although direct combustion has higher energy conversion efficiency than indirect techniques, it suffers from some technical limitations and causes operating problems in thermal conversion systems such as high ash content (13.25- 18.66%), low ash melting point (700- 800 °C), high alkali index (1.75- 2.09 kg alkali/GJ) and severe sinter and slag formation at 900-1000 °C due to the presence of potassium, chlorine and silicon in the straw, where the ash composition analysis revealed that silica (49.99 -

65.43 %) was the foremost component, followed by K_2O (13.01 - 18.14 %), and Cl (4.18 - 7.54 %).

The seal of Universitas Granada is a circular emblem. It features a central shield with a crown on top, flanked by two lions. The shield is supported by two columns. The outer ring of the seal contains the Latin text 'UNIVERSITAS GRANATAE' at the top and '1531' at the bottom, separated by small squares.

CHAPTER 4

**EFFECT OF WATER WASHING ON THE
CHARACTERISTICS OF RICE STRAW**

The previous chapter of rice straw characterization concluded that rice straw has high ash content, alkali values and its combustion showed some problems such as sinter and slag formation. This composition depends on the variation of growing location, or soil but also it depends on harvesting time, cultivation and storage conditions such as its exposure to rain washing and soil contamination. There are different pretreatment processes to reduce troublesome compounds and, in consequence, such problems before straw combustion, for example water washing (Bakker et al. 2002; Jenkins et al. 1996; Soest 2006). The main objective of this chapter is investigating the effect of washing on the characteristics of rice straw and its thermal behavior.

1. INTRODUCTION

For using rice straw to generate energy efficiently and solve the problems related to troublesome compounds that cause operating problems in thermal conversion systems such as high ash content, sinter and slag formation, it is necessary to develop processes to overcome the difficulties caused by these problems (Abril et al., 2009; Baxter et al., 1998; Fu et al., 2009; Jenkins et al., 1996). Soil and mineral contamination for the straw during storage and handling may lead to higher ash content (Gilber et al. 2009; Lehtikangas 2001). In consequence, the straw should be carefully collected and stored to avoid mineral contamination and it could be treated before its use by means such as by chemical and biological pretreatments to reduce the problems related to high silica and lignin content or by water washing to reduce alkali and alkaline compounds or (Bakker et al. 2002; Jenkins et al. 1996; Soest 2006).

Using additives for rice straw such as kaolin or blending rice straw with other fuels such as coal may be suggested solutions to enhance combustion efficiency of boilers and to

control fouling and slag formation (Picco et al., 2010). However, practical experiences with co-combustion of rice straw show a certain increase of slagging tendency in high temperature part of the boiler, comparing with coal combustion (Pronobis, 2005), meanwhile, co- combustion of rice straw with wood based fuel may be beneficial and may reduce fouling (Thy et al., 2004).

Because washing of rice straw with water is a possible way of reducing the content of the undesirable compounds which cause these problems, the main objective of the present chapter is to investigate the effect of washing on the characteristics of rice straw and its ash by using the analysis applied in the previous chapter for the different rice straw samples.

2. MATERIAL AND METHODS

According to Deng et al. (2013), water washing appears to be a more controllable manner than natural rain washing and washing with tap water and distilled water makes no difference to element removal, washing the straw samples with tap water is used in this study as a simple and an effective method to remove a large part of troublesome elements from biomass fuels. So, samples from the different rice straws used in the previous chapter were collected and cut to 10 cm then washed with flushed tap water and dried at 105 °C to a constant weight then characterized using the same methods that were described in section 2 of the previous chapter.

3. RESULTS AND DISCUSSION

3.1. Straw and ash analysis

The characteristics of the washed rice straw samples were compared with their characteristics before washing (Table 12) and the variations in the characteristics due to

washing have been summarized in Table 14. Initially, soil contamination may be high and may result in an increase in the percentage of some elements for the unwashed straw and due to washing this percentage decreases but also may increase for other main constituent components of the straw such as C and H, where the removing of the other surface elements by water washing result in an increase of their contents as a percentage of the whole straw.

After washing the straw, almost all the washed straw samples showed an increase in carbon, hydrogen and VM content. The variation in carbon content has not been detected in Murcia samples, while it increased in the other samples with ratios reached to 16.45 % in case of Valencia straw. Hydrogen content has been decreased in Murcia samples with 1.62 % ratio, otherwise, its content increased in the rest of the samples with ratios reached to 8.47 % in Valencia straw. On the other hand, VM increased in all samples with different ratios ranged from 0.42 % in case of Murcia straw to 3.42 % for Valencia straw. Although 23.81 % increase in nitrogen content has been detected in Andalusia straw, its content decreased in the rest of straw samples with ratios ranged from 10.00 % in Murcia straw to 59.38 % in Egypt straw. Similar results were found with other authors (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Lee et al., 2005; Saddawi et al., 2012).

Reduction in ash contents has been observed for all the samples by washing the straw, however the reduction percentage in ash content due to washing depended on the type of sample; it reached from 10.66% in the case of sample from Murcia straw to about 19.77 % in Andalusia straw (Table 14). Ash content reduction was due to that washing the straw extracts large amounts of alkali metals, chlorine, in addition to variable

amounts of sulfur, phosphorus and other elements (Table 15) caused by contamination of the straw with soil (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Kargbo et al., 2009; Skrifvars et al., 2005). Table 15 shows that the washing was very efficient in chlorine removal and was significant in the other elements; the chlorine, magnesium and phosphorous removal ratios reached to about 87 %, 39% and 35 %, respectively in Valencia straw. About 60 % sodium and sulfur removal were recorded in Andalusia and Egypt straw, respectively; finally potassium removal ratio reached about 50% in Murcia, Valencia and Andalusia straw, where the potassium can be dissolved very well in water (Lee et al., 2005).

Table 14. The variation in the parameters due to straw washing

Parameter	Egypt	Murcia	Valencia	Andalusia
Ash content	- 17.06	- 10.66	- 15.80	- 19.77
HHV	+ 5.29	+ 1.84	+ 7.82	+ 7.89
VM	+ 1.81	+ 0.42	+ 3.42	+ 0.97
C	+ 3.59	--	+ 16.45	+ 3.83
H	+ 2.58	- 1.62	+ 8.47	+ 2.72
N	- 59.38	- 10.00	- 32.52	+ 23.81
Alkali index	- 43.46	- 55.43	- 60.77	- 63.24

-- No variation has been detected; the negative values indicate reduction percentage in the parameter value due to washing; the positive values indicate increasing percentage in the parameter value due to washing

After washing, the heating value increases with a percentage varied from 1.84 % in the case of the sample from Murcia to 7.89 % in Andalusia straw. The increase in HHV may be correlated to the decrease in the ash content of the washed straws (Jenkins et al., 1996). Table 14 shows that the highest reduction in ash content with the highest

increase in HHV were occurred in Andalusia straw, whenever, Murcia straw recorded the lowest ash reduction and lowest increase in HHV due to washing. Moreover, the compositional changes after washing such as the increase of carbon values of the washed straw, as shown in Table 14, lead to modest increases in heating value (Bakker et al., 2002).

Table 15. Percentage of inorganic elements in ash and removal ratio due to washing

Parameter	Egypt		Murcia		Valencia		Andalusia	
	Ash (%)	R ^a (%)	Ash (%)	R ^a (%)	Ash (%)	R ^a (%)	Ash (%)	R ^a (%)
Na	2.30	35.65	0.73	40.08	1.61	52.86	2.02	59.95
K	10.80	26.14	12.92	49.48	11.25	49.38	15.06	49.09
Mg	1.35	21.98	1.36	--	2.93	38.80	2.03	17.97
P	0.30	7.80	0.42	--	0.78	34.83	0.45	--
S	0.50	59.44	0.69	30.26	1.43	55.24	0.82	25.46
Cl	5.40	59.04	4.18	80.82	4.70	86.96	7.54	82.90

^a) Removal (%)

-- No removal has been detected

3.2. ESEM inspection

Figure 17 and 18 show the ESEM results for washed Egypt straw and its ash, respectively. Comparing with ESEM inspection in Figure 12 and 13 for the unwashed samples, washing did not have a significant effect on the straw and ash microstructure, but it did cause changes in chemical composition. As shown in the Figure 17, C and Si represented the dominant components at the selected spots, and significant loss of Cl and K has been observed. On the other hand, all the selected spots in Figure 18 of the selected ash sample consist primarily of Si and small amounts of other elements

including C, O, Mg and Na were also presented. A considerably high amount of Ca was detected at spot 1. Both Si and Ca appear to reside largely in the plant cell wall of rice straw (Miles et al., 1995; Soest, 2006), for which reason the washing practice did not effectively remove them. Meanwhile, markedly lower contents of Cl and K were observed by ESEM for the washed samples when compared to the unwashed one, supporting the results obtained in Table 15.

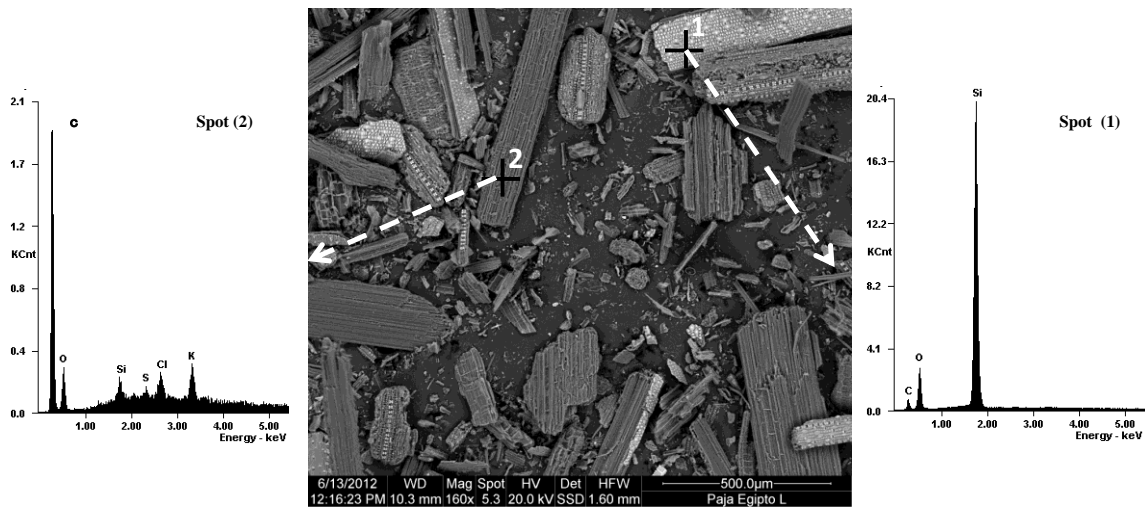


Figure 17. ESEM inspection for washed Egypt straw

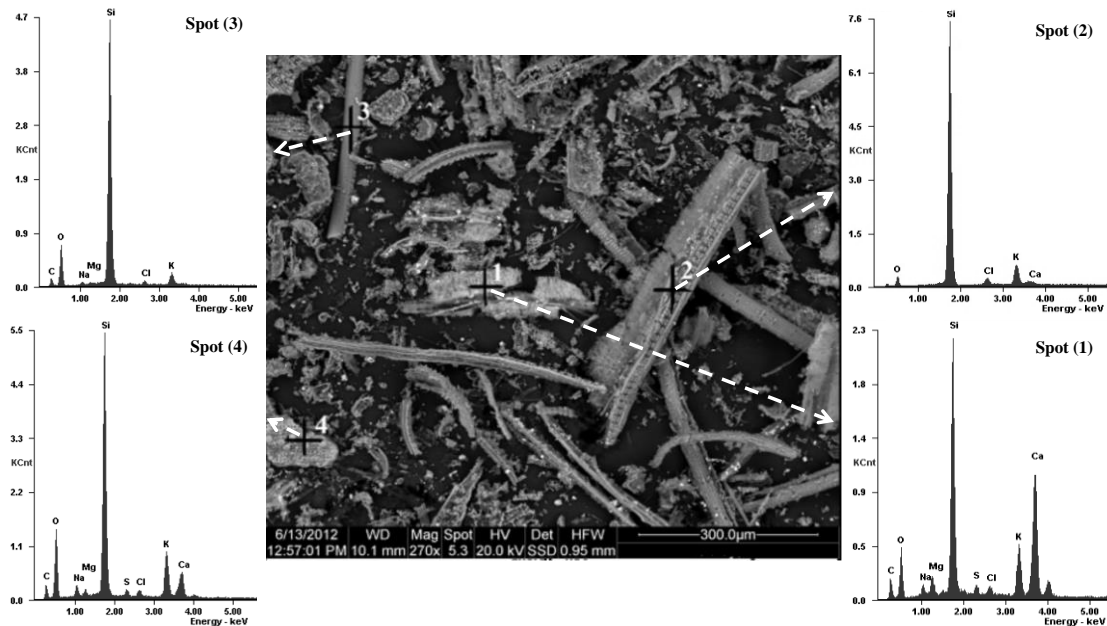


Figure 18. ESEM inspection for ash of the washed sample

3.3. TGA/ DSC analysis

To discuss the effect of washing on the thermal behavior of straw and its ash in detail, the thermogravimetric curves (TGA/ DSC) of the washed and unwashed straw samples and their corresponding ash obtained at 550 °C were analyzed.

3.3.1. TGA/ DSC of straw samples

As one example of the different rice straws, Figure 19 shows TGA and DSC thermograms of washed and unwashed Egypt rice straw. TGA profiles showed lower degradation residues, namely char, in the washed straw compared to the unwashed straw. This may be due to the lower metals content in the washed straw that acts as a catalyst in the formation of char (Raveendran et al., 1995). In contrast, the DSC profile for the washed straw recorded higher exothermic peak than the unwashed straw. This may be due to increase volatiles content in the washed straw compared to the unwashed straw (Lee et al., 2005), see Table 14.

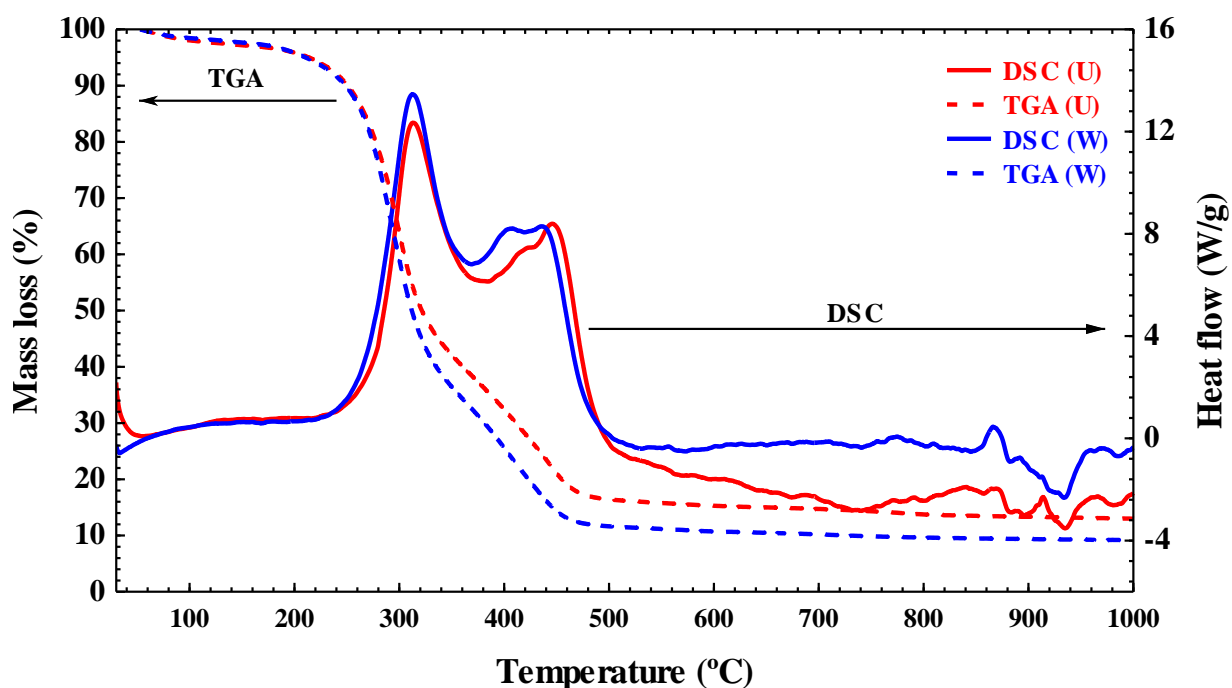


Figure 19. TGA and DSC thermograms of washed (W) and unwashed (U) Egypt straw.

3.3.2. TGA/ DSC of ash samples

TGA curves in Figure 20 showed changes in mass loss of the ash samples with increasing temperature, essentially in the same order as found in previous work (Fang and Jia, 2012). An initial mass loss occurred at temperatures lower than 200 °C because of the evaporation of water, which was readily absorbed in the atmosphere by the much smaller ash particles before testing (Fang and Jia, 2012). The mass loss at 200 °C in the unwashed sample was higher than that for the washed sample (2.80% versus 1.20%). It may be that the moisture in the unwashed samples is absorbed by components such as chlorine and potassium, present together in greater concentrations than in the washed samples (Lee et al., 2005; Skrifvars et al., 2005).

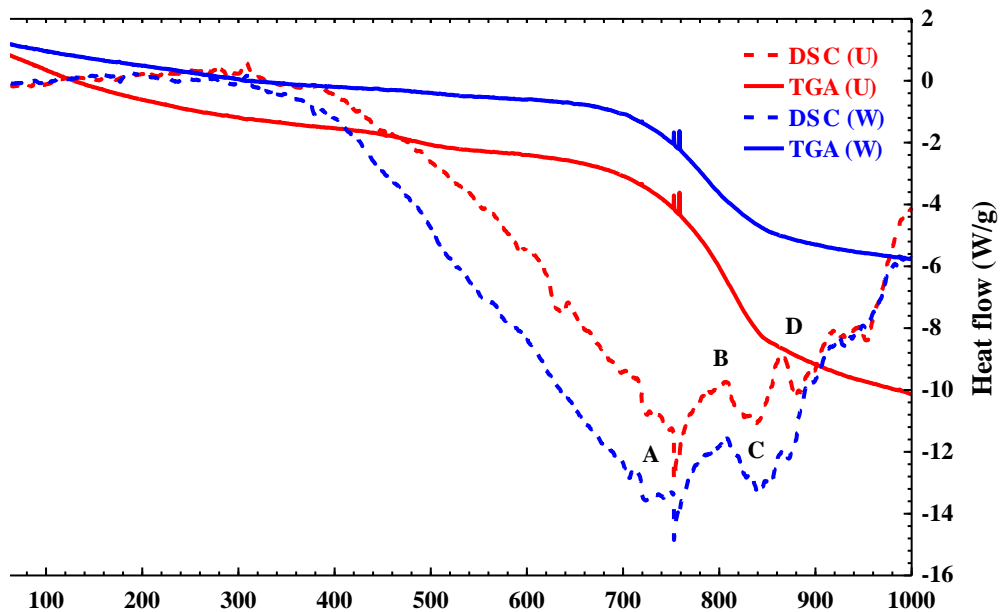


Figure 20. TGA and DSC for ash of washed (W) and unwashed (U) Egypt straw.

Since the ash samples tested were obtained at 550 °C, a very low rate of mass loss was observed from 200 up to 700 °C, only about a 3.60 % loss in the ash mass of the unwashed sample. This loss may be attributed to the oxidation of some organic

components that had not been completely burnt, and to the evaporation of some inorganic matter from the ash with further increases in temperature (Fang and Jia, 2012). After 700 °C and up to 850 °C, a significant increase in mass loss (5.50% and 7.70% for washed and unwashed samples, respectively) was observed. This may be due to the higher deposition rate of char particles of unwashed straw during the higher combustion temperature (Bakker et al., 2002), and also to the removal and decomposition reaction of inorganic components such as chlorine and potassium (Fang and Jia, 2012), which are found together and in greater proportions in the unwashed samples, as indicated by ash composition and ESEM analyses.

The potassium starts to be released at a low rate at very low temperatures, but is then rapidly released as the temperature increases up to 800 °C (Knudsen et al., 2004; Skrifvars et al., 2005). The potassium absorbed from the soil mainly remains as ions in fresh plants; when the plants wither, the potassium may exist in simple salts such as KCl and K₂SO₄, which have high activity and strong migration characteristics at high temperatures (Yu et al., 2010). A high content of potassium salts is retained in ash after completion of combustion, and at high-temperatures the potassium salts may evaporate and volatilize into gas or react with silicon, calcium, or other elements to form complex silicates after 800 °C (Baxter et al., 1998; Fang and Jia, 2012). The minor mass loss observed from 850 °C up to 1000 °C (1.33% and 2.51% for the washed and unwashed samples, respectively) can be attributed to the evaporation of KCl and reaction between Si and KCO₃, which decomposes after 1000° C (Masia et al., 2007; Szemmelveisz et al., 2009).

As seen in Figure 20, DSC curves for the ash samples recorded maximum endothermic

peaks as melting points in the range 700 °C to 800 °C, represented at zone (A). In agreement with Wanger (2009) and as indicated in the figure, the melting peaks was followed by an exothermic decomposition reaction represented in zone (B); then evaporation of the decomposition product represented at zone (C) was followed by a crystallization exothermic peak represented at (D), which was only observed for the unwashed sample and not detected in the washed one.

This crystallization peak could indicate sintering formation occurring with the ash of the unwashed sample, as discussed in the section of sintering and slagging tendencies of the unwashed samples. No significant changes in melting temperature were observed between the washed and unwashed samples. Yet the fact that the unwashed sample recorded a lower heat flow rate may be associated with the higher ash-related problems of the unwashed samples: this would result in low thermal conductivity, retarding the rate of heat transfer (Jenkins et al., 1996; Zbogar et al., 2009; Zygarlicke et al., 2000).

3.4. Sintering and slagging tendencies

The appearance and behavior of the washed straw samples were observed by combustion at different temperature (550-1000 °C) in muffle furnace. The ash of the washed samples obtained at 550 °C had a grey color (Figure 21a). With the increasing combustion temperature up to 700 °C, the ash had a lighter grey color and became close to white when the furnace temperature was increased to 1000 °C (Figure 21b). Unlike the unwashed samples, the ash of the washed samples was easy to remove and did not show sinter and slag formation as found by Bakker et al. (2002) and Jenkins et al. (1996). This could be explained by the reduction of some undesirable compounds, especially potassium, after straw washing. Moreover, an improvement in alkali index

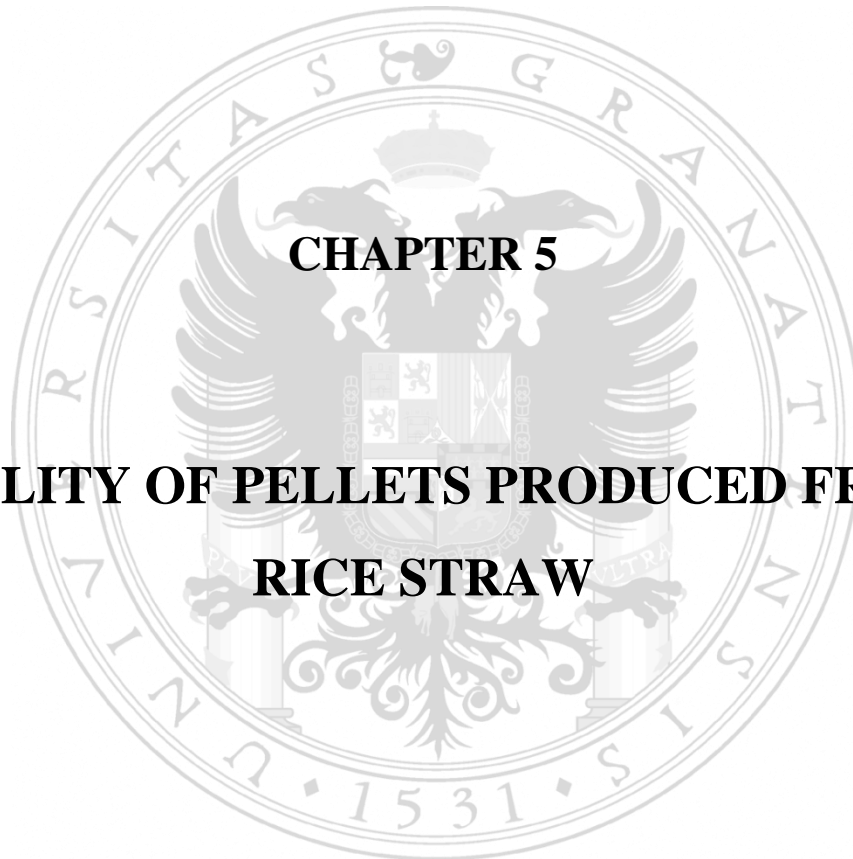
values was observed for the washed samples, especially for Andalusian straw, for which the ratio improved by approximately 63.24%, see Table 14. Washing therefore leads to significant changes in inorganic composition and substantially improves combustion behavior (Bakker et al., 2002; Jenkins et al., 1996; Lee et al., 2005).



Figure 21. Ash photos of washed straw samples: a) at 550 °C; and b) at 1000 °C

4. CONCLUSIONS

Rice straw has high ash content, alkali index and its combustion causes operating problems such as sinter and slag formation so the effect of washing on the characteristics of rice straw and its ash were investigated. The results have showed significant improvement in the thermal behavior and reduction in the ash contents, chlorine, alkali metals, and sintering formation for the washed straw in comparison to the unwashed straw. After washing, chlorine and potassium removal ratio reached to about 87 and 50 %, respectively. Reduction in ash content and increasing in HHV reached to about 19.77 % and 7.89 %, respectively. Moreover, reduction ash sintering formation and improvement in the alkali index value was observed for the washed samples, the ratio improved by approximately 63.24%. In consequence it is possible conclude that washing rice straw with water is a feasible option to reduce the content of troublesome compounds that cause sinter and slag formation.



CHAPTER 5

**QUALITY OF PELLETS PRODUCED FROM
RICE STRAW**

Due to its low bulk density, rice straw is difficult to handle, transport, store, and utilize in its original form. The densified rice straw by means of techniques such as pelleting, can be easily handled and can reduce the costs of transportation, handling and storage. Moreover, the densification process also provides potential storage for off-season utilization. However, pellets' quality depends on the properties of the feedstock and quality management of the manufacturing process (Gilbert et al., 2009). Considering that wood pellets from forestry residues already has successfully established technologies and markets for production and consumption in some European countries, it is necessary to focus on studying the pelletization of agricultural biomass, which is periodically planted and harvested and then may have a great energy potential especially in rural areas. This chapter investigated the best operational conditions to produce rice straw pellets, according to the final mechanical and physical characteristics of pellets.

1. INTRODUCTION

The utilization of rice straw for energy production faces a major hurdle in terms of the cost and logistics of collecting, transporting, handling and storage, particularly because of its low density. The bulk density of rice straw is around 75 kg/m^3 (Kargbo et al., 2010), and it is roughly 40 kg/m^3 for the loose straw (Mani et al., 2006).

To solve these problems, rice straw could be processed by densification techniques such as extrusion, pelletizing, and roll briquetting. In the extruder, the raw material is conveyed and compressed by a screw or a piston through a die to form compacts of cylindrical or other shapes. Meanwhile, the pelletizer consists of a hard steel die that is perforated and one or two rollers. By rotating the die and/or the rollers, the feedstock is forced through the perforations to form densified pellets. In the briquetting roller press,

the feedstock falls in between two rollers rotating in opposite direction and is compacted into pillow-shaped briquettes (Li and Liu, 2000).

Pelletization is the most common densification process used for solid fuel applications, moreover, the pellets have drawn attention due to its superiority over raw biomass in terms of its physical and combustion characteristics. It increases the bulk density of biomass from an initial value of 40-200 kg/m³ to a final bulk density of 600-800 kg/m³ (Oberberger and Thek, 2004). It makes easier the handling of biofuels and can reduce the costs of transportation and storage; moreover, it provides potential storage for off-season utilization (Ewida et al., 2006; Gilbert et al., 2009; Kaliyan and Vance Morey, 2009). Finally, given their uniform shape and size and their high energy and bulk density, pellets can be easily handled using standard equipment, with less dust formation, and can be easily adopted for usage in different energy conversion systems (Gilbert et al., 2009; Kaliyan and Vance Morey, 2009; Vinterbäck, 2004).

Pellet qualities depend not only on the raw material characteristics (Arshadi et al., 2008; Carone et al., 2011; Gilbert et al., 2009; Rhén et al., 2005), but also on the operating conditions, which can be controlled during production (Arshadi et al., 2008; Gilbert et al., 2009; Lehtikangas et al., 2001; Rhén et al., 2005). For example, the moisture content, when optimal, serves as a binding agent, facilitates heat transfer, and aids in the thermal softening and self-bonding of individual particles in the pellet (Kaliyan and Vance Morey, 2009; Larsson et al., 2008; Mani et al., 2003; Rhén et al., 2005). A liquid or solid binder, which forms a bridge and causes a chemical reaction to make strong inter-particle bonding, can be added to the feed to increase or minimize the variations in pellet quality (Marrero, 1999; Tabil, 1996).

Furthermore, an increase in the temperature inside the pellet press generated by the friction between the straw and the die, can act in combination with the moisture content of the straw, softening the components, activating the inherent binders or added binder and affecting the self-bonding processes, hence affecting the pellet quality (Gilbert et al., 2009; Rhén et al., 2005). The pelletiser die hole size is known to have an important effect on the pellets moisture content, while the temperatures reached during the pelletisation process can also determine pellet quality (García-Maraver et al., 2011; Rhén et al., 2005; Theerarattananoon et al., 2012; Wu et al., 2011). One challenge in biomass pelletisation is therefore to keep these parameters in the range where high quality pellets are produced with minimal energy input and at a high pellet mill capacity (Stelte et al., 2011).

Research studies on pelletizing rice straw are few to date. In consequence the main objective of this chapter is the analysis of the effect of pelletisation conditions on rice straw pellet quality. The influence of production factors on pellet properties is studied using full factorial design methodology, moreover, the quality of pellets was evaluated by comparing their properties with respective standard limits.

2. MATERIAL AND METHODS

2.1. Production process of pellets

The rice straw used in this study was obtained from Andalusia, Spain. The straw size was reduced to less than 4mm using a VIKING electric garden shredder with a chipping unit and 2500 W power (GE150). Different feeding material and operating conditions were used and described below.

2.1.1. Feeding material conditions

2.1.1.1. *Binder*

The selection of a binder depends fundamentally on its cost and environmental friendliness (Marrero, 1999; Tabil, 1996). Ewida et al. (2006) studied the effect of five bonding materials (starch, sodium silicates, latex, phenol-formaldehyde and molasses) on rice straw pellet strength, the results showing that starch is the best bonding material, due to the strength and combustion characteristics. Maize starch is reportedly a better additive for power consumption per unit of pellet output, when compared to other additives (Kuokkanen et al., 2011; Mediavilla et al., 2012), due to its lubricating ability (Tarasov et al., 2013). According to Austrian standards for energetic pellets ÖNORM M 7135 (2003), an additive less than 2% (by weight) is allowed as a guideline, this percentage moreover proving economical, especially for such a high cost binder as starch. Thus, the binder (maize starch, in white powder form) was added to the milled straw in ratios of 0%, 1% and 2% by weight (S0, S1, and S2, respectively).

2.1.1.2. *Feeding material moisture*

The moisture content of feeding material (M_f) was adjusted to be 12%, 15% and 17% (M1, M2, and M3, respectively) in view of references (Liu et al., 2013; Kargbo et al., 2009; Tarasov et al., 2013; PelHeat, 2010). M_f was adjusted by spraying water over the straw and mixing very well, then measuring the moisture content.

2.1.2. Operating conditions

After fitting-out the rice straw, the pellets were produced using the well-proven flat die pelleting press KAHL 14-175, with a nominal power of 3 kW and a feeding rate of 50

kg/h. Two different conditions regarding temperature and size of dies were used. These operating conditions are justified below.

2.1.2.1. Temperature

An increase in temperature inside the pellet press is produced by the friction between the straw and the die, within a temperature range of 20 °C to 80 °C. In this research, the two levels of temperature (T) were used (T1 <50 °C and T2 >50 °C).

2.1.2.2. Size of dies

The following three dies with different diameter/compression length were used to produce the pellets:

D1: diameter 6 mm and compression length 20 mm (6/20)

D2: diameter 6 mm and compression length 24 mm (6/24)

D3: diameter 8 mm and compression length 32 mm (8/32).

2.2. Analysis of pellets

Produced pellets were allowed to cool in the ambient air and stored for two days before characterization. Previous to laboratory analysis, a sample splitter was used to subdivide the samples and ensure a representative sample. Then the following pellet parameters were analyzed, according to European norms: moisture content, pellet size, pellet and bulk densities, hardness and durability.

All property analyses were run in triplicate, taking the average values. Results were compared with the standard values established for straw pellets indicated in the non-

woody pellet norm (UNE-EN ISO 17225-6, 2014) to determine any possible restrictions on the use of the rice straw pellets. Table 16 summarizes the guidelines established for all study parameters.

Table 16. Parameters and guidelines published in UNE-EN ISO 17225-6 (2014), including specifications non-woody pellets.

Parameter	Guideline
Diameter (mm)	Die diameter \pm 1.00
Length (mm)	$3.15 \leq \text{Length} \leq 40.00$
Moisture content (%)	≤ 10.00
Durability (%)	≥ 97.50
Bulk density (kg/m³)	≥ 600
Additive (%)	Declare type and quantity

2.2.1 Moisture content of pellets

Moisture content of pellets (M_p) was determined by means of an air oven at 105 ± 2 °C to a constant weight, following UNE-EN 14774-2 (2010).

2.2.2 Pellet size

In order to determine dimensions, according to UNE-EN 16127 (2012), the length (L_p) and diameter (D_p) of the pellet were measured using a digital Vernier caliper CLD-150. Pellets size distribution in percentage was studied by screening 100 g of random samples of pellets through 16, 8, 4 and 2.5 mm circular holes.

2.2.3. Pellet density

The pellet density, according to UNE-EN 15150 (2012), was determined by weighing the individual pellet using a precision digital balance and calculating its volume based on the length and diameter previously determined.

2.2.4. Bulk density

To determine the bulk density, the volume and the weight of the pellet samples were measured according to UNE-EN 15103 (2010), using a laboratory balance and graduated cylinder.

2.2.5. Hardness

Hardness is defined as the maximum crushing load a pellet can withstand before cracking or breaking. It was measured using a hand-operated durometer (Amandus Khal mod. 21465) working between 0 and 100 kgf. A single pellet was located between two plates and a progressively increasing load was applied until fracturing. This test simulates the compressive stress due to the weight of pellets on top of the pellets underneath during storage in bins or silos, and crushing of pellets in a screw conveyor (Li and Liu, 2000; Gilbert et al., 2009).

2.2.6. Durability

The durability was determined according to UNE-EN 15210-1 (2010) using a New Holmen tester, which simulates pneumatic handling. This device pneumatically circulates 100 mg of pellets at 70 mbar for 60 seconds, acting as a sieving process, causing the pellets to collide with each other and with hard surfaces within the perforated hopper. The fines pass through a 3.15-mm sieve and the pellets are collected

and re-weighed upon completion of the cycle. This value was then compared against the sample weight prior to sieving, and the difference was expressed as a percentage corresponding to the durability of the pellets.

2.3. Experimental design and data analysis

Multivariate analysis has become an important tool for obtaining valuable and statistically significant models for any phenomenon by performing a minimum set of well-chosen experiments. With a given number of assays, analytical information can be obtained regarding the importance of each variable and the effect of their interactions. Thus, a three-level full factorial design was employed to investigate the effect of M_f (M1, M2, and M3) and starch ratio (S) (S0, S1, and S2) on the pellet properties produced from each die (D1, D2, and D3) at two levels of temperature (T1 and T2), with a total of 54 experiments run, using *Statistica* software version 8 (Table 17). Consequently, the equation of the polynomial regression design and the 2-way interaction effects of four predictor variables M_f , S, T, die size (D) is fitted by the following equation:

$$Z = \beta_0 + \beta_1 M_f + \beta_2 M_f^2 + \beta_3 S + \beta_4 S^2 + \beta_5 T + \beta_6 D + \beta_7 D^2 + \beta_8 M_f \times S + \beta_9 M_f \times T + \beta_{10} M_f \times D + \beta_{11} S \times T + \beta_{12} S \times D + \beta_{13} T \times D \quad (7)$$

where Z represents the pellet property as a response of variable effect, and β_i ($i = [0, 13]$) are regression coefficients that are useful in generating the relationship between variables and property response.

Table 17. Full factorial design of experiments.

Exp. No.	D	M_f	S	T
1	D1	M1	S0	T1
2	D1	M1	S1	T1
3	D1	M1	S2	T1
4	D1	M2	S0	T1
5	D1	M2	S1	T1
6	D1	M2	S2	T1
7	D1	M3	S0	T1
8	D1	M3	S1	T1
9	D1	M3	S2	T1
10	D1	M1	S0	T2
11	D1	M1	S1	T2
12	D1	M1	S2	T2
13	D1	M2	S0	T2
14	D1	M2	S1	T2
15	D1	M2	S2	T2
16	D1	M3	S0	T2
17	D1	M3	S1	T2
18	D1	M3	S2	T2
19	D2	M1	S0	T1
20	D2	M1	S1	T1
21	D2	M1	S2	T1
22	D2	M2	S0	T1
23	D2	M2	S1	T1
24	D2	M2	S2	T1
25	D2	M3	S0	T1
26	D2	M3	S1	T1
27	D2	M3	S2	T1
28	D2	M1	S0	T2
29	D2	M1	S1	T2
30	D2	M1	S2	T2
31	D2	M2	S0	T2

Table 17. Full factorial design of experiments (continued).

Exp. No.	D	M_f	S	T
32	D2	M2	S1	T2
33	D2	M2	S2	T2
34	D2	M3	S0	T2
35	D2	M3	S1	T2
36	D2	M3	S2	T2
37	D3	M1	S0	T1
38	D3	M1	S1	T1
39	D3	M1	S2	T1
40	D3	M2	S0	T1
41	D3	M2	S1	T1
42	D3	M2	S2	T1
43	D3	M3	S0	T1
44	D3	M3	S1	T1
45	D3	M3	S2	T1
46	D3	M1	S0	T2
47	D3	M1	S1	T2
48	D3	M1	S2	T2
49	D3	M2	S0	T2
50	D3	M2	S1	T2
51	D3	M2	S2	T2
52	D3	M3	S0	T2
53	D3	M3	S1	T2
54	D3	M3	S2	T2

3. RESULTS AND DISCUSSIONS

The production of pellets under different feeding and operating conditions resulted in forty-five samples of pellets; nine experimental cases (37-39, 46-48 and 52-54) involving die D3 proved unfeasible for actual pellet production. Table 18 shows the

properties of pellets for different experiments developed according to the previous section, results are analyzed and discussed below.

3.1. Quality of pellet properties

3.1.1. Durability

Durability is one of the most important quality factor. High durability means high quality pellets (Kaliyan and Vance Morey, 2009; UNE-EN 14588, 2011) low durability leads to problems such as disturbances within the pellet feeding systems, dust emission, and an increased risk of fire and explosions during pellet handling and storage (Temmerman et al., 2006). In consequence, norms recommend a durability value ≥ 97.5 % (Table 16). The durability values of the pellets obtained in this study varied greatly depending on the feeding and operating conditions, giving values between 55.24% and 99.31%, though five samples achieved the standard level.

3.1.2. Hardness

This parameter was not included in the norm, and in fact is not limited by any pellet quality norm. Although it is important during handling and storage, hardness has a negative effect on the feeding processes as well, where higher values imply difficulty operating the boiler during combustion tests due to an occasional blocking of the screw conveyor (Gilbert et al., 2009; Li and Lui, 2000; Maraver 2013). According to the results obtained in previous work (Arshadi et al., 2008; Carone et al., 2011; Carroll and Finnan, 2012; Lehtikangas, 2001; Zamorano et al., 2011), the hardness values involving various materials may reach 25 kgf, while the ideal hardness ensuring high quality pellets is 22 kgf. In our study, the hardness values of the pellets were between 17 and 22 kgf, which are lower than or equal to the recommended ideal value.

3.1.3. Bulk density

The bulk density is significant for pellet storage and transport as well as combustion efficiency (Gilbert et al., 2009; Kaliyan and Vance Morey, 2009; Vinterbäck, 2004). The norm recommends bulk density $\geq 600 \text{ kg/m}^3$ (Table 16). Results obtained by Liu et al. (2013) showed that the bulk density of cylindrical rice straw pellets having 6 mm diameter and produced at 15% M_f was 640 kg/m^3 . In the present contribution, bulk density values ranged between 490 and 750 kg/m^3 , only eight samples of produced pellets did not attain the standard.

3.1.4. Pellet density

The norm did not include guideline values for this parameter. However, in view of the limits established by German standards (DIN EN 15270, 2007; DIN 51731, 1996) and the results of previous works (Arshadi et al., 2008; Carone et al., 2011; Carroll and Finnan, 2012; Lehtikangas, 2001; Liu et al., 2013; Zamorano et al., 2011), the pellet density of rice straw and other materials may reach 1500 kg/m^3 , although the ideal value for a high quality pellet is 1200 kg/m^3 . Extremely high pellet density is not good for combustion efficiency, as access to oxygen is prevented when the pellet elements are very tightly packed (Tarasov et al., 2013).

Variation in the pellet density values in this case ranged between 1030 and 1290 kg/m^3 . Although some values were lower than the ideal one, most were near it. We could therefore conclude that there was no important deviation from the pellet density value of reference.

Table 18. Pellet properties (response) according to design of experiments.

Exp. No.	M _p (%)	D _p (mm)	L _p (mm)	L _p /D _p	Hardness (kgf)	Durability (%)	Pellet density (kg/m ³)	Bulk density (kg/m ³)	Particle size distribution (%)			
									16-8 mm	8-4 mm	4-2.5 mm	<2.5 mm
1	11.10	6.04	26.33	4.36	18.33	58.88	1270	630	4.04	94.00	0.92	1.03
2	11.21	6.09	27.34	4.49	21.33	85.77	1250	650	6.16	93.47	0.16	0.22
3	11.28	6.06	28.48	4.70	21.33	85.60	1260	640	7.37	91.65	0.49	0.49
4	13.60	6.21	26.70	4.30	21.33	93.85	1280	630	13.09	86.74	0.05	0.12
5	13.80	6.11	26.40	4.32	20.67	95.73	1170	640	6.16	93.47	0.16	0.22
6	13.95	6.09	27.41	4.50	21.00	90.47	1030	650	12.19	86.77	0.66	0.51
7	15.75	6.12	28.52	4.66	21.50	96.24	1210	610	3.56	96.22	0.07	0.15
8	15.96	6.15	27.00	4.39	21.17	92.58	1130	600	4.17	95.53	0.18	0.12
9	16.10	6.15	24.48	3.98	21.50	91.84	1150	570	2.85	96.52	0.31	0.32
10	10.70	6.11	26.33	4.31	18.67	66.25	1230	610	4.74	93.72	0.71	0.83
11	10.81	6.11	25.11	4.11	19.17	79.16	1180	610	3.70	95.23	0.46	0.61
12	10.79	6.16	27.54	4.47	20.33	74.52	1150	580	4.10	95.03	0.41	0.46
13	12.57	6.12	24.05	3.93	20.83	92.97	1280	640	9.38	90.52	0.05	0.05
14	12.70	6.10	27.27	4.47	21.00	94.84	1100	630	10.22	89.75	0.00	0.03
15	12.85	6.13	25.38	4.14	21.00	93.50	1170	610	7.27	90.47	0.01	0.05
16	15.43	6.26	26.67	4.26	21.00	91.94	1140	560	1.66	98.27	0.01	0.06
17	15.24	6.14	26.22	4.27	21.33	94.79	1130	590	4.38	95.56	0.00	0.06
18	15.24	6.15	24.54	3.99	21.83	94.70	1130	540	4.38	95.49	0.06	0.08
19	10.81	6.24	25.08	4.02	17.00	55.24	1150	560	3.25	95.40	0.55	0.80
20	10.33	6.06	24.72	4.08	20.33	80.82	1260	670	2.05	97.21	0.30	0.45
21	11.72	6.11	25.42	4.16	20.67	82.53	1180	640	2.11	97.66	0.24	0.26
22	11.90	6.10	25.13	4.12	21.33	79.23	1230	620	5.86	93.46	0.51	0.16
23	12.33	6.05	27.23	4.50	21.00	85.26	1260	690	5.95	93.27	0.39	0.40

Note: Hardness, pellet density, and particle size distribution do not have guidelines in the norm.

Bold values indicate that the results achieved the standard levels of the norm.

Table 18. Pellet properties (response) according to design of experiments (Continued)

Exp. No.	M _p (%)	D _p (mm)	L _p (mm)	L _p /D _p	Hardness (kgf)	Durability (%)	Pellet density (kg/m ³)	Bulk density (kg/m ³)	Particle size distribution (%)			
									16-8 mm	8-4 mm	4-2.5 mm	<2.5 mm
24	13.52	6.02	24.44	4.06	22.00	92.22	1270	670	4.80	95.01	0.08	0.11
25	12.38	6.30	23.69	3.76	19.33	79.07	1120	490	3.70	96.00	0.20	0.10
26	16.15	6.16	23.53	3.82	20.00	92.30	1200	630	7.60	91.90	0.17	0.33
27	16.33	6.12	25.40	4.15	21.00	97.06	1210	630	8.37	91.56	0.03	0.04
28	10.67	6.16	25.19	4.09	19.00	73.73	1180	570	3.46	96.23	0.18	0.13
29	10.12	6.13	25.75	4.20	21.00	86.45	1210	610	2.13	97.25	0.35	0.27
30	10.49	6.08	24.99	4.11	21.50	91.88	1250	660	2.06	97.81	0.03	0.10
31	10.60	6.16	26.24	4.26	21.67	90.25	1180	630	4.66	95.15	0.13	0.06
32	11.91	6.06	26.30	4.34	21.00	93.32	1240	690	6.54	93.34	0.03	0.09
33	12.00	6.04	24.64	4.08	22.00	94.93	1280	680	4.50	95.43	0.02	0.05
34	12.35	6.38	24.88	3.90	19.00	78.60	1100	420	2.71	96.57	0.42	0.30
35	14.19	6.02	25.52	4.24	21.00	98.20	1230	630	9.91	90.07	0.00	0.02
36	14.90	6.19	23.89	3.86	21.00	97.51	1170	610	7.26	92.75	0.00	0.00
37	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
38	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
39	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
40	11.52	8.19	18.43	2.25	19.50	90.69	1150	660	98.01	1.88	0.04	0.08
41	12.30	8.03	19.67	2.45	20.00	92.55	1290	750	96.50	3.19	0.10	0.20
42	12.37	8.04	19.22	2.39	21.00	96.00	1240	740	96.56	3.35	0.03	0.05
43	12.00	8.08	18.34	2.27	21.00	91.37	1160	670	91.52	7.78	0.41	0.30
44	13.67	8.14	19.37	2.38	21.00	93.07	1180	660	96.79	3.13	0.04	0.04
45	14.80	8.09	20.14	2.49	21.00	99.31	1260	740	95.16	4.75	0.07	0.02
46	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE

Note: Hardness, pellet density, and particle size distribution do not have guidelines in the norm.

Bold values indicate that the results achieved the standard levels of the norm.

NE: Pellets do not exist.

Table 18. Pellet properties (response) according to design of experiments (Continued)

Exp. No.	M _p (%)	D _p (mm)	L _p (mm)	L _p /D _p	Hardness (kgf)	Durability (%)	Pellet density (kg/m ³)	Bulk density (kg/m ³)	Particle size distribution (%)			
									16-8 mm	8-4 mm	4-2.5 mm	<2.5 mm
47	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
48	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
49	11.49	8.22	19.07	2.32	20.67	95.54	1130	630	99.01	0.67	0.01	0.02
50	12.00	8.07	20.09	2.49	21.00	97.93	1240	750	98.67	1.27	0.02	0.04
51	12.50	8.04	18.57	2.31	21.00	97.50	1230	740	97.72	2.23	0.02	0.03
52	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
53	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
54	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE

Note: Hardness, pellet density, and particle size distribution do not have guidelines in the norm.

Bold values indicate that the results achieved the standard levels of the norm.

NE: Pellets do not exist.

3.1.5. Moisture content of pellet

The values of M_p of pellets produced in this research ranged from 10.12% to 16.33%. These values were on the “safe storage” side of the 20% threshold preventing bacterial growth (Lehtikangas, 2000), material degradation and self-heating, which in the worst case scenario could result in self-ignition (Rhén et al., 2005). Still, all the values were above the level ($\leq 10\%$) established in the norm (Table 16).

The high M_p values obtained can be attributed to the elevated M_f necessary for pelletisation, as well as the low temperature range under which the pellets were produced (Carone et al., 2011). To meet the standard level requirements, the M_p should be reduced by immediate cooling of the pellets by means of forced air (Turner, 1995).

3.1.6. Pellet size

Pellet size is determinant of pellet strength, as longer pellets can be more easily broken (Tarasov et al., 2013). Pellet dimensions are important factors in the context of fuel feeding properties and combustion processes. Thinner pellets allow for a more uniform combustion rate than thicker ones. The shorter the pellets, the easier the continuous flow can be arranged, and the L_p/D_p ratio is of particular relevance if pneumatic feeding systems are used (Lehtikangas, 2001; Obernberger and Thek, 2004). The norm sets the diameter limit (die diameter ± 1 mm) and length range (between 3.15 and 40 mm).

Visual observations of the pellets sufficed to reveal differences among pellet sizes for the different dies (Figure 22). The particle size distribution of pellets length was analyzed and the results showed that no particles were obtained more than 16 mm size and the higher percentage of particles (more than 90 %) was obtained between 4 and

8mm for D1 and D2, meanwhile, was retained between 8 and 16mm size for D3, see Table 18. Pellet length varied between 18.34 and 28.52 mm. Meanwhile, pellet diameter ranged between 6.02 and 6.38 mm for the hole diameter of 6 mm, and between 8.03 and 8.22 mm in the case of a die hole diameter of 8 mm. The slight increase in diameter indicates that the pellets actually expanded after release from the die (Carone et al., 2011). Despite such variations, all dimension values of the pellets obtained were well within the limits established by the norm.

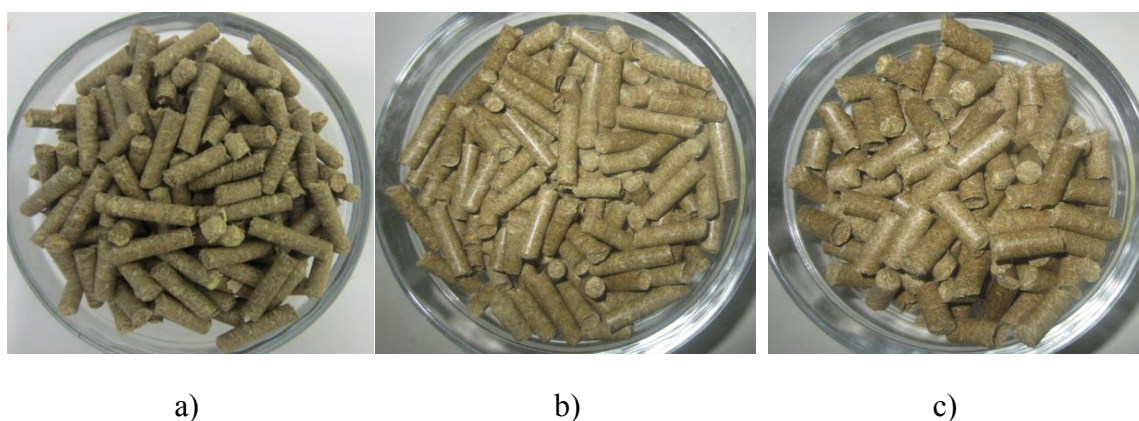


Figure 22. Pellets photos for the different dies a) D1, b) D2, and c) D3 at M3 and S2.

3.2. Effect of feeding and operation conditions on pellet properties

After recording the results summarized in Table 18, the effects of feeding and operating conditions on the pellet quality properties (durability, hardness, bulk density, pellet density, M_p , and dimensions) were assessed statistically using Pareto charts, t-values of quadratic (Q) or/and linear (L) variables interactions are represented by columns and the line going across the columns with a confidence level 95% indicates how large the variable effect has to be statistically significant, see Figure 23. The regression equation coefficients for the different variables and their interactional effects are presented in Tables 19 and 20. Furthermore, different relationships between certain pellet properties were discerned, as illustrated in Figure 24.

3.2.1. Durability

All feeding and operational variables significantly affected durability, as reflected in Figure 23a. Starch had the most substantial effect, its addition or increase resulting in enhanced durability, as found by previous studies (Ståhl et al., 2012; Tarasov et al., 2013; Tumuluru et al., 2011). The significant effect of M_f on durability reported by Tarasov et al. (2013) and Larsson et al. (2008), was confirmed, our results showed that in most cases, increasing M_f resulted in significantly higher durability values. Likewise in line with previous findings (Fasina, 2008; Kaliyan and Vance Morey, 2009; Lehtikangas, 2001; Serrano et al., 2011; Theerarattananon et al., 2011; Zafari et al., 2012), durability was found to increase with greater moisture content until reaching maximum durability; a further increase in moisture content led to a decrease in durability in some cases in the present study.

The initial increase in durability with an increase in moisture can be attributed to the binding forces of the water molecules strengthening the bonds between individual particles in the pellets (Theerarattananon et al., 2011). Water acts as a film-type binder by strengthening and promoting bonding via Van der Waal's forces, that is, by increasing the contact area of the particles (Mani et al., 2003). Further increases in moisture beyond the optimal range would depend on the type of biomass and the processing conditions, potentially reducing the intermolecular forces; even much higher moisture content would cause a biphasic mixture (liquid and solid phase) and cause intermolecular forces to disappear entirely, resulting in swelling and disintegration of the pellets (Fasina, 2008; Zafari et al., 2012).

On the other hand, increasing the processing temperature gave rise to better pellet durability in most cases, as found by Rhén et al. (2005) and Tumuluru et al. (2011). Finally, the die size clearly influenced durability. Higher durability values were observed in conjunction with greater die size, in line with previous studies of durability correlated to die size (Rhén et al., 2005; Smith et al., 1977; Tabil and Sokhansanj, 1996; Theerarattananoon et al., 2012). However, Tumuluru et al. (2011) and Theerarattananoon et al. (2011) found that smaller die size resulted in higher durability, as observed for some values obtained under the same feeding conditions but with different die size.

Table 19. Regression coefficients of the variables for durability, hardness, and bulk density of pellets produced

	Durability			Hardness			Bulk density		
	β_i	Std Err	P-value	β_i	Std Err	P-value	β_i	Std Err	P-value
Intercept	+88.17	1.03	0.00	+20.55	0.15	0.00	+639.53	6.55	0.00
M_f	+13.52	2.78	0.00	+0.93	0.40	0.03	-33.27	17.60	0.07
M_f²	+4.61	1.82	0.02	+0.54	0.26	0.05	+49.87	11.53	0.00
S	+11.07	2.14	0.00	+1.37	0.31	0.00	+62.79	13.55	0.00
S²	+3.74	1.74	0.04	+0.12	0.25	0.63	+32.33	11.02	0.01
T	+3.81	1.80	0.04	+0.20	0.26	0.45	-18.79	11.41	0.11
D	+5.30	2.82	0.07	-0.27	0.41	0.52	+76.37	17.88	0.00
D²	-3.89	1.87	0.05	-0.05	0.27	0.86	-32.63	11.87	0.01
M_f×S	-6.66	2.64	0.02	-0.98	0.38	0.02	+5.77	16.76	0.73
M_f×T	-1.83	2.20	0.41	-0.15	0.32	0.64	-4.63	13.92	0.74
M_f×D	-4.67	3.92	0.24	-0.30	0.57	0.60	+16.62	24.83	0.51
S×T	-1.88	2.03	0.36	-0.12	0.29	0.68	+5.22	12.85	0.69
S×D	+2.52	2.73	0.36	+0.16	0.40	0.68	+59.76	17.32	0.00
T×D	+3.05	2.34	0.20	+0.37	0.34	0.28	+4.69	14.81	0.75
R²		0.79			0.86			0.79	
Q²		0.71			0.68			0.70	

M_f: Feeding moisture content, S: Starch ratio, T: Temperature, D: Die size, R²: Goodness of fit, and Q²: Goodness of prediction.

Note: Numbers in bold print are statistically significant

Table 20. Regression coefficients of the variables for pellet density, M_p , and L_p/D_p of pellets produced

	Pellet density			M_p			L_p/D_p		
	β_i	Std Err	P-value	β_i	Std Err	P-value	β_i	Std Err	P-value
Intercept	+1195.20	9.35	0.00	+12.50	0.11	0.00	+3.59	0.03	0.00
M_f	-28.71	25.14	0.26	+3.50	0.29	0.00	-0.08	0.09	0.36
M_f^2	+25.67	16.47	0.13	-0.61	0.19	0.00	+0.06	0.06	0.33
S	+32.68	19.36	0.10	+1.08	0.22	0.00	+0.07	0.07	0.32
S^2	+11.67	15.74	0.46	+0.12	0.18	0.49	+0.10	0.06	0.10
T	-16.17	16.29	0.33	-0.59	0.19	0.00	-0.04	0.06	0.50
D	+10.47	25.54	0.68	-1.02	0.29	0.00	-1.96	0.09	0.00
D^2	+18.63	16.95	0.28	-0.36	0.19	0.07	+0.76	0.06	0.00
$M_f \times S$	+1.73	23.95	0.94	+0.68	0.27	0.02	-0.14	0.09	0.12
$M_f \times T$	+5.17	19.88	0.80	-0.17	0.23	0.45	+0.00	0.07	0.96
$M_f \times D$	+50.70	35.47	0.16	-1.23	0.40	0.00	+0.10	0.13	0.42
$S \times T$	+16.46	18.35	0.38	-0.24	0.21	0.26	-0.05	0.07	0.43
$S \times D$	+102.53	24.75	0.00	+0.66	0.28	0.03	+0.08	0.09	0.40
$T \times D$	+5.14	21.15	0.81	+0.28	0.24	0.26	+0.11	0.08	0.15
R^2		0.74			0.93			0.96	
Q^2		0.44			0.90			0.95	

M_f : Feeding moisture content, S: Starch ratio, T: Temperature, D: Die size, R^2 : Goodness of fit, and Q^2 : Goodness of prediction.

Note: Numbers in bold print are statistically significant

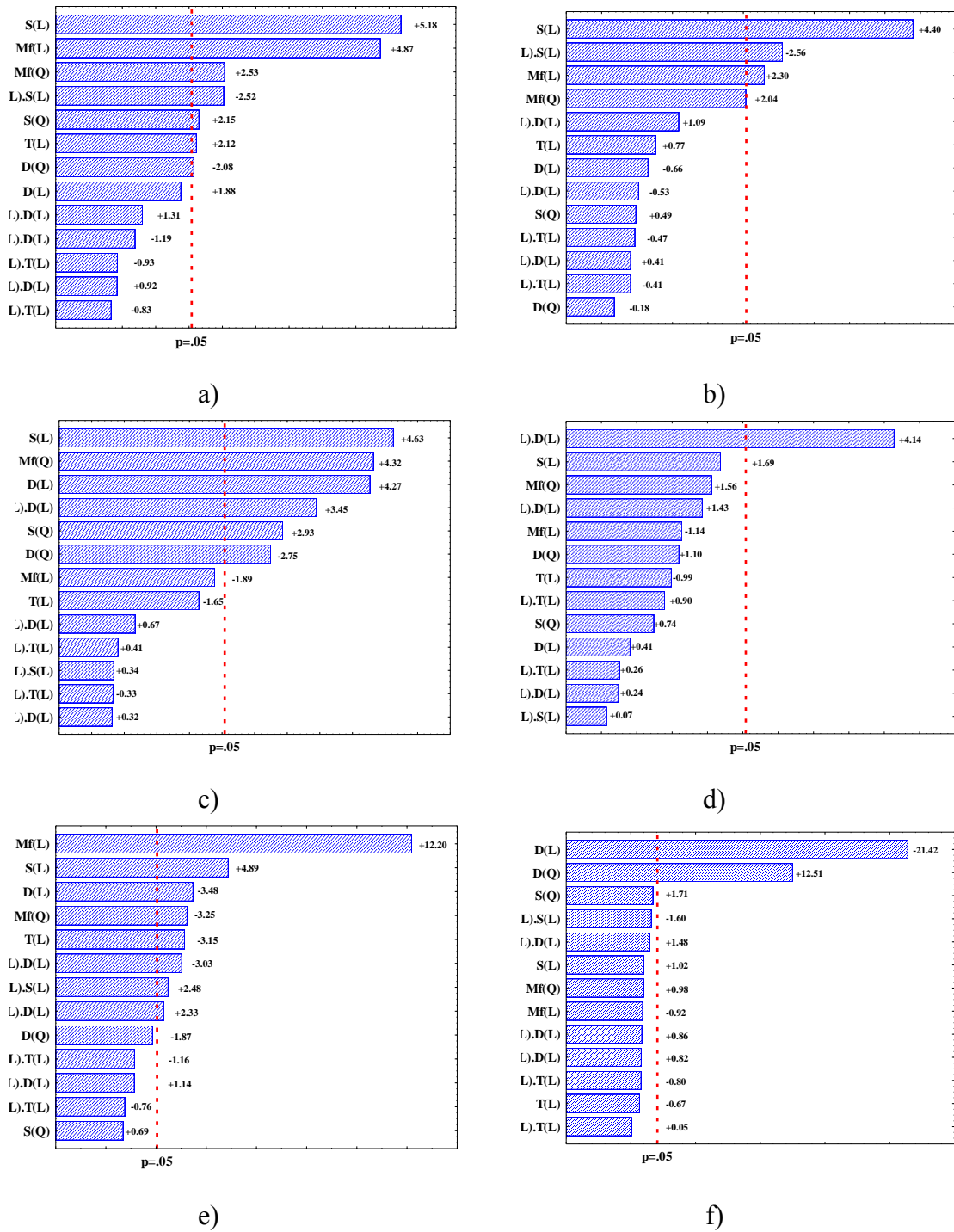


Figure 23. Variable effects on pellet properties a) durability, b) hardness, c) bulk density, d) pellet density, e) M_p and f) L_p/D_p ratio.

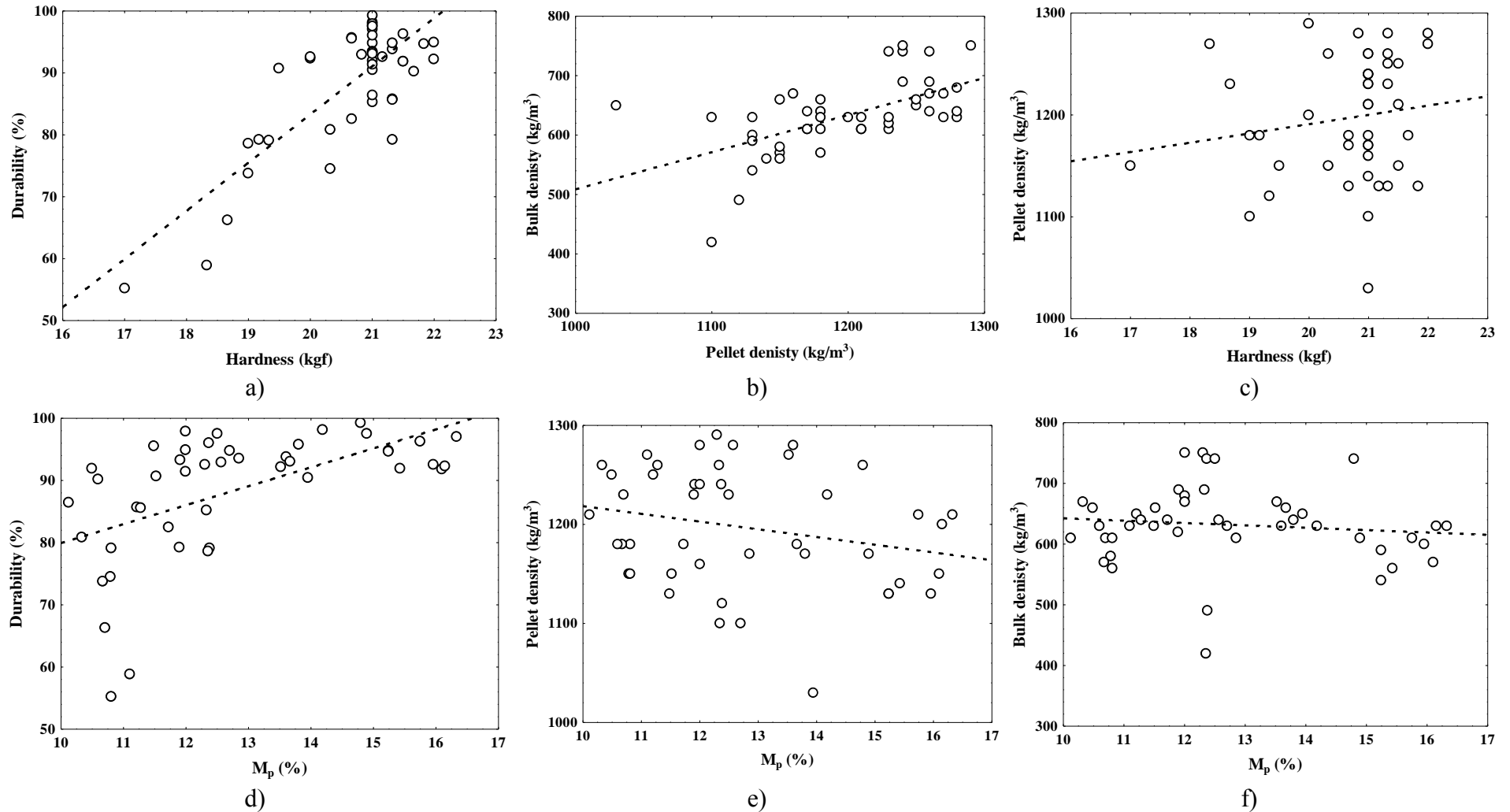


Figure 24. Relations between pellet properties a) durability/hardness, b) bulk density/pellet density, c) pellet density/hardness, d) durability/ M_p , e) pellet density/ M_p , f) bulk density/ M_p .

3.2.2. Hardness

Although die size and the temperature of the process affected hardness values to some extent (Carone et al., 2011; Gilbert et al., 2009; Larsson et al., 2008; Rhén et al., 2005; Shankar and Bandyopadhyay, 2005; Stelte et al., 2011), hardness was more significantly affected by M_f and starch ratio, as found by Sokhansanj et al. (2005) and Kaliyan and Vance Morey (2009). Moreover, starch exerted a dominant effect when compared to the other variables, as seen in Figure 23b. The effects of the different variables on hardness values were quite similar to those of durability, and indeed, a clear relation between hardness and durability was detected. As is evident in Figure 24a, durability was positively related with hardness for most values obtained in this study. The hardness and durability are two distinct pellet quality measures used to assess the effectiveness of the inter-particle bonds created during the densification process (Kaliyan and Vance Morey, 2009; Thomas et al., 1996). Richards (1990) observed direct relationships between the hardness and durability of pellets. Tabil and Sokhansanj (1996) and Wood (1987) found that the logarithm of hardness and durability of feed pellets had a linear relationship. However, Tabil et al. (1996) also observed that some of the pellets with high durability had low hardness values, a finding likewise derived from some values obtained in the present study.

3.2.3. Bulk density

Bulk density was significantly affected by starch ratio, followed by M_f and die size, as shown in Figure 23c. In contrast, the temperature effect was not significant and almost negligible for some cases, as found by Larsson et al. (2008). For most cases studied, the bulk density increased with increasing starch ratio, as reported by Tarasov et al. (2013). Bulk density values increased with a higher initial M_f , but decreased after a certain point

of high M_f , as described in previous studies (Fasina, 2008; Larsson et al., 2008; Theerarattananoon et al., 2011; Tumuluru et al., 2011; Zafari et al., 2012). This is because pellets expanded and increased in volume when they absorbed more moisture (Theerarattananoon et al., 2011). Greater bulk density values with greater die size were also observed by Wu et al. (2011) and Theerarattananoon et al. (2012).

3.2.4. Pellet density

Although the pellet density was more affected by the starch ratio, followed by M_f , die size, and finally temperature, no variables had a significant effect on it. As seen in Figure 23d, the effect of the different variables on pellet density was similar to that on bulk density; furthermore, pellet density values are positively correlated and affect bulk density (Fasina, 2008; Larsson et al., 2008; Theerarattananoon et al., 2011; Tumuluru et al., 2011; Zafari et al., 2012), as reflected in Figure 24b. Pellet density was also found to increase with increasing hardness values, see Figure 24c, in line with the results of Rhén et al. (2005) and Carone et al. (2011).

3.2.5. Moisture content of pellets

The M_p , significantly affected by all feeding and operation variables of study, was most markedly influenced by M_f . Figure 23e shows that increasing M_f coincided with a substantial increase in M_p , as found by Tumuluru et al. (2011) and Serrano et al. (2011). Meanwhile, M_p slightly increased with a greater starch ratio, otherwise decreased (with higher die size and higher temperature range (Carone et al., 2011). In most cases, M_p was positively correlated to durability values and negatively correlated to pellet and bulk density values, as seen Figure 24d, e, and f, and as reported by Fasina (2008) and Theerarattananoon et al. (2011).

3.2.6. Pellet size

The L_p/D_p ratio was significantly affected only by die size; the other variables showed a minor effect, seen in Figure 23f. Pellet diameter was close to die hole diameter with the effect of different variables. Pellet length decreased markedly with increasing die compression length. Meanwhile, increasing starch ratio and M_f can make particles agglomerate better, providing for longer pellets, as obtained by Serrano et al. (2011) and Carone et al. (2011). Otherwise, a higher processing temperature leads to a reduction in the expansion of pellets, meaning lesser pellet length (Carone et al., 2011).

3.3 The best conditions for producing high quality pellets

According to the analysis of results presented here, the properties of pellets most affected by the specific operating and feeding conditions involved in production would be M_p , durability and bulk density. Hardness, pellet density and the dimensions of pellets were not significantly altered by most of the conditions tested. In fact, all pellet dimension values were within the limits set forth in the prescriptive norms. None of the M_p achieved the standard level. Although hardness and pellet density are not addressed by the norm, our results gave values near the ideal ones recommended by previous studies.

In consequence, the best conditions for producing high quality pellets are found to be well within the recommended limits established for durability and bulk density values. Furthermore, pellet durability, a key quality factor (Kaliyan and Vance Morey, 2009; UNE-EN 14588, 2011), was used to determine high quality pellets suggesting the best condition. Five manufacturing conditions achieved the standard limits of durability, as highlighted in bold in Table 18. In any case, the use of a die size of 8 mm diameter and

a compression length of 32 mm, in conjunction with 17% of feeding material moisture content, 2% of starch and an operation temperature lower than 50 °C produced the pellets of rice straw of the highest quality, featuring the characteristics summarized in Table 21.

Table 21. The best conditions for producing high quality pellets of rice straw

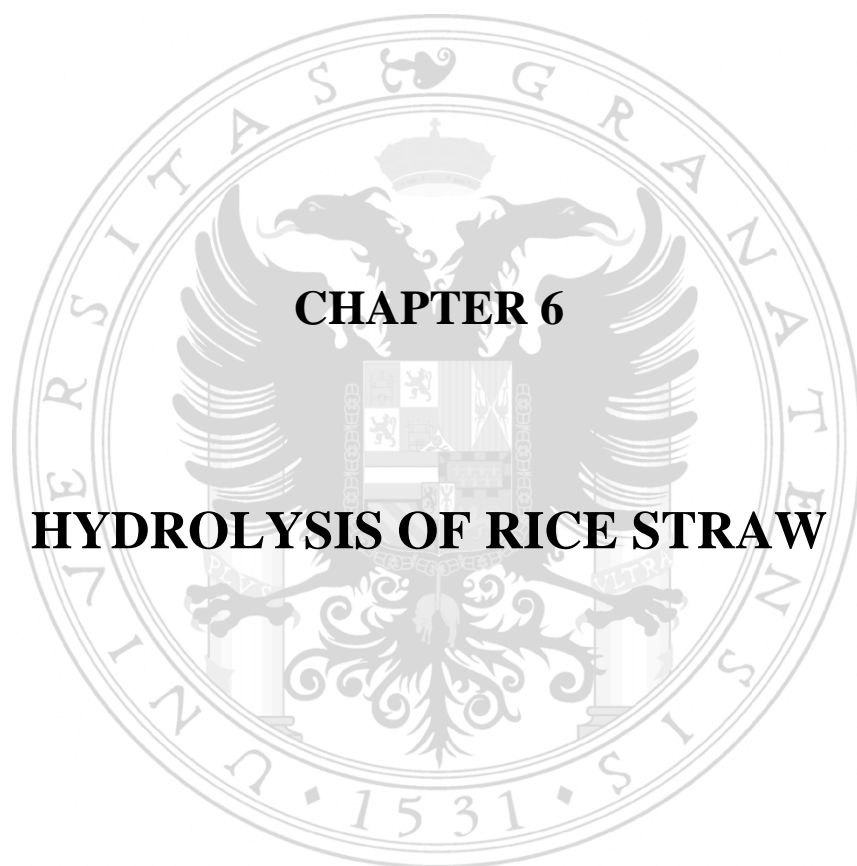
Manufacturing conditions					Pellet properties					
Exp. No.	D (mm/mm)	M _f (%)	S (%)	T (°C)	Hardness (kgf)	Durability (%)	Pellet density (kg/m ³)	Bulk density (kg/m ³)	M _p (%)	L _p /D _p
45	8/32	17	2	< 50	21.00	99.31	1260	740	14.80	2.49

M_f: Feeding moisture content, S: Starch ratio, T: Temperature, D: Die size

4. CONCLUSIONS

The influence of densification parameters on the quality properties of rice straw pellets was evaluated according to the European Standards for non-woody biomass:

- The results showed significant effects of the feeding and operating conditions studied (M_f , starch binder ratio, operating temperature, and flat die size) on the pellets' properties (hardness, durability, bulk density, pellet density, M_p and dimensions). The durability, hardness and bulk density values are the most affected by M_f and starch ratio; on the other hand, die size and M_f showed a high significant influence on dimensions and M_p , respectively. Furthermore, positive relationships were observed between some pairs of the quality parameters analyzed such as hardness and durability or pellet and bulk density values.
- Despite the fact that all the dimension values fulfilled the limits of the norm, the M_p did not achieve the threshold established by the standard due to the fact that an initially high moisture content was necessary for the agglomeration between particles. Hardness and pellet density are not addressed by the norms, but the results obtained were near the ones recommended by previous studies. Considering the results, relationships and guidelines obtained, it can be deduced that the highest pellets' quality is that corresponding with the sample of durability 99.31%, which was obtained with the following operating conditions: 2% starch, 17% M_f , $T < 50$ °C and die size (8/32).



CHAPTER 6

HYDROLYSIS OF RICE STRAW

Recently, rice straw is regarded as a promising starting material for 2nd generation bioethanol production that represents one of the most important bioenergy forms of rice straw. Hydrolysis of rice straw is a preliminary step for bioethanol production and pelleting was recently shown to enhance the pretreatment and hydrolysis without affecting the quality of sugars for fermentation. In this sense, analysis of the effect of pelleting on hydrolysis and saccharification of rice straw represented the main objective of this chapter.

1. INTRODUCTION

Rice straw is one of the most abundant lignocellulosic wastes by-products worldwide, with an annual availability of 731 million tons globally, and provides an alternative substrate to produce several value added products (Burton and Fincher, 2014; Karimi et al., 2006b; Yao et al., 2007; Liu et al., 2012). Recently, rice straw is regarded as a promising starting material for 2nd generation bioethanol production, because of its abundance, cost-effectiveness and high cellulosic content that can be readily hydrolysed into fermentable sugar (Binod et al., 2010; Sánchez and Cardona, 2008). Globally, rice straw can potentially produce 205 billion litres bioethanol per year, which is about 5% of total consumption. It is the largest amount from a single biomass feedstock (Yoswathana et al., 2010).

Rice straw conversion to ethanolic biofuel is limited by its low bulk density and the associated handling, transportation and storage costs. Pelleting increases the biomass density by almost ten-fold, thereby, facilitates handling and lowers storage costs (Hess et al., 2007; Tumuluru et al., 2011). In addition, the high shearing force and frictional heating during the pelleting of lignocellulose partially deconstruct its complex structure;

this alteration of lignocellulose during pelleting was recently shown to enhance the pretreatment and hydrolysis without affecting the quality of sugars for fermentation (Guragain et al., 2013; Rijal et al., 2012; Theerarattananon et al., 2012).

On the other hand, pretreatment is necessary to obtain ultimately high degree of fermentable sugars, where this process aids to break down the lignin structure and disrupt the crystalline structure of cellulose (Aderemi et al., 2008; Aly and Megeed, 2008; Binod et al., 2010; Mosier et al., 2005; Patel et al., 2007). Among various pretreatment approaches, microbial pretreatment offers advantages such as low-capital cost, low energy, no chemicals requirement, and mild environmental conditions. However, the main drawback of employing microorganisms in pretreatment is the low hydrolysis rate obtained in most biological materials compared to other technologies (Alvira et al., 2010). Investigations on microbial lignocellulose decomposition, successfully identified several *actinomyete* species which secrete a range of hydrolysing enzymes for delignification of feedstock and enhanced sugar recovery (Abdulla and El-Shatoury, 2007; Anderson et al., 2012; Xu and Yang, 2010). Compared to fungi which may possibly mineralize lignin, *actinomycetes* have an added advantage of recovery of depolymerised lignin, which is an important industrial raw material (Saritha et al., 2013).

In this context, the present study attempted to evaluate the combination of pelleting and microbial hydrolysis for improving the saccharification process. Rice straw was used as a model substrate, and a consortium of 5 preselected *actinomyete* strains was employed with pelleting under different conditions. Effectiveness of hydrolysis was evaluated by

comparing pelleted and unpelleted straw in terms of total saccharification efficiency and sugar recovery from biomass feedstock.

2. MATERIAL AND METHODS

2.1. Rice straw and pellets sampling

The rice straw used in this study was obtained from Andalusia, Spain. The characteristics of the used straw samples were presented in Table 12. According to the operation and feeding conditions of a previous work of pellets in Chapter 5, two samples of pellets (P1 and P2) were selected only different on percentage of binder used to manufacturer them (Table 22).

Table 22. Feeding and operation conditions to produce pellet samples

Pellet sample	Feeding conditions		Operation conditions	
	M _f (%)	S (%)	D (mm/mm)	T (°C)
Sample 1 (P1)	15	0	(6/24)	50-80
Sample 2 (P2)	15	2	(6/24)	50-80

M_f: Feeding moisture content, S: Starch ratio, T: Temperature, D: Die size (diameter/compression length).

2.2. Characterization of the *actinomyce* consortium

The straw-degrading *actinomyce* consortium was named SAC and consisted of seven *actinomyce* strains. The strains were selected based on their efficient cellulolytic abilities in previous investigations (Abdulla and El-Shatoury, 2007).

2.2.1. DNA extraction and phylogenetic analysis of the strains

Individual strains of SAC were grown in starch casein broth at 28 °C, 120 rpm, for 2-4 days, until mycelial growth is obtained before sporulation stage. About 100 mg of

harvested mycelia were washed in saline solution (NaCl 0.085%). DNA extraction was carried out using the EZ-10 Spin Column Plant PCR kit (Bio Basic Inc, Canada) according to the manufacturer's instructions. The 16S rRNA gene of the strains was amplified in 20 μ l reactions using the universal bacterial primers 27F-AGAGTTTGATCMTG GCTCAG and 1492R-GGTTACC TTGTTACGACTT (Saritha et al., 2013). DNA sequencing was carried out by Macrogen Labs Ltd., Korea. Amplification and sequencing conditions were performed as described by Trujillo et al. (2010). The sequences obtained were compared with those in the GenBank database using the BLAST search program. The sequences of the isolates and those of their most closely related taxa retrieved from GenBank were aligned using the CLUSTAL X program (Thompson et al., 1997) and checked for alignment inconsistencies. The phylogenetic trees were inferred using the neighbour-joining method (Saitou and Nei, 1987) and was visualized using software package TreeView X (Page, 1996).

2.2.2. Enzymatic activities of the consortium

Enzymatic activities of individual strains of SAC were measured as activity index (diameter of clear zone/diameter of growth). Lignin peroxidases were determined as described by Niladevi and Prema (2005) using Azura B plate assay on peptone agar medium and clear zones were measured after incubation at 28 °C for 7 days. Amylase, cellulase, carboxymethyl cellulase and hemicellulase activities were determined according to Williams and Wellington (1982). *Actinomycetes* grown on starch agar medium for 14 days at 28 °C were covered by Gram's iodine solution and clear halos around the amylase-positive colonies were scored. Cellulolytic ability was measured as clearing of the cellulose agar medium around colonies after 21 days of incubation at 28 °C. Strains inoculated into carboxymethyl cellulose (CMC) basal medium for 9 days at

28 °C were covered with 1% aqueous hexadecyl trimethyl ammonium bromide to score carboxymethyl cellulase activity. Strains grown on xylan-containing agar medium for 21 days at 28 °C were evaluated for hemicellulase production by clear zones formation.

2.2.3. Cellulose saccharification by SAC individuals

Spore suspensions of each strain was inoculated into cellulose broth and incubated at 28 °C, 120 rpm. After 10 days, 3 ml hydrolysates were centrifuged for 10 min at room temperature. The reducing sugar (RS) was determined using Nelson-Somogyi method (Somogyi, 1945). The degree of cellulose saccharification (DCS) was calculated using the following equation (Vallander and Eriksson, 1985):

$$\text{DCS (\%)} = [(\text{RS} \times \text{V} \times 0.89) / (\text{M})] \times 100 \quad (8)$$

where RS in the hydrolysate estimated as glucose, in g/l; V is the liquid volume of the hydrolysate, in ml (the factor 0.89 is used to convert monosaccharide to polysaccharide due to water uptake during hydrolysis); and M is the weight of cellulose, in mg.

2.3. Hydrolysis of rice straw by SAC

2.3.1. Preparation of the consortium

The strains were activated from spore suspensions in yeast extract dextrose broth and incubated at 28 °C, 100 rpm for 5 days. Mycelia were harvested by centrifugation, washed twice in phosphate buffer and adjusted to consistent cell concentration (of absorbance 2.0 at 540 nm).

2.3.2. Hydrolysis batch experiment

The use of SAC in hydrolysis of the pelleted and shredded straw, with and without starch additive, was carried out in sterilized 0.5-L flasks; containing 10% pellets or 2 mm shredded straw, in a total volume 70 ml of 1 M potassium phosphate buffer (PH 7). The *actinomycetes* consortium (1 ml mycelia suspension from each strain at $A_{540} = 2$) was inoculated into the flasks and incubated at 28 °C for 7 days. Un-inoculated control flasks were included and the experiment was performed in triplicate. On daily basis, supernatant samples were taken for monitoring straw hydrolysis. Total carbohydrate content (TC) was determined using phenol sulphuric acid method (DuBois et al., 1956) and RS was determined as above mentioned. Total saccharification (TSac) (cellulose and hemicellulose conversion to RS) was calculated by using the following equation (Schilling et al., 2009):

$$\text{TSac (\%)} = (\text{RS} / \text{TC before hydrolysis}) \times 100 \quad (9)$$

Actual RS yield in the hydrolyzed samples was calculated by subtracting the reducing sugar content present in the control samples from the corresponding consortium-inoculated samples.

At the end of experiment, inoculated and control straw samples were washed with deionized water and kept at 4 °C for examination by scanning electron microscopy, at Housing and building national research center, Giza, Egypt.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the SAC consortium

In the present study, strains of the developed consortium were confirmed by 16SrDNA analysis as strains of *Streptomyces* (3 strains), *Nocardiopsis* (2 strains), *Nocardioides* (1 strain) and *Micomonospora* (1 strain); exhibiting a similarity between 89-99% with the nearest phylogenetic neighbour strains. The phylogenetic relationship is shown in Table 23 and Figure 25. Strain 97-SAC had a high similarity value with *Streptomyces griseoruben*. This species was reported to release a series of enzymes, including cellulase, xylanase and ligninase, simultaneously, resulting in weight loss about 76% of straw in 30 days (Prasad et al., 2013). It was also found to partially degrade lignin from paddy straw, resulting in its solubilization in high amounts (Saritha et al., 2013).

Table 23. The 16S rDNA sequences of SAC isolates and the similar sequences from NCBI BLAST.

Isolate Code	Closest type strain	Similarity rate (%)
61-SAC	<i>Nocardiopsis lucentensi</i> DSM44048	89
11-SAC	<i>Nocardiopsis composta</i> KS9	89
85-SAC	<i>Streptomyces azureus</i> NRRL B2655	99
97-SAC	<i>Streptomyces griseorubens</i> NBRC 12780	92
105-SAC	<i>Streptomyces variabilis</i> NRRL B-3984	95
38- SAC	<i>Micromonospora pisi</i> GUI 15	94
7-SAC	<i>Nocardioides agariphilus</i> MSL 28	90

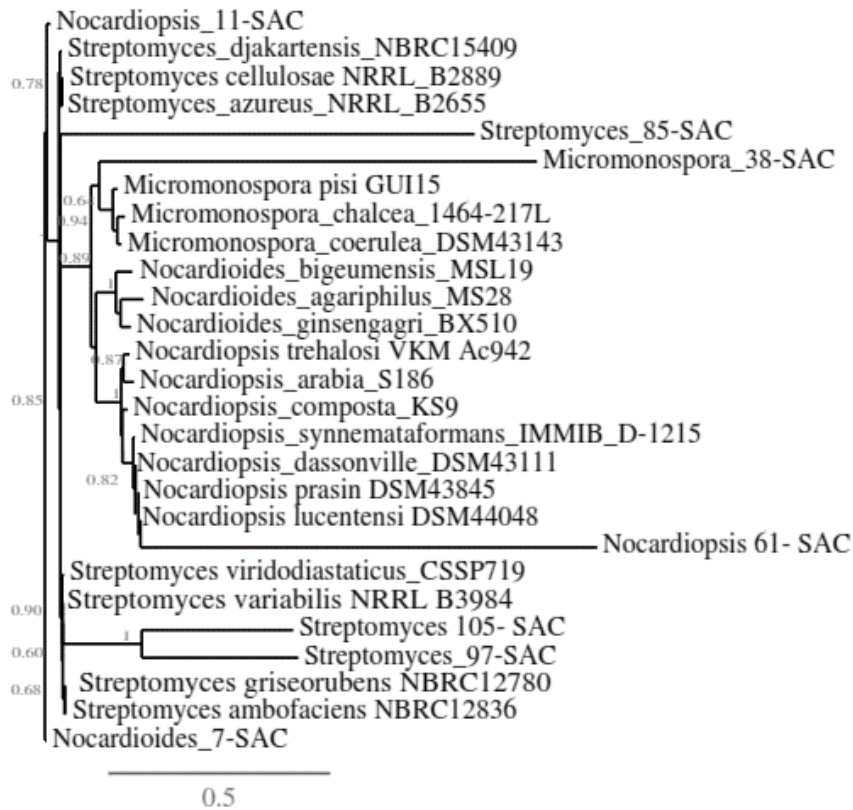


Figure 25. Phylogenetic tree of 16S rDNA sequences from the SAC and their most similar GenBank sequences. Only bootstrap values above 50% were displayed.

All individuals of the developed SAC showed abilities to produce lignin peroxidases (1.0 – 3.6 index) and to hydrolyze a broad range of cellulose/hemicellulose derived compounds as shown in Table 24. *Actinomycetes* are known to selectively cleave lignin and facilitate enzymatic attack of cellulose for sugar release (Abdel-Hamid et al., 2013). It was particularly notable that, *Streptomyces* 85-SAC and *St.* 97-SAC were highly efficient in cellulose saccharification - 83.8 and 69.6%, respectively - although not likewise efficient in lignin hydrolysis. While, the principally high ligninolytic ability of *Micromonospora* 38 - that was phylogenetically similar to *M. pisi* GUI 15 at 94.0 % - was in agreement with previous studies; as discussed in the comprehensive review by Hirsch and Valdés (2010). This actually indicates that a consortium would be more effective in lignocellulose degradation than individual strains, where degradation is

enforced by the synergistic action of the consortium enzymes. In addition, hydrolysis of lignocelluloses by microbial consortia has been proposed as a highly efficient approach, because it avoids feedback regulation and metabolite repression problems (Ling et al., 2014; Soundar and Chandra, 1987).

Table 24. Extracellular lignocellulytic enzymes activity and degree of cellulose saccharification (DCS) of individual strains of the *actinomycete* consortium SAC.

Enzyme ^{a)}	SAC individual strain						
	<i>Np 61</i>	<i>Np 11</i>	<i>St 85</i>	<i>St 97</i>	<i>St 105</i>	<i>M 38</i>	<i>Nd 7</i>
Lignin peroxidases	1.1	1.5	1.4	1.2	1.0	3.6	2.4
Amylase	3.0	2.7	2.0	2.0	2.0	3.0	2.6
Caboxymethylcellulase	--	--	1.5	2.0	3.0	--	--
Hemicellulases	--	1.0	1.5	3.0	3.1	3.0	1.0
Cellulases	3.1	2.1	2.3	2.6	2.0	2.0	2.0
DCS (%)	27.8	22.5	83.8	69.6	22.3	17.1	22.0

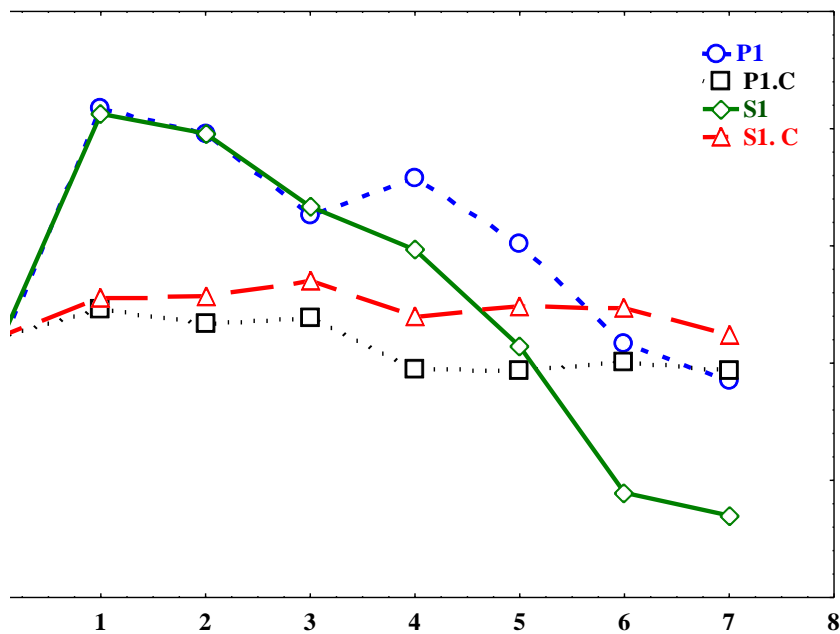
^{a)} Activity index (diameter of clear zone / diameter of growth).
--: No activity.

3.2. Efficiency of SAC in straw hydrolysis

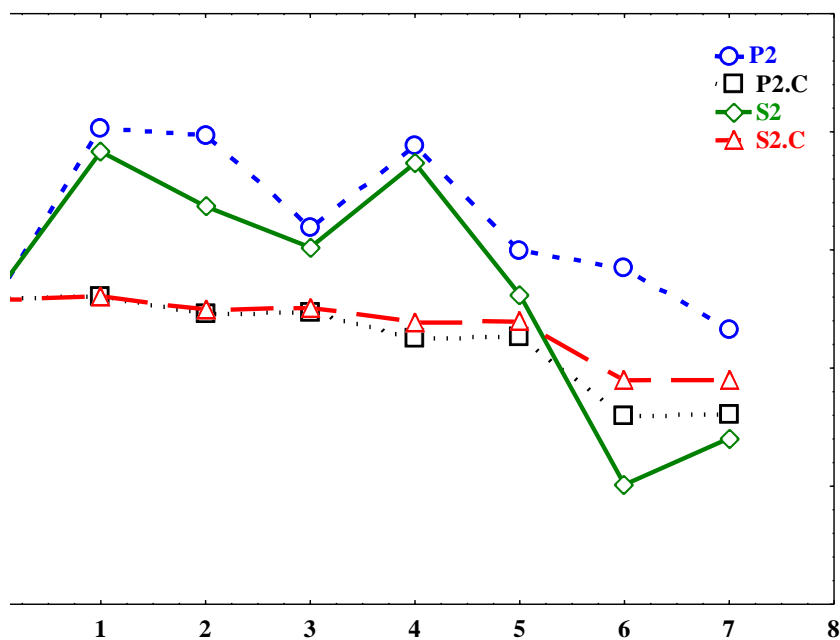
Figure 26a and b show the influence of the *actinomycete* consortium SAC on saccharification of unpelleted and pelleted rice straw samples compared to the shredded and control corresponding straw samples. Results indicated a highly significant effect ($P = 0.0006$) of the consortium in the saccharification process over 4 days, compared to the control samples, where, the saccharification rate reached to about 40% with 60% efficiency for both pelleted and unpelleted straw. There are reports about delignification

and saccharification, to varying extents, of different lignocellulosic substrates by *actinomycetes* (Saratale et al., 2012; Saritha et al., 2013)

The results indicated that SAC could excrete a set of lignocellulose hydrolyzing enzymes during the 4-days period. Nevertheless, subsequent incubation to the 7th day showed sharp reduction in saccharification in all experimental settings, which was an indication of insufficient enzymatic activity. There are several factors that can affect the consortium ability to degrade lignocellulose; due to affecting the level of enzymes synthesis and excretion. Major factors include: the levels of cellulose and hemicelluloses, monomeric content ratios and composition of the lignin (Abdel-Hamid et al., 2013). In the present study, component analysis of the straw demonstrated low N percentage and high C/N ratio of the lignocellulosic materials; indicating that nitrogen could represent a limiting factor for the consortium to sustain growth. According to Castillo and Torstensson (2007), a C/N ratio of approximately 30, is the recommended ratio for efficient microbial growth and consequently, straw hydrolysis. In this context, the high C/N ratio (65.5) and high lignin content (20.6%), in rice straw, are expected to affect the growth and activity of the microbial consortium, subsequently leading to limited saccharification after the 4th day. Similar results were reported for microbial degradation of plant residues, in which lignocellulosic material with elevated lignin content led to limited degradation process (Castillo et al., 1997; Diez et al., 2013).



a)



b)

Figure 26. Total saccharification of pelleted (P) / shredded straw (S), samples 1 without starch (a) and samples 2 with starch addition (b), using SAC at different experimental settings compared to corresponding uninoculated control samples denoted by C.

3.3. Influence of pelleting on the hydrolysis process

It was worth noting that, the starch-amended pellets (P2) represented the best setting for straw hydrolysis using SAC, where three saccharification peaks occurred over the 4-days period. The total saccharification averaging 35 and 34% in P2 and P1, respectively; compared to 33 and 32% in the corresponding shredded samples S2 and S1, see Figure 26a and b. This indicates the positive effect of pelleting and the starch additive on degradation of the straw. The starch is expected to provide an easily accessible carbon source to maintain a rapid rate of consortium growth, allowing for production of hydrolytic enzymes that are responsible for saccharification. Additionally, the mechanical effect of pelleting has likely contributed to facilitate the action of hydrolyzing enzymes. Rijal et al. (2012) and Theerarattananon et al. (2012) showed similar results for sugars yields with pelleting and indicated that pelleting of lignocellulosic biomass can be used as a preliminary pretreatment step to increase hydrolysis yields.

3.4. Actual reducing sugar yield

Increases in RS can be attributed to reduction in particle size and cellulose crystallinity during mechanical processing (Dasari and Berson, 2007; Rijal et al., 2012). Therefore, in the present experiment the actual RS yield was calculated to specify the hydrolysis effect by the consortium as shown in Figure 27. The actual RS yield from starch-amended pellets (P2) increased steadily with an average 500 mg/g over two day and another peak of 440 mg/g fermentable sugar on the 4th day. Although the yield from shredded straw (S1) lasted for 2 days (av. 740 mg/g), it sharply depleted afterward. The reducing sugars released from SAC pretreated straw were significantly higher as compared to respective lignocelluloses within 4 days. For example, RS yield was

509.65 mg/g from paddy straw by the fungus *Myrothecium roridum* (Tiwari et al., 2013), 449 mg/g from sugarcane bagasse by the fungus *Ceriporiopsis subvermispora* (Sasaki et al., 2011) and 379 mg/g from paddy straw by the *actinomycete Streptomyces griseorubens* (Saritha et al., 2013).

The negative RS net values, particularly towards the end of experiment, are an indication of lower sugar content in the samples than their corresponding uninoculated samples. This observed depletion of sugars could be attributed to its consumption by the consortium for maintaining their growth, at the point where lignocellulose hydrolyzing enzymes are not sufficiently excreted. However, further studies will be directed to optimize various physicochemical parameters for achieving maximum enzymes and reducing sugar production.

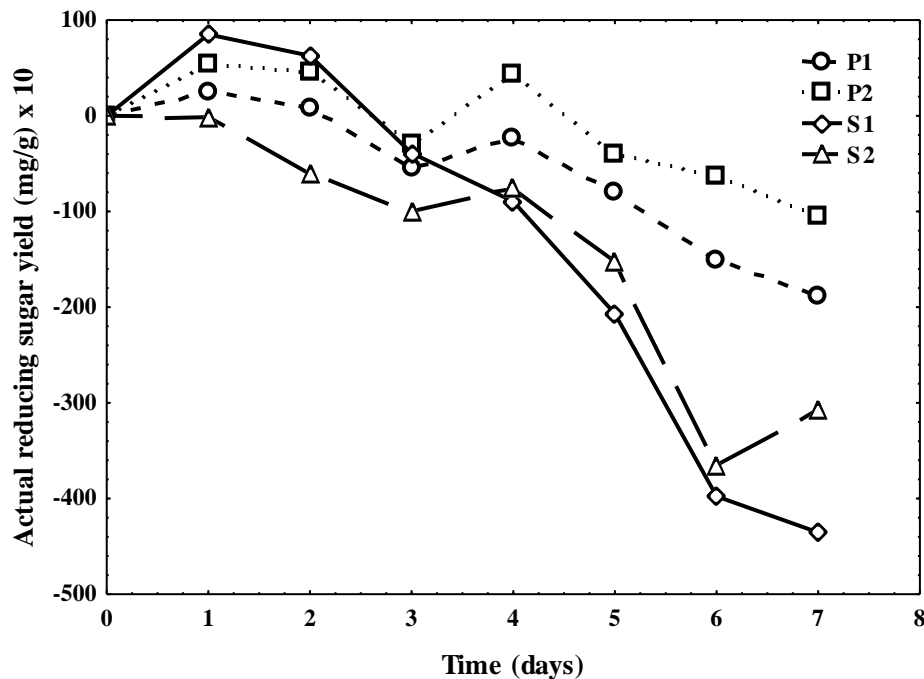


Figure 27. Actual RS yield of pelleted and shredded straw during straw hydrolysis by the *actinomycete* consortium SAC.

Uninoculated and SAC inoculated straw pellets were examined by scanning electron microscopy after 7 days of the hydrolysis experiment. The consortium mycelia appeared to be highly capable of penetrating the interior layers, causing disintegration and deformation of the structural components of rice straw as compared to the uninoculated straw (Figure 28 a and b). The micrographs confirm the partial degradation of rice straw by the *actinomycete* consortium.

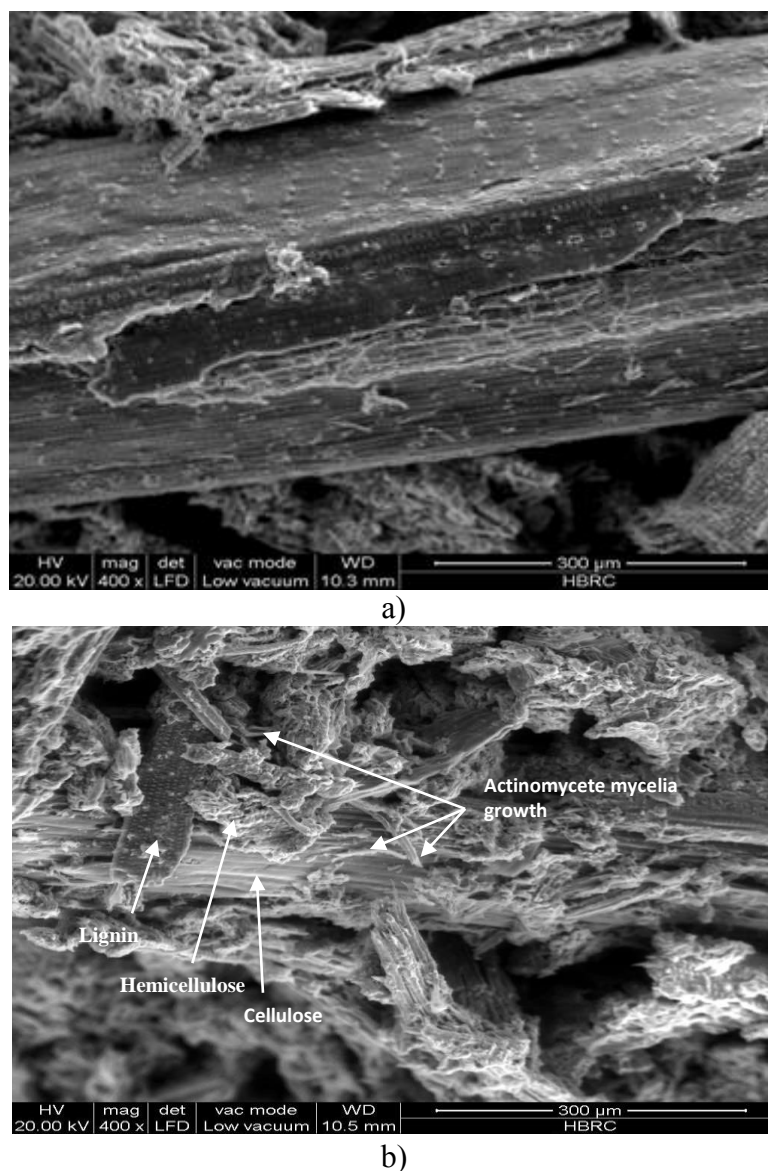


Figure 28. Scanning electron micrograph of rice straw pellets after 7 days of the hydrolysis experiment. a) un-inoculated; b) inoculated with the SAC consortium.

4. CONCLUSION

Rice straw is regarded as a promising starting material for 2nd generation bioethanol production. Densification of rice straw into uniform pellets can provide easy handling, transportation and storage costs reduction, and help disrupting its lignin-carbohydrate complex prior to microbial hydrolysis.

The applied *actinomycete* consortium had the ability of penetrating and disintegrating the interior layers of rice straw and the results showed it had a high significant effect in increasing saccharification efficiency, especially over 4 days from experiment start.



CONCLUSIONES

A continuación se exponen las conclusiones más importantes obtenidas en este trabajo, que han sido clasificadas en cinco secciones de acuerdo con los objetivos específicos establecidos en la investigación:

- a) Evaluación de la cantidad de biomasa producida en Egipto y estudio de su potencial energético.
- b) Caracterización de la paja de arroz para la producción energética como fuente de energía renovable.
- d) La influencia de los parámetros de densificación de las propiedades de calidad de los pellets de paja de arroz.
- e) Análisis del efecto del proceso de densificación en la hidrólisis y sacarificación de pellets fabricados con paja de arroz.

Con respecto de al análisis de la evaluación cuantitativa de los recursos de biomasa y su energía potencial en Egipto se ha concluido:

- Este país produce una cantidad considerable de biomasa procedente de cultivos agrícolas, residuos sólidos urbanos, lodos de depuradora y biomasa animal, con un contenido energético teórico total de 416.9×10^{15} J. Concretamente la biomasa seca producida a partir de los residuos agrícolas, estimada en 12.33 millones de toneladas/año, permitiría generar 185.75×10^{15} J, un 44.60% del potencial energético teórico.
- Del total de biomasa seca procedente de los residuos agrícolas, el 63.75% se genera en el cultivo del arroz. Por tanto la paja de arroz podría ser considerada

una buena candidata como fuente de energía renovable en Egipto, mediante la aplicación de procesos de conversión termoquímicos y bioquímicos.

- El uso de esta biomasa como biocombustible permitiría reducir la dependencia de Egipto de los combustibles fósiles así como las emisiones de CO₂, en el marco de las políticas de potenciación del uso de energías renovables puestas en marcha en el país.

En cuanto a la caracterización y comportamiento térmico de la paja de arroz, se obtuvieron las siguientes conclusiones:

- Las características de la paja de arroz dependen de la variación de lugar de cultivo, tiempo de cosecha, suelo, cultivo y las condiciones de almacenamiento. Concretamente su contenido de cenizas y composición fueron las características que mostraron mayor diferencias entre las muestras estudiadas.
- El análisis termogravimétrico mostró que la paja de arroz tiene un gran potencial para producir energía; no obstante su análisis químico puso de manifiesto un alto contenido de ceniza (13.25 - 18.66%) así como la presencia de compuestos alcalinos (1.75 - 2.09 álcali kg/GJ), entre ellos SiO₂ y K₂O. La combinación de estos componentes a altas temperaturas da lugar a la sinterización de las cenizas y por tanto a problemas en el funcionamiento de los equipos de combustión.
- El uso del proceso de lavado como método de pretratamiento para mejorar el comportamiento térmico de la paja de arroz ha mostrado la reducción de componentes precursores en la sinterización de las cenizas, tales como K y Cl; este resultado se ha traducido en un menor valor en el contenido de cenizas y del índice que determina la presencia de compuestos alcalinos del 19.77% y 63.24%, respectivamente. Estos valores suponen una mejora significativa en el

comportamiento térmico y la reducción de procesos de sinterización para las muestras lavadas.

Con respecto a los efectos de las variables relacionadas con la producción de pellets fabricados con paja de arroz en la calidad de los mismos, y de acuerdo a los límites establecidos en la *Norma UNE-EN ISO 17225-6:2014 sobre Biocombustibles sólidos. Especificaciones y clases de combustibles. Parte 6: Clases de pellets de origen no leñoso*, se pudo concluir lo siguiente:

- Los resultados mostraron un efecto significativo de las condiciones de operación (M_f , proporción de almidón como aditivo, temperatura de operación y tamaño de matriz) sobre las propiedades del pelet final (dureza, durabilidad, densidad real y aparente, M_p y dimensiones). La durabilidad, dureza y densidad aparente fueron los parámetros más afectados por la M_f y el contenido en almidón. Por otro lado, el tamaño de la matriz y la M_f mostraron gran influencia en las dimensiones del pellet y la M_p . Además, se observaron relaciones directamente proporcionales entre algunas parejas de parámetros tales como durabilidad y dureza o densidad real y aparente.
- A pesar de que los requisitos referentes a las dimensiones del pelet fueron alcanzados para todas las muestras fabricadas, los valores de M_p superaban el límite establecido debido al hecho de que eran necesarios valores altos de humedad en la alimentación para favorecer la aglomeración entre partículas. Por su parte, la dureza y la densidad del pelet no están limitadas por norma, pero los valores obtenidos estaban dentro de los rangos recomendados en estudios previos. Considerando los resultados obtenidos, la interrelación entre parámetros y los valores límite para cada uno de ellos, se puede deducir que la muestra de

pelet de paja de arroz de mayor calidad es aquella con un 99.31% de durabilidad, correspondiéndose por tanto con las siguientes condiciones de operación: 2% almidón, 17% humedad de la materia prima (paja de arroz), menor que 50 °C de temperatura de funcionamiento de la pelletizadora, y matriz de dimensiones 8/32.

Finalmente el análisis del efecto del proceso de densificación en la hidrólisis y sacarificación de pellets fabricados con paja de arroz utilizando un consorcio de actinomicetos lignocelulolíticas, permitió concluir:

- El consorcio *actinomiceto* aplicado tuvo la capacidad de penetrar y desintegrar las capas interiores de la paja de arroz. El valor de la tasa de sacarificación ha sido del 40% y, en el caso de pellets con aditivo de almidón, el aumento de la eficiencia de la sacarificación alcanzó el 55%.



CONCLUSIONS

The most important contributions that deduced from this work can be classified in five sections, according to the specific objectives of the research:

- a) The development of a quantitative appraisal of biomass resources and their energy potential in Egypt.
- b) Characterization of rice straw as a renewable energy source.
- c) Pretreatment of rice straw using washing process to improve its thermal behavior.
- d) The influence of densification parameters on the quality properties of rice straw pellets.
- e) Analysis of the effect of pelleting on hydrolysis and saccharification of rice straw

With regards to the analysis of the quantitative appraisal of biomass resources and their energy potential in Egypt:

- This country produces a considerable amount of biomass with a total theoretical energy content of 416.9×10^{15} J.
- The dry biomass produced from bioenergy crop residue sources has been estimated at about 12.33 million tons/year, of which 63.75% is produced from rice straw. This source represents the highest percentage (44.60%) of the total theoretical potential energy in Egypt, followed by municipal solid wastes, which could produce 41.70% from an annual amount of 34.6 million tons. The rest of the total theoretical potential energy could be produced from animal and sewage wastes.
- In consequence rice straw would represent a good candidate as a renewable energy source in Egypt which could be used as a clean fuel and would decrease the

dependence on fossil fuel; its energy can be recovered in other different forms such as bio-oil, biogas, and syngas.

Concerning the characterization and thermal behavior of rice straw, the following conclusions were deduced:

- The characterization of rice straw is an important step to determine its properties and potential applications as renewable energy source. The characteristics depend on the variation of growing location, harvesting time, soil, cultivation and storage conditions.
- The characteristics of rice straw samples collected from different regions showed that the ash content and its composition is the most important difference between the samples; moreover, the thermal behavior and composition has not showed important differences.
- Despite the thermogravimetric analysis of rice straw showed how it has a great potential to produce energy, the chemical analysis showed high ash contents (13.25 - 18.66%) and alkali index values (1.75 - 2.09 kg alkali/GJ). This represents obstacles that can cause some operating problems in thermal conversion systems such as sintering and slag formation which appeared at combustion of rice straw at high temperatures (900-1000 °C).
- The ash analysis revealed that silica was the foremost component, followed by K_2O , and that these two components are combined at high combustion temperatures and associated with ash sintering problems.

In relation to the use of washing process as pretreatment method to improve rice straw thermal behavior, the following conclusions have been deduced:

- Water washing of rice straw showed reduction in the ash content and alkali index value with percentages reached to 19.77% and 63.24%, respectively, so the washing process resulted in a reduction of some sintering precursor components in the ash samples, such as K and Cl with percentages 50% and 87%, respectively. In consequence a significant improvement in thermal behavior and reduction in sintering formation was observed for the washed samples.

With regards to the influence of densification parameters on the quality properties of rice straw pellets and according to the thresholds established by UNE-EN ISO 17225-6:2014 about Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets, it has been concluded the following:

- The results showed significant effects of the feeding and operating conditions studied (M_f , starch binder ratio, operating temperature, and flat die size) on the pellets' properties (hardness, durability, bulk density, pellet density, M_p and dimensions). The durability, hardness and bulk density values are the most affected by M_f and starch ratio; on the other hand, die size and M_f showed a high significant influence on dimensions and M_p , respectively. Furthermore, positive relationships were observed between some pairs of the quality parameters analyzed such as hardness and durability or pellet and bulk density values.
- Despite the fact that all the dimension values fulfilled the limits of the norm, the M_p did not achieve the threshold established by the standard due to the fact that an initially high moisture content was necessary for the agglomeration between particles. Hardness and pellet density are not addressed by the norms, but the

results obtained were near the ones recommended by previous studies. Considering the results, relationships and guidelines obtained, it can be deduced that the highest pellets' quality is that corresponding with the sample of durability 99.31%, which was obtained with the following operating conditions: 2% starch, 17% M_f, T < 50 °C and die size (8/32).

Finally through the analysis of the effect of pelleting on hydrolysis and saccharification of rice straw using a consortium of lignocellulolytic *actinomyces*, it has been possible to conclude that:

- The applied *actinomyces* consortium had the ability of penetrating and disintegrating the interior layers of rice straw, showed saccharification rate reached to 40%, and in the case of pellets with starch additive, increased efficiency of saccharification by 55%.

The seal of the University of Granada is a circular emblem. It features a central shield with a crown on top, flanked by two eagles with spread wings. The shield is supported by two columns. The text 'UNIVERSITAS GRANATAE' is written around the top inner edge, and '1531' is at the bottom. The word 'UNIVERSITAS' is also written vertically on the right side.

LÍNEAS FUTURAS DE INVESTIGACIÓN

LÍNEAS FUTURAS DE INVESTIGACIÓN

De acuerdo con el trabajo desarrollado en este estudio, se han observado algunos aspectos que requieren un estudio y un análisis más detallado. Por lo tanto, se proponen a continuación las líneas de investigación siguientes:

- Estudiar la evaluación del ciclo de vida del uso de pellets de paja de arroz en Egipto, tanto en procesos de combustión como para la extracción de bioetanol
- Proponer experimentos pilotos para analizar el comportamiento térmico de los pellets de paja de arroz a escala real y las emisiones gaseosas y de partículas generadas.
- Analizar técnicas alternativas para mejorar el comportamiento térmico de la paja de arroz tales como procesos de pretratamiento químico, co-combustión con otro material, o el uso de aditivos.



FUTURE LINES OF RESEARCH

FUTURE LINES OF RESEARCH

According to the developed work in this study, there have been observed some aspects that need more detailed study and analysis. Therefore, they are proposed below as future lines of research:

- Study the life cycle assessment of the implementation of rice straw pellets techniques in Egypt in combustion process as well as to bioethanol extraction
- Pilot experiments to analyze thermal behavior of rice straw pellets at real scale: emissions study
- The use of techniques to improve the thermal behavior of rice straw: such as chemical pretreatment processes, co-combustion with another material or using fuel additives.



REFERENCES

- Abbasi T, 2010, Biomass energy and the environmental impacts associated with its production and utilization. *Renewable and Sustainable Energy Reviews*, 14, 919-937.
- Abdel Halim AS, Metwally E, El-desoukky MM, 2003, Environmental pollution study around a large industrial area near Cairo-Egypt. *Journal of Radio Analytical and Nuclear Chemistry*, 257(1), 123-124.
- Abdel-Hamid AM, Solbiati JO, Cann IKO, 2013, Insights into Lignin Degradation and its Potential Industrial Applications. *Advances in Applied Microbiology*, 82, 1-28.
- Abdrabo MA, 2008, Assessment of economic viability of solid waste service provision in small settlements in developing countries: Case study Rosetta, Egypt. *Waste Management*, 28, 2503-2511.
- Abdulla HM, El-Shatoury SA, 2007, Actinomycetes in rice straw decomposition. *Waste Management*, 27(6), 850-853
- Abo-State MA, Ragab AM, EL-Gendy NS, Farahat LA, Madian HR, 2014, Bioethanol Production from Rice Straw Enzymatically Saccharified by Fungal Isolates, *Trichoderma viride* F94 and *Aspergillus terreus* F98. *Soft*, 3, 19-29.
- Abou-Sekkina MM, Issa RM, Bastawisy AEM, El-Helece WA, 2010, Characterization and Evaluation of Thermodynamic Parameters for Egyptian Heap Fired Rice Straw Ash (RSA). *International Journal of Chemistry*, 2(1), 81-88.
- Abril D, Navarro E, Abril A, 2009, Rice straw Consequences of its management and use alternatives. *Agronomia*, 17, 69-79.
- Aderemi BO, Abu E, Highina BK, 2008, The kinetics of glucose production from rice straw by *Aspergillus niger*. *African Journal of Biotechnology*, 7(11), 1745-1752.
- Ahmed HK, Abouzeid M, 2001, Utilization of wind energy in Egypt at remote areas. *Renewable Energy*, 23(3-4):595-604.

- Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ, 2010, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, 101(13), 4851-4861
- Aly HF, Megeed EM, 2008, Lignocellulosic Biomass Conversion Technologies to Biofuels, Potentials in Egypt, Report Submitted to UNIDO-Cairo-Egypt, IMC.
- Amigun B, Sigamoney R, Von Blottnitz H, 2008, Commercialisation of biofuel industry in Africa: a review. *Renewable and Sustainable Energy Reviews*, 12, 53-68.
- Anderson I , Abt B , Lykidis A , Klenk H, Kyrpides N, Ivanova N, 2012, Genomics of Aerobic Cellulose Utilization Systems in Actinobacteria. *PLoS ONE*, 7(6), e39331.
- Arafat S, Afify A, Aboelghar M, Belal A, 2010, Rice crop monitoring in Egyptian Nile delta using Egyptsat-1 data, National Authority for Remote Sensing and Space Sciences, Joint U.S. Egypt workshop for Space Technology & Geo-information for Sustainable Development, NARSS-Cairo.
- Aref AA, Combustion characteristics of biomass fuels, 1995, Bull Faculty Engineering, Minia University, 126-138.
- Arshadi M, Gref R, Geladi P, Dahlgvist SA, Lestander T, 2008, The influence of raw material characteristics on the industrial pelletizing process and pellet quality. *Fuel Process Technology*, 89, 1442-1447.
- Badger PC, 2002, Ethanol from Cellulose: A General Review, Trends in New Crops and New Uses (Eds: J. Janick, A. Whipkey), ASHS Press, Alexandria, VA, 17-21.
- Badran MF, El-Haggag SM, 2006, Optimization of municipal solid waste management in Port Said – Egypt. *Waste Management*, 26, 534–545.
- Baird MS, Eng MA, 1993, Energy fact sheet. The Energy Educators of Ontario.

- Bakker RR, Jenkins BM, Williams RB, 2002, Fluidized Bed Combustion of Leached Rice Straw. *Energy Fuel*, 16, 356-365.
- Balat M, Balat M, Kirtay E, Balat H, 2009, Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems. *Energy Conversion and Management*, 50, 3147-3157.
- Balat M, Balat H, Oz C, 2008, Progress in bioethanol processing. *Progress in Energy and Combustion Science*, 34, 551-573.
- Balat M, Ayar G, 2003, Biomass Energy in the World, Use of Biomass and Potential Trends. *Energy Sources*, 27, 931-940.
- Bapat DW, Kulkarni SV, Bhandarkar VP, 1997, Design and operating experience on fluidized bed boiler burning biomass fuels with high alkali ash. In: Preto FDS, editor. *Proceedings of the 14th International Conference on Fluidized Bed Combustion*, Vancouver, New York, NY: ASME, 165-74.
- Basso B, Ritchie JT, 2005, Impact of compost, manure and inorganic fertilizer on nitrate leaching and yield for a 6-year maize–alfalfa rotation in Michigan, *Agriculture, Ecosystems & Environment*, 108, 329-341.
- Baxter LL, Miles TR, Miles Jr TR, Jenkins BM, Milne T, Dayton D, Bryers RW, Oden LL, 1998, The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Process Technology*, 54, 47-78.
- Bilbao R, Mastral JF, Aldea ME, Ceamons, J, 1997, Kinetic study for the thermal decomposition of cellulose and pine sawdust in an air atmosphere. *Journal of Analytical and Applied Pyrolysis*, 39, 53-64.
- Bilgen S, Keles S, Kaygusuzb A, Saric A, Kaygusuza K, 2008, Global warming and renewable energy sources for sustainable development: A case study in Turkey. *Renewable and Sustainable Energy Reviews*, 12, 372-396.

- Binod P, Sindhu R, Singhania RR, Vikram S, Devi L, Nagalakshmi S, Kurien N, Sukumaran RK, Pandey, 2010, A. Bioethanol production from rice straw: An overview. *Bioresource Technology*, 101, 4767-4774.
- Black M, Richter GM, 2010, Mapping out global biomass projections, technological developments and policy innovations. *Rothamsted Research*, 1-21.
- Blasi CD, Branca C, Santoro A, Hernandez EG, 2001, Pyrolytic behavior and products of some wood varieties. *Combustion and Flame*, 124, 165-177.
- Bryers RW, 1996, Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Progress in Energy and Combustion Science*, 22, 20-120.
- Burton RA, Fincher GB, 2014, Plant cell wall engineering: applications in biofuel production and improved human health. *Current Opinion in Biotechnology*, 26, 79-84.
- Bushra M, 2000, Regional study on policies and institutional assessment of solid waste management in Egypt. *Blue Plan*. Regional Activity Centre, Sophia Antipolis.
- Buzarovska A, Bogoeva-Gaceva G, Grozdanov A, Avella M, Gentile G, Errico M, 2008, Potential use of rice straw as filler in eco-composite materials. *Australian Journal of Crop Science*, 2, 37-42.
- Calvo LF, Otero M, Jenkins BM, Morán A, Garcia AI, 2004, Heating process characteristics and kinetics of rice straw in different atmospheres. *Fuel Processing Technology*, 85, 279-291.
- Cao Y, Wang Y, Riley JT, Pan WP, 2006, A novel biomass air gasification process for producing tar-free higher heating value fuel gas. *Fuel Processing Technology*, 87, 343-353.

- CAPMS, 2013, Central Agency for Public Mobilization and Statistics.
http://www.capmas.gov.eg/pages_ar.aspx?pageid=708.
- Carone MT, Pantaleo A, Pellerano A, 2011, Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of *Olea Europaea* L. *Biomass and Bioenergy*, 35, 402-10.
- Carroll JP, Finnan J, 2012, Physical and chemical properties of pellets from energy crops and cereal straws. *Biosystem Engineering*, 112, 151-9.
- Castillo M, Ander P, Stenstrom J, 1997, Lignin and manganese peroxidase activity in extracts from straw solid substrate fermentations. *Biotechnology Techniques*, 11(9), 701-706.
- Castillo MDP, Torstensson L, 2007, Effect of biobed composition, moisture, and temperature on the degradation of pesticides. *Journal of Agricultural and Food Chemistry*, 55(14), 5725-5733.
- CEA, Country Environmental Analysis, 2002, Arab Republic of Egypt, Water and Environment Department, the Middle East and North Africa Region. A World Bank Document
- Chakraverty A, Banerjee HD, Pandey SK, 1987, Studies on thermal decomposition of rice straw. *Thermochimica Acta*, 120, 241-255.
- Chou C, Lin S, Peng C, Lu W, 2009, The optimum conditions for preparing solid fuel briquette of rice straw by a piston-mold process using the Taguchi method. *Fuel Processing Technology*, 90, 1041-1046.
- Cooper CJ, Laing CA, 2007, A macro analysis of crop residue and animal wastes as a potential energy source in Africa. *Journal of Energy South Africa*, 18, 10-19.
- CPH, EEOC, 2000, Central Public Health and Environmental Engineering Organization. Manual on municipal solid waste management. Energy recovery

- from municipal solid waste. Ministry of Urban Development, Government of India.
- Dael MV, Passel SV, Pelkmans L, Guisson R, Reumermann P, Luzardo NM, Witters N, Broeze J, 2013, A techno-economic evaluation of a biomass energy conversion park. *Applied Energy*, 104 , 611-622
- Dasari RK, Berson RE, 2007, The effect of particle size on hydrolysis reaction rates and rheological properties in cellulosic slurries. *Applied Biochemistry and Biotechnology*, 137, 289-299.
- Datnoff LE, Deren CW, Snyder GH, 1997, Silicon fertilization for disease management in Florida. *Crop Protection*, 16, 525-531.
- De Kam MJ, Morey RV, Tiffany DG, 2009, Biomass integrated gasification combined cycle for heat and power at ethanol plants. *Energy Conversion and Management*, 50, 1682-1690.
- Delivand KM, Barz M, Gheewala S, 2011, Logistics cost analysis of rice straw for biomass power generation in Thailand. *Energy*, 36, 1435-1441.
- Demirbas M, Mustafa B, Balat H, 2009, Potential contribution of biomass to the sustainable energy development. *Energy Conversion and Management*, 50, 1746-1760.
- Demirbas A, 2005, Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Progress in Energy and Combustion Science*, 31, 171-192.
- Demirbas A, 2001a, Relationships between lignin contents and heating values of biomass. *Energy Conversion and Management*, 42(2), 183-188.
- Demirbas A, 2001b, Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Conversion and Management*, 42, 1357-1378.

- Deng L, Zhang T, Che D, 2013, Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. *Fuel Processing Technology*, 106, 712–720.
- Diez MC, Tortella GR, Briceño G, Castillo M, Díaz J, Palma G, Altamirano C, Calderón C, Rubilar O, 2013, Influence of novel lignocellulosic residues in a biobed biopurification system on the degradation of pesticides applied in repeatedly high doses. *Electronic Journal of Biotechnology* 2013; 16(6), 1-11.
- DIN 51731, 1996, Testing of solid fuels, compressed untreated wood. Requirements and testing. Berlin, Germany: DeutschesInstitutfürNormung.
- DIN EN 15270, 2007, Pellet burners for small heating boilers. Definitions, requirements, testing, marking. Berlin, Germany: DeutschesInstitutfürNormung.
- DuBois M, Gilles K, Hamilton J, Rebers P, Smith F, 1956, Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, 28(3), 350-356.
- EEAA, Egyptian Environmental Affairs Agency, 2012, Estimated GHG inventory in Egypt.
- EEAA, UNFCCC, Egyptian Environmental Affairs Agency and United Nations Framework Convention on Climate Change, 2010, Egypt National Environmental, Economic and Development Study (NEEDS) for climate change.
- EEAA, Egyptian Environmental Affairs Agency, 2005, Egypt state of the environment in 2004, Cairo, Egypt.
- EIB, European Investment Bank, 1999, Cairo sludge disposal study. Mediterranean Technical Assistance Programme for the Execution of the Greater Cairo Wastewater Project.

- El Saeidy E, 2004, Renewable energy in agriculture in Egypt, Technological Fundamentals of Briquetting Cotton Stalks as a Biofuel. Doctoral thesis, Berlin University.
- El-Khayat MM, Ameen EE, 2010, Renewable energy in Egypt - challenges and prospects. Thermal Issues in Emerging Technologies, ThETA 3, Cairo, Egypt, 19-22, 277-280.
- Elliot D, 1997, Energy, society and environment: technology for a sustainable future. London: Routle Publishing, 1-35.
- El-Mashad HM, van Loon WKP, Zeeman G, Bot GPA, Lettinga G, 2003, Reuse potential of agricultural wastes in semi-arid regions: Egypt as a case study. Reviews in Environmental Science and Biotechnology, 1, 53-66.
- Elmassry I, 2006, Sunny outlook in Egypt: potential and opportunities for cogeneration, Cogeneration and On-site Power Production
- EL-Shimy M, 2009, Viability analysis of PV power plants in Egypt. Renewable Energy, 34, 2187-2196.
- Elsobki M, Wooders P, Sherif Y, 2009, Clean energy investment in developing countries. In: Wind power in Egypt. Winnipeg, Manitoba, Canada International Institute for Sustainable Development Energy, 85, 430-438.
- EQI, Environmental Quality International, 2005, Alternative methods for solid waste management and treatment and disposal of wastewater. Environmental Services for Improving Water Quality Management, Ministry of Water Resources & Irrigation, United States Agency for International Development.
- EEA, European Environment Agency, 2007, Greenhouse gas emission trends and projections in Europe. Tracking Progress towards Kyoto Targets. EEA Report No. 5/2007. Copenhagen: EEA.

- Ewida KT, El-Salmawy H, Atta NN, Mahmoud MM, 2006, A sustainable approach to the recycling of rice straw through pelletization and controlled burning. *Clean Technology and Environmental Policy*, 8, 188-197.
- Faaij APC, 2008, Sustainable Biofuels. Presentation at Rockefeller Bellagio Conference on North-South Biopact, Bellagio, Italy.
- Fang X, Jia L, 2012, Experimental study on ash fusion characteristics of biomass. *Bioresource Technology*, 104, 769-774.
- Fasina OO, 2008, Physical properties of peanut hull pellets. *Bioresource Technology*, 99, 1259-66.
- Fernández JM, Plaza C, Polo Sb, Plante AF, 2012, Use of thermal analysis techniques (TG–DSC) for the characterization of diverse organic municipal waste streams to predict biological stability prior to land application. *Waste Management*, 32, 158-164.
- Field CB, Campbell JE, David B, 2007, Biomass energy: the scale of the potential resource. *Lobell Trends in Ecology and Evolution*, 23(2), 65-72.
- Field CB, Raupach MR, 2004, *The global carbon cycle: integrating humans, climate, and the natural world*, Washington: Island Press.
- Fischer G, Schrattenholzer L, 2001, Global bioenergy potentials through 2050. *Biomass and Bioenergy*, 20 (3), 151-159.
- Fitzgerald GJ, Scow KM, Hill JE, 2000, Fallow season straw and water management effects on methane emissions in California rice. *Global Biogeochemical Cycles*, 14, 767-776.
- Fletcher SR, 2004, *Global Climate Change: The Kyoto Protocol*. CRS Report for congress. Congressional Research Service.

- Franki P, Brown A, Dobrotkova Z, 2013, Global tracking framework: sustainable energy for all. *Renewable energy*, Chapter 4, 193-250.
- Fu P, Hu S, Xiang J, Sun LS, Yang T, Zhang AC, Zhang JY, 2009, Mechanism study of rice straw pyrolysis by Fourier transform infrared technique. *Chinese Journal of Chemical Engineering*, 17(3), 522-529
- Fujino J, Yamaji K, Yamamoto H, 1999, Biomass-balance table for evaluating bioenergy resources. *Applied Energy*, 63(2), 75-89.
- Gadde B, Menke C, Wassmann R, 2009, Rice straw as a renewable energy source in India, Thailand, and the Philippines: Overall potential and limitations for energy contribution and greenhouse gas mitigation. *Biomass and Bioenergy*, 33(11), 1532–1546.
- García-Maraver A, Popov V, Zamorano M, 2011, A review of European standards for pellet quality. *Renewable Energy*, 36, 3537-3540.
- Ghazy M, Dockhorn T, Dichtl N, 2009, Sewage sludge management in Egypt: current status and perspectives towards a sustainable agricultural use, *World Academy of Science. Engineering and Technology*, 57, 299-307.
- Gilbert P, Ryu C, Sharifi V, Swithenbank J, 2009, Effect of process parameters on pelletisation of herbaceous crops. *Fuel*, 88, 1491-7.
- Grubor BD, Oka SN, Ilic MS, Dakic DV, Arsic BT, 1995, Biomass FBC combustion-bed agglomeration problems. In: Heinschel KJ, editor. *Proceedings of the 13th International Conference on Fluidized Bed Combustion*, Orlando, FL, New York, NY: ASME, 515–22.
- GTZ, 2010, Integration of large amounts of renewable electricity in the Egyptian energy grid – capacity building for management and engineer – technical level (Egypt-RE-Grid).

- GTZ, 2006, International Services. Technical/policy note on agricultural waste management in Egypt.
- Guragain YN, Wilson J, Staggenborg S, McKinney L, Wang D, Vadlani PV, 2013, Evaluation of pelleting as a pre-processing step for effective biomass deconstruction and fermentation. *Biochemical Engineering Journal*, 77,198-207.
- Hall DO, Rosillo-Calle F, Williams RJ, Woods J, 1993, Biomass for energy: supply prospects. *Renewable energy: sources for fuels and electricity*. Earthscan, London, 593-651.
- Hamdy YA, 1998, The current situation of Egyptian agricultural wastes. In: *Proc Anaerobic Treatment of Solid Wastes Workshop*, Mansoura University, Egypt, 1-5.
- Hamouda YA, 2012, Wind energy in Egypt: Economic feasibility for Cairo. *Renewable and Sustainable Energy Reviews*, 16, 3312-3319
- Hashiramoto O, 2007, Wood-product trade and policy issue. *Cross-sectoral policy developments in forestry*, 24-35.
- Hess JR, Wright CT, Kenney KL, 2007, Cellulosic biomass feedstocks and logistics for ethanol production. *Biofuels, Bioproducts and Biorefining*, 1, 181-190.
- Hirsch AM, Valdés M, 2010, *Micromonospora*: An important microbe for biomedicine and potentially for biocontrol and biofuel. *Soil Biology and Biochemistry*, 42(4), 536-542
- Hoogwijk M, 2004, On the global and regional potential of renewable energy sources. PhD thesis, Utrecht University, Utrecht, The Netherlands, 256.
- Hoogwijk M, Faaij A, Van den Broek R, Berndes G, Gielen D, Turkenburg W, 2003, Exploration of the ranges of the global potential of biomass for energy. *Biomass and Bioenergy*, 25(2), 119-133.

- Hulteberg PC, Karlsson HT, 2009, A study of combined biomass gasification and electrolysis for hydrogen production. *International Journal of Hydrogen Energy*, 34, 772-782.
- Iakovou E, Karagiannidis A, Vlachos D, Toka A, Malamakis A, 2010, Waste biomass-to-energy supply chain management: A critical synthesis. *Waste Management*, 30, 1860-1870.
- Ibrahim A, 2012, Renewable energy sources in the Egyptian electricity market: A review. *Renewable and Sustainable Energy Reviews*, 16, 216- 230.
- IEA (International energy agency), 2014, Key world energy statistics.
- IEA (International energy agency), 2012, Key world energy statistics.
- Igoni AH, Ayotamuno MJ, Eze CL, Ogaji SOT, Probert SD, 2008, Designs of anaerobic digesters for producing biogas from municipal solid-waste. *Appl. Index Mundi, Egypt Electricity*.
- IndexMundi, 2012, http://www.indexmundi.com/egypt/electricity_production.html.
- IPCC, 2000, Special report on emissions scenarios. Intergovernmental panel on climate change. Cambridge Univ. Press, Cambridge, UK.
- Jaccard M, Nyboer J, Sadownik B, 2002, The cost of climate policy. Toronto: UBC Press.
- Jenkins BM, Baxter LL, Miles Jr TR, Miles TR, 1998, Combustion properties of biomass. *Fuel Processing Technology*, 54, 17-46.
- Jenkins BM, Bakker RR, Wei JB, 1996, On the properties of washed straw. *Biomass and Bioenergy*, 10, 177-200.
- Jung S, Kang B, Kim J, 2008, Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a

- fluidized bed and a char separation system. *Journal of Analytical and Applied Pyrolysis*, 82, 240-247.
- Kadam KL, Forrester LH, Jacobson WA, 2000, Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. *Biomass and Bioenergy*, 18, 369-389.
- Kaliyan N, Vance Morey R, 2009, Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy*, 33, 337-59.
- Kalt G, Kranzl L, 2011, Assessing the economic efficiency of bioenergy technologies in climate mitigation and fossil fuel replacement in Austria using a techno economic approach. *Applied Energy*, 88, 3665-84.
- Karagiannidis A, Wittmaier M, Langer S, Bilitewski B, Malamakis A, 2009, Thermal processing of waste organic substrates: developing and applying an integrated framework for feasibility assessment in developing countries. *Renewable and Sustainable Energy Reviews*, 13(8), 2156-2162.
- Karaj S, Rehl T, Leis H, Müller J, 2010, Analysis of biomass residues potential for electrical energy generation in Albania. *Renewable and Sustainable Energy Reviews*, 14, 493-499.
- Karekezi S, Kithyoma W, 2006, *Bioenergy and Agriculture: Promises and Challenges. Bioenergy and the Poor*. In: 2020 Vision for Food, Agriculture, and the Environment. International Food Policy Research Institute, Washington DC, USA.
- Kargbo FR, Xing J, Zhang Y, 2010, Property analysis and pretreatment of rice straw for energy use in grain drying?: A review. *Agriculture and Biology Journal of North America*, 1, 195-200.

- Kargbo FR, Xing J, Zhang Y, 2009, Pretreatment for energy use of rice straw: A review. *African Journal of Agricultural Research*, 4, 1560-1565.
- Karimi K, Kheradmandinia S, Taherzadeh MJ, 2006a, Conversion of rice straw to sugars by dilute acid hydrolysis. *Biomass and Bioenergy*, 30, 247-253.
- Karimi K, Emtiazi G, Taherzadeh MJ, 2006b, Ethanol production from dilute-acid pretreated rice straw by simultaneous saccharification and fermentation with *Mucor indicus*, *Rhizopus oryzae*, and *Saccharomyces*. *Enzyme and Microbial Technology*, 40(1), 138-144.
- Khalil A, Mubarak A, Kaseb S, 2010, Road map for renewable energy research and development in Egypt. *Journal of Advanced Research*, 1, 29-38.
- Khalil A, 2007, Renewable energy sector in Egypt. Energy research center report. Cairo University.
- Klass DL, 2004, Biomass for renewable energy and fuels. *Encyclopedia of Energy*, 1, 192-212.
- Klass DL, 1998, Waste biomass resource abundance, energy potential, and availability. In: *Biomass for renewable energy fuels and chemicals*. USA: E-Publishing Inc, 137-158.
- Knauf M., Moniruzzaman M, 2004, Lignocellulosic Biomass Processing: Perspective, *International Sugar Journal*, 106(1263), 147-150.
- Knudsen JN, Jensen PA, Dam-Johansen K, 2004, Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy and Fuel*, 18, 1385-1399.
- Kobayashi N, Guilin P, Kobayashi J, Hatano S, Itaya Y, Mori S, 2008, A new pulverized biomass utilization technology. *Powder Technology*, 180(3), 272-283.

- Kopsahelis N, Agouridis N, Bekatorou A, Kanellaki M, 2007, Comparative study of spent grains and delignified spent grains as yeast supports for alcohol production from molasses. *Bioresource Technology*, 98, 1440-1447.
- Koufopoulos CA, Maschio GA, 1989, Lucchesi, Kinetic modelling of the pyrolysis of biomass and biomass components. *The Canadian Journal of Chemical Engineering*, 67, 75–84.
- Kuligowski K, Poulsen TG, Rubæk GH, Sørensen P, 2010, Plant-availability to barley of phosphorus in ash from thermally treated animal manure in comparison to other manure based materials and commercial fertilizer. *European Journal of Agronomy*, 33, 293-303.
- Kuokkanen M, Vilppo T, Kuokkanen T, Stoor T, Niinimäki J, 2011, Additives in wood pellet production a pilot-scale study of binding agent usage. *Bioresources*, 6, 4331-4355.
- Ladanai S, Vinterbäck J, 2009, Global potential of sustainable biomass for energy. SLU Report 013 ISSN, 1654-9406.
- Larsson SH, Thyrel M, Geladi P, Lestander TA, 2008, High quality biofuel pellet production from pre-compacted low density raw materials. *Bioresource Technology*, 99, 7176-82.
- Lasheen MR, Ammar NS, 2009, Assessment of metals speciation in sewage sludge and stabilized sludge from different wastewater treatment plants, Greater Cairo, Egypt. *Journal of Hazard Material*, 164, 740-749.
- Lashof DA, Tirpak DA, 1990, Policy Options for Stabilising Global Climate, Hemisphere Publishing Corp. N.Y. 810.

- Lee K, Kang B, Park Y, Kim J, 2005, Influence of Reaction Temperature, Pretreatment, and a Char Removal System on the Production of Bio oil from Rice Straw by Fast Pyrolysis, Using a Fluidized Bed, *Energy Fuel*, 19, 2179-2184.
- Lee R, 2002, Environmental impacts of energy use. In: Bent R, Orr L, Baker R, editors. *Energy: science, policy, and the pursuit of sustainability*. Washington: Island Press, 77.
- Lehtikangas P, 2001, Quality properties of pelletised sawdust, logging residues and bark. *Biomass and Bioenergy*, 20, 351-360.
- Lehtikangas P, 2000, Storage effects on pelletised sawdust, logging residues and bark. *Biomass and Bioenergy*, 19, 287-93.
- Lequerica JL, Valles S, Flors A, 1984, Kinetics of rice methane fermentation. *Biotechnology and Bioengineering*, 19, 70-74.
- Li Y, Liu H, 2000, High-pressure densification of wood residues to form an upgraded fuel. *Biomass and Bioenergy*, 19, 177-86.
- Liang C, Yi S, Yi C, Yong-hao L, Fang L, Wen-guang W, 2009, Effect of Equivalence Ratio on Gasification Characteristics in a Rice Straw Two stage Gasifier, (School of Mechanical Engineering, Shanghai Jiao Tong University, Minhang District, Shanghai 200240, China).
- Ling H, Teo W, Chen B, Su Jan Leong S, Chang MW, 2014, Microbial tolerance engineering toward biochemical production: from lignocellulose to products. *Current Opinion in Biotechnology*, 29, 99-106
- Liu X, Liu Z, Fei B, Cai Z, Jiang Z, Liu X, 2013, Comparative Properties of Bamboo and Rice Straw Pellets. *Bioresources*, 8, 638-47.

- Liu Y, Guo Y, Gao W, Wang Z, Ma Y, Wang Z, 2012, Simultaneous preparation of silica and activated carbon from rice husk ash. *Journal of Cleaner Production*, 32, 204-209
- Liu Z, Xu A, Zhao T, 2011, Energy from Combustion of Rice Straw: Status and Challenges to China. *Energy and Power Engineering*, 3, 325-331.
- Liu NA, Fan W, Dobashi R, Huang L, 2002, Kinetic modeling of thermal decomposition of natural cellulosic materials in air atmosphere. *Journal of Analytical and Applied Pyrolysis*, 63, 303-325.
- Mahammad FA, 2007, Financing wind park projects - experience from Egypt; (Private communication).
- Mahmoud SA, 2009, Electricity sector in Egypt. Egyptian Electricity Holding Company. DSM and EE workshop.
- Maiga AS, Chen GM, Wang Q, Xu JY, 2008, Renewable energy options for a Sahel country: Mali. *Renewable and Sustainable Energy Reviews*, 12, 564-574.
- Maldonado J, Sherif S, 2010, Egypt livestock and products annual. GAIN Report, USDA Foreign Agriculture Service. Global Agriculture Information Network.
- Mani S, Tabil LG, Sokhansanj S, 2006, Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. *Biomass and Bioenergy*, 30, 648-54.
- Mani S, Tabil LG, Sokhansanj S, 2003, An Overview of Compaction of Biomass Grinds. *Power Handling Process*, 15, 2.
- Maraver AG, Optimization of the pelletization process of agricultural wastes originating from olive farms for their application in domestic boilers, Doctoral thesis, Granada University, Spain, 2013. Marrero TR, 1999, Theory and application of binders: an

- update. Proceedings of the Institute for Briquetting and Agglomeration, 26, 103-109.
- Masia AAT, Buhre BJP, Gupta RP, Wall TF, 2007, Characterizing ash of biomass and waste. *Fuel Processing Technology*, 88, 1071-1081.
- Mat SB, 2003, Biomass energy utilization and environment protection – commercial reality and outlook. Transtherm Engineering and Construction Sdn Bhd, Malaysia.
- Matsumura Y, Minowa T, Yamamoto H, 2005, Amount, availability, and potential use of rice straw (agricultural residue) biomass as an energy resource in Japan. *Biomass and Bioenergy*, 29,347-354.
- Kendry P, 2002a, Energy production from biomass (part 1): overview of biomass. *Bioresource Technology*, 83, 37-46
- McKendry P, 2002b, Energy production from biomass (part 2): conversion technologies. *Bioresource Technology*, 83(1), 47-54.
- Mediavilla I, Esteban LS, Fernández MJ, 2012, Optimisation of pelletisation conditions for poplar energy crop. *Fuel Processing Technology*, 104, 7-15.
- Mielenz JR, 2001, Ethanol production from biomass: technology and commercialization status. *Current Opinion in Microbiology*, 4, 324–329.
- Miles TR, Miles Jr TR, Baxter L, Bryers R, Jenkins B, Oden L, 1995, Alkali Deposits, A Summary Report for National Renewable Energy Laboratory, NREL Subcontract No. TZ-2-11226-1, p 73.
- Miner R, 2010, Biomass Carbon Neutrality. National Council for Air and Stream Improvement (NCASI).
- Mortensen NG, Said US, Badger J, 2005, Wind atlas for Egypt. In: Measurements and modelling 1991-2005. Cairo/Roskilde: NREA and Egyptian Meteorological Authority/Risø National Laboratory.

- Mosier N, Wyman CE, Dale BD, Elander RT, Lee YY, Holtzapple M, Ladisch CM, 2005, Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 96, 673-686.
- Mubarak A, Khalil A, Mostert W, Kaseb S, 2006, Renewable Energy Sector in Egypt (Tender IMC/PS_217), Energy Research Center (ERC), Final Report, Industrial Modernization Center (IMC), (I), 1-88.
- Murphy ML, 2001, Retrofit of coal-fired power boilers using fluidized bed biomass gasification. *Energy products of IDAHO*, Coeur d'Alene, Idaho, USA, 208, 765-1611.
- Mussatto SI, Roberto IC, 2004, Optimal experimental condition for hemicellulosic hydrolyzate treatment with activated charcoal for xylitol production. *Biotechnology Progress*, 20, 134-139.
- Nakhla DA, Hassan MG, Haggag S, 2013, Impact of biomass in Egypt on climate change. *Natural Science*, 5(6), 678-684.
- Niladevi KN, Prema P, 2005, Mangrove actinomycetes as the source of ligninolytic enzymes. *Actinomycetologica*, 19(2), 40-47
- NREA, 2002. Implementation of renewable energy technologies - opportunities and barriers. Egypt country study.
- NREA, 2000, Implementation of renewable energy technologies (RETs) – project opportunities and barriers. Egypt Country Study. Final Report to UNEP Collaborating Centre on Energy and Environmen. Denmark: Risø National Laboratory.
- Obernberger I, Thek G, 2004, Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behavior. *Biomass and Bioenergy*, 27, 653-669.

- ÖNORM M, 2003, 7135. Compressed wood or compressed bark in natural state, pellets and briquettes. Requirements and test specifications. Vienna, Austria: Österreichisches.
- Oregon EC, 2009, Dairy manure anaerobic digester feasibility study report. Albany.
- Page RDM, 1996, TreeView: An application to display phylogenetic trees on personal computers. *Computer Applications in the Biosciences*, 12, 357-358.
- Patel SJ, Onkarappa R, Shobha' KS, 2007, Comparative Study of Ethanol Production from Microbial Pretreated Agricultural Residues. *Journal of Applied Sciences and Environmental Management*, 11(4), 137-141.
- Patlitzianas KD, 2011, Solar energy in Egypt: Significant business opportunities, *Renewable Energy*, 36, 2305-2311.
- PelHeat, 2010, Biomass pellet production guide.
- Peng F, Song H, Jun X, Lushi S, Tao Y, Anchao Z, Junying Z, 2009, Mechanism Study of Rice Straw Pyrolysis by Fourier Transform Infrared Technique. *Chinese Journal of Chemical Engineering*, 17, 522-529.
- Picco D, 2010, Thermal efficiency report, Tenbiore Project, (Ref. No. 1206.011A-09).
- Potgieter JG, 2011, Agricultural residue as a renewable energy resource. *Renewable and sustainable energy studies*, Stellenbosch University.
- Prasad P, Singh T, Bedi S, 2013, Characterization of the cellulolytic enzyme produced by *Streptomyces griseorubens* (Accession No. AB184 139) isolated from Indian soil. *Journal of King Saud University – Science*, <http://dx.doi.org/10.1016/j.jksus.2013.03.003>
- Prescott J, 2013, Climate change: a framework for a global agreement in 2015, council of Europe, Doc. 13362, Committee on Social Affairs, 10 December 2013, United Kingdom.

- Pronobis M, 2005, Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass and Bioenergy*, 28, 375-383.
- Rath J, Steiner G, Wolfinger MG, Staudinger G, 2002, Tar cracking from fast pyrolysis of large beech wood particles. *Journal of Analytical and Applied Pyrolysis*, 62, 83-92.
- Raveendran K, Ganesh A, Khilar KC, 1995, Influence of mineral matter on biomass pyrolysis characteristics. *Fuel*, 74, 1812-1822.
- Ravindranath NH, Sathaye JA, 2002, *Climate change and developing countries*. New York: Kluwer Academic Publishers, 1-150.
- Reith JH, den Uil H, van Veen H, de Laat WTAM, Niessen JJ, de Jong E, Elbersen HW, Weusthuis R, van Dijken JP, Raamsdonk L, 2002, Co-production of bio-ethanol electricity and heat from biomass residues. 12th Eur Conf Technology Exhibition on Biomass for Energy, Industry and Climate Protection, Amsterdam, Netherlands.
- Ren J, Li F, Li Q, Wu J, 2008, Experiment study on the combustion characteristics of maize stalk biomass fuel. In: 9th Asia-Pacific Int Symp Combustion and Energy Utilization, China. *Renewable and Sustainable Energy Reviews*, 13, 2156-2162.
- Rentizelas A, Karellas S, Kakaras E, Tasiopoulos I, 2009, Comparative techno economic analysis of ORC and gasification for bioenergy applications. *Energy Conversion and Management*, 50, 674-81.
- Rhén C, Gref R, Sjöström M, Wästerlund I, 2005, Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets. *Fuel Processing Technology*, 87, 11-16.

- Richards SR, 1990, Physical testing of fuel briquettes. *Fuel Processing Technology*, 25, 89-100.
- Rijal B, Igathinathane C, Karki B, Yu M, Pryor C, 2012, Combined effect of pelleting and pretreatment on enzymatic hydrolysis of switchgrass. *Bioresource Technology*, 116, 36-41.
- Rogner HH, 2000, Energy Resources. *World Energy Assessment*. J. Goldemberg, UNPD, Washington, District of Columbia, USA, 135-171.
- Rosie CC, Gavrilesco M, Macoveanu M, 2008, biomass - an important renewable source of energy in Romania. *Environmental Engineering and Management Journal*, 7(5), 559-568.
- Saddawi A, Jones JM, Williams A, Coeur CL, 2012, Commodity Fuels from Biomass through Pretreatment and Torrefaction: Effects of Mineral Content on Torrefied Fuel, Characteristics and Quality. *Energy and Fuel*, 26, 6466- 6474.
- Said N, El-Shatoury SA, Díaz, LF, Zamorano M, 2013a, Quantitative appraisal of biomass resources and their energy potential in Egypt. *Renewable and Sustainable Energy Reviews*, 24, 84-91.
- Said N, Bishara T, García-Maraver A, Zamorano M, 2013b, Effect of water washing on the thermal behavior of rice straw. *Waste Management*, 33, 2250-2256.
- Said N, Zamorano M, El-shatoury SA, 2012, Renewable energy potential from biomass residues in Egypt. *World bioenergy conference*, 29-31 May, Jonkoping, Sweden.
- Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S, 2011, A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews*, 15, 2262–2289.
- Saitou N, Nei M, 1987, The neighbor-joining method: a new method for reconstructing phylogenetic trees. *Molecular Biology and Evolution*, 4, 406-425.

- Salama L, 2004, Egypt. Response to a Check List Submitted by the European Commission, MED BEST Report, Ministry of Foreign Trade and Industry.
- Sánchez OJ, Cardona CA, 2008, Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresource Technology*, 99, 5270-5295.
- Saratale GD, Saratale RG, Oh SE, 2012, Production and characterization of multiple cellulolytic enzymes by isolated *Streptomyces* sp. MDS. *Biomass and Bioenergy*, 47, 302-315.
- Saritha M, Arora A, Singh S, Nain L, 2013, *Streptomyces griseorubens* mediated delignification of paddy straw for improved enzymatic saccharification yields. *Bioresource Technology*, 135, 12-17.
- Sarkar N, Ghosh SK, Bannerjee S, Aikat K, 2012, Bioethanol production from agricultural wastes: An overview. *Renewable Energy*, 37, 19-27.
- Sasaki C, Takada R, Watanabe T, Honda Y, Karita S, Nakamura Y, Watanabe T, 2011, Surface carbohydrate analysis and bioethanol production of sugarcane bagasse pretreated with the white rot fungus, *Ceriporiopsis subvermispora* and microwave hydrothermolysis. *Bioresource Technology*, 102(21), 9942-9946.
- Schilling JS, Tewalt JP, Duncan SM, 2009, Synergy between pretreatment lignocellulose modifications and saccharification efficiency in two brown rot fungal systems. *Applied Microbiology and Biotechnology*, 84(3), 465-75.
- Schröder J, 2005, Revisiting the agronomic benefits of manure: a correct assessment and exploitation of its fertilizer value spares the environment. *Bioresource Technology*, 96, 253–261.
- Selim TH, 2009, Egypt's carbon emissions and the Kyoto Protocol, Egypt, energy and the environment. Adonis & Abbey Ltd.

- Serrano C, Monedero E, Lapuerta M, Portero H, 2011, Effect of moisture content, particle size and pine addition on quality parameters of barley straw pellets. *Fuel Processing Technology*, 92, 699-706.
- Shankar TJ, Bandyopadhyay S. Process, 2005, Variables during Single Screw Extrusion of Fish and Rice Flour Blends. *Journal of Food Processing and Preservation*, 29, 151-164.
- Sharma A, Khare SK, Gupta MN, 2001, Hydrolysis of rice hull by crosslinked *Aspergillus niger* cellulose. *Bioresource Technology*, 78, 281- 284.
- Shawky BT, Mahmoud MG, Ghazy EA, Asker MS, Gada S, Ibrahim GS, 2011, Enzymatic hydrolysis of rice straw and corn stalks for monosugars production. *Journal of Genetic Engineering and Biotechnology*, 9, 59–63.
- Shehata AM, 2002, Effect of particle size and firing load on characteristics of heat transfer in square fluidized bed combustor. MSc, Cairo University, Egypt.
- Singh A, 1996, A Study of Reaction Kinetics for Thermochemical Conversion of Rice Straw, University of California, Davis.
- Skrifvars BJ, Yrjas P, Kinni J, Siefen P, Hupa M, 2005, The Fouling Behavior of Rice Husk Ash in Fluidized-Bed Combustion. 1. Fuel Characteristics. *Energy Fuel*, 19, 1503-1511.
- Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D, 2012, Determination of Structural Carbohydrates and Lignin in Biomass. *Laboratory Analytical Procedure (LAP)*, 1-18
- Smeets EMW, Faaij APC, Lewandowski IM, Turkenburg WC, 2007, A bottom-up assessment and review of global bio-energy potentials to 2050. *Progress in Energy and Combustion Science*, 33, 56-106.

- Smeets E, Faaij A, Lewandowski I, 2004, A quick scan of global bioenergy potentials to 2050. An analysis of the regional availability of biomass resources for export in relation to the underlying factors. Report NWS-E; 2004-109, Utrecht University, Netherlands.
- Smith IE, Probert SD, Stokes RE, Hansford RJ, 1977, The briquetting of wheat straw. *Journal of Agricultural Engineering Research*, 22, 105-111.
- Soest PJV, 2006, Rice straw, the role of silica and treatments to improve quality. *Animal Feed Science and Technology*, 130, 137-171.
- Sokhansanj S, Mani S, Bi X, Zaini P, Tabil L, 2005, Binderless Pelletization of Biomass, ASAE Annual International Meeting, Tampa, FL, ASAE Paper No. 056061. ASAE, 2950 Niles Road, St. Joseph, MI 49085-9659 USA, July 17-20.
- Somogyi M, 1945, A new reagent for the determination of sugars. *Journal of Biological Chemistry*, 160, 61-73.
- Sosnowski P, Wieczorek A, Ledakowicz S, 2003, Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes. *Advances in Environmental Research*, 7, 609-616.
- Soundar S, Chandra TS, 1987, Cellulose degradation by a mixed bacterial culture. *Journal of Industrial Microbiology*, 2, 257-265.
- Ståhl M, Berghel J, Frodeson S, Granström K, Renström R, 2012, Effects on Pellet Properties and Energy Use When Starch Is Added in the Wood-Fuel Pelletizing Process. *Energy and Fuels*, 26, 1937-45.
- Stahl R, Ramadan AB, 2007, Fuels and chemicals from rice straw in Egypt. Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft Wissenschaftliche Berichte FZKA 7361, Fuels, <http://bibliothek.fzk.de/zb/berichte/FZKA7361.pdf>.

- Stelte W, Holm JK, Sanadi AR, Barsberg S, Ahrenfeldt J, Henriksen UB, 2011, A study of bonding and failure mechanisms in fuel pellets from different biomass resources. *Biomass and Bioenergy*, 35, 910-918.
- Summers DM, 2001, Using Rice Straw for Energy Production: Economics, Energetics and Emissions, Department of Biological and Agricultural Engineering, University of California, One Shields Ave., Davis, CA, USA 95616.
- Sun Z, Jin Bao-Sheng J, Ming-Yao Z, Ren-Ping L, Yong Z, 2008, Experimental study on cotton stalk combustion in a circulating fluidized bed. *Applied Energy*; 85, 1027-1040.
- Sun Y, Cheng J, 2002, Hydrolysis of lignocellulosic materials for ethanol Production: a review. *Bioresource Technology*, 83, 1-11.
- Sun XF, Sun R, Sun JX, 2002, Acetylation of Rice Straw with or without Catalysts and Its Characterization as a Natural Sorbent in Oil Spill Cleanup. *Journal of Agricultural and Food Chemistry*, 50, 6428-6433.
- Suramaythangkoo T, Gheewala SH, 2010, Potential alternatives of heat and power technology application using rice straw in Thailand. *Applied Energy*, 87, 128-133.
- Suramaythangkoo T, Gheewala SH, 2008, Potential of practical implementation of rice straw-based power generation in Thailand. *Energy Policy*, 36, 3183-3187.
- Szemmelveisz K, Szucs I, Palotas AB, Winkler L, Edings EG, 2009, Examination of the combustion conditions of herbaceous biomass. *Fuel Processing Technology*, 90, 839-847.
- Tabil LG, Sokhansanj S, 1996, Process conditions affecting the physical quality of alfalfa pellets. *Applied Engineering in Agriculture*, 12, 345-350.

- Tabil LG, 1996, Binding and pelleting characteristics of alfalfa. Ph.D. dissertation. Saskatoon, Saskatchewan, CA: Department of Agricultural and Bioresource Engineering, University of Saskatchewan.
- Tarasov D, Shahi C, Leitch M, 2013, Effect of Additives on Wood Pellet Physical and Thermal Characteristics: A Review. Hindawi Publishing Corporation ISRN Forestry, 1-6.
- Tchobanoglous G, Theisen H, Vigil S, 1993, Integrated solid waste management. New York: McGraw-Hill.
- Temmerman M, Rabier F, Jensen P, Hartmann H, Bohm T, 2006, Comparative study of durability test methods for pellets and briquettes. *Biomass and Bioenergy*, 30, 964-72.
- Theerarattananoon K, Xu F, Wilson J, Staggenborg S, Mckinney L, Vadlani P, Pei Z, Wang D, 2012, Effects of the pelleting conditions on chemical composition and sugar yield of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. *Bioprocess and Biosystems Engineering*, 35, 615-23.
- Theerarattananoon K, Xu F, Wilson J, Ballard R, Mckinney L, Staggenborg S, Vadlanib P, Peid ZJ, Wang D, 2011, Physical properties of pellets made from sorghum stalk, corn stover, wheat straw, and big bluestem. *Industrial Crops and Products*, 33, 325-32.
- Thomas M, van der Poel AFB, 1996, Physical quality of pelleted animal feed 1. Criteria for pellet quality. *Animal Feed Science and Technology*, 61, 89-112.
- Thompson JD, Gibson TJ, Plewniak F, Jeanmougin F, Higgins DG, 1997, The clustalX windows interface: flexible strategies for multiple sequence alignment aided by quality analysis tools. *Nucleic Acids Research*, 24, 4876-4882.

- Thy P, Jenkins BM, Williams RB, Leshner CE, 2004, Slag formation and potassium volatilization from rice straw blended wood fuel, Preprints of Papers- American Chemical Society. Division of Fuel Chemistry, 49(1), 89- 91.
- Tiwari R, Rana S, Singh S, Arora A, Kaushik R, Agrawal VV, Saxena A, Nain A, 2013, Biological delignification of paddy straw and *Parthenium* sp. using a novel micromycete *Myrothecium roridum* LG7 for enhanced saccharification. *Bioresource Technology*, 135, 7-11.
- Trujillo ME, Alonso-Vega P, Rodríguez R, Carro L, Cerda E, Alonso P, Martínez-Molina E, 2010, The genus *Micromonospora* is widespread in legume root nodules: the example of *Lupinus angustifolius*. *International Society for Microbial Ecology Journal*, 4, 1265-1281.
- Tumuluru JS, Sokhansanj S, Wright CT, Boardman RD, Yancey NA, 2011, A Review on Biomass Classification and Composition, Co-Firing Issues and Pretreatment Methods, ASABE Annual International Meeting.
- Turner R, 1995, Bottom line in feed processing: achieving optimum pellet quality. *Feed Manager*, 46, 30-3.
- UNE-EN 14588, 2011, Solid biofuels, Terminology, definitions and descriptions.
- UNE-EN 14774-2, 2010, Solid biofuels, Determination of moisture content, simplified method.
- UNE-EN 14775, 2010, Solid biofuels, Determination of ash content.
- UNE-EN 14918, 2011, Solid biofuels, Determination of calorific value.
- UNE-EN ISO 17225- 1, 2014, Solid biofuels. Fuel specification and classes. Part 1: general requirements.
- UNE-EN ISO 17225-6, 2014, Solid biofuels, Fuel specification and classes- Part 6: Graded non-woody pellets.

- UNE-EN 15103, 2010, Solid biofuels, Determination of bulk density.
- UNE-EN 15104, 2011, Solid biofuels, Determination of total content of carbon, hydrogen and nitrogen, Instrumental methods.
- UNE-EN 15148, 2010, Solid biofuels, Determination of the content of volatile matter.
- UNE-EN 15150, 2012, Solid biofuels, Determination of particle density.
- UNE-EN 15210-1, 2010, Solid biofuels, Determination of mechanical durability of pellet and briquettes- part 1: pellets.
- UNE-EN 15290, 2011, Solid biofuels, Determination of major elements.
- UNE-EN 16127, 2012, Solid biofuels, Determination of length and diameter of pellets.
- UNEP, United Nations Environmental Programme, 2009, Converting Waste Agricultural Biomass into a Resource, Compendium of Technologies, International Environmental Technology Centre, Japan.
- UNEP, United Nations Environment Programme, 2003, Global Environment Outlook 3. London: Earthscan Publications.
- UNFCCC, United Nations Framework Convention on Climate Change, 2010, Egypt second national communication.
- Vallander L, Eriksson KEL, 1985, Enzymic saccharification of pretreated wheat straw. *Biotechnology and Bioengineering*, 27, 650-659
- Velis CA, Longhurst PJ, Drew GH, Smith R, Pollard SJT, 2009, Biodrying for mechanical-biological treatment of wastes: a review of process science and engineering. *Bioresource Technology*, 100, 2747-2761.
- Vinterbäck J, 2004, Pellets 2002: the first world conference on pellets. *Biomass and Bioenergy*, 27, 513-520.
- Vlesenko EY, Ding H, Labavitch JM, Shoemaker SP, 1997, Enzymatic hydrolysis of pretreated rice straw. *Bioresource Technology*, 59, 109-119.

- Vojdani F, 2010, Biomass and waste characterization as a potential energy sources in Iran. Proc Third Int Symp Energy from Biomass and Waste, Venice, Italy; 8-11.
- Wanger M, 2009, Thermal Analysis in practice. Schwerzenbach: Mettler Toledo collected applications, (Chapter 7)
- Wattanasiriwech S, Wattanasiriwech D, Svasti J, 2010, Production of amorphous silica nanoparticles from rice straw with microbial hydrolysis pretreatment. Journal of Non-Crystalline Solids, 356 (25-27), 1228-1232.
- WEC, 1994, New renewable energy sources. A guide to the future. World Energy Council/Kogan Page Ltd, London, UK.
- Werther J, Saenger M, Hartge EU, Ogada T, Siagi Z, 2000, Combustion of agricultural residues. Progress in Energy and Combustion Science, 26, 1-27.
- Wilkie AC, Castro HF, Cubinski KR, Owens JM, Yan SC, 2004, Fixed-film anaerobic digestion of flushed manure after primary treatment: wastewater production and characterization. Biosystems Engineering, 89, 457-471.
- Williams ST, Wellington EMH, 1982, Actinomycetes. In: Page, A. L. (ed), methods of soil analysis. Part 2. Chemical and microbiological properties-Agronomy monograph no. 9, ASA-SSSA, Madison, USA, 969-987.
- Wolfson R, Schneider SH, 2002, Understanding climate science. In: Climate change policy: a survey. Washington: Island Press, 3-52.
- Wongjewboot I, Kangsadan T, Kongruang S, Burapatana V, Pripanapong P, 2010, Ethanol Production from Rice Straw Using Ultrasonic Pretreatment. International Conference on Chemistry and Chemical Engineering (ICCCE).
- Wood JF, 1987, The functional properties of feed raw materials and their effect on the production and quality of feed pellets. Animal Feed Science and Technology, 18, 1-17.

- World Bank, 2009. World Development Indicators (WDI). <http://web.worldbank.org/>.
- Wu MR, Schott DL, Lodewijks G, 2011, Physical properties of solid biomass. *Biomass and Bioenergy*, 35, 2093-2105.
- Xu J, Yang Q, 2010, Isolation and characterization of rice straw degrading *Streptomyces griseorubens* C-5. *Biodegradation*, 21(1), 107-116.
- Xu C, Etcheverry T, 2008, Hydro-liquefaction of woody biomass in sub- and supercritical ethanol with iron-based catalysts. *Fuel*, 87, 335-345.
- Xuereb P, 1997, Biogas a fuel produced from waste. www.synapse.net.mt/miwm/newsletter/3836.asp.
- Yan J, Lin T, 2009, Biofuels in Asia. *Applied Energy*, 86, S1-S10.
- Yao R, Qi B, Deng S, Liu N, Peng S, Cui Q, 2007, Use of surfactants in enzymatic hydrolysis of rice straw and lactic acid production from rice straw by simultaneous saccharification and fermentation. *Bioresources*, 2(3), 389-398.
- Yoswathana N, Phuriphat P, Treyawutthiwat P, Eshtiaghi M, 2010, Bioethanol, Production from Rice Straw. *Energy Research Journal*, 1(1), 26-31.
- Youssef MA, Wahid SS, Mohamed MA, Askalany AA, 2009, Experimental study in Egyptian biomass combustion in circulating fluidized bed. *Applied Energy*, 86, 2644-2650.
- Yu C, Qin J, Xu J, Nie H, Luo Z, Cen K, 2010, Straw Combustion in Circulating Fluidized Bed at Low-Temperature: Transformation and Distribution of Potassium, Wiley Online Library, 88, 874-880.
- Yu ZS, Ma XQ, Ao L, 2008, Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis. *Biomass and Bioenergy*, 32(11), 1046-1055

- Zafari A, Kianmehr MH, 2012, Effect of raw material properties and die geometry on the density of biomass pellets from composted municipal solid waste. *Bioresources*, 7, 4704-4714.
- Zamorano M, Popov V, Rodríguez ML, García-Maraver A, 2011, A comparative study of quality properties of pelletized agricultural and forestry lopping residues. *Renewable energy*, 36, 3133-3140
- Zannoun MS, 2009, Egypt's renewable energy strategy, achievements and programs. New and Renewable Energy Authority (NREA), Egypt.
- Zbogar A, Frandsen F, Jensen PA, Glarborg P, 2009, Shedding of ash deposits. *Progress in Energy and Combustion Science*, 35, 31-56.
- Zhaosheng Y, Xiaoqian M, Ao L, 2008, Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis. *Biomass and bioenergy*, 32, 1046-1055.
- Zheng YH, Li ZF, Feng SF, Lucas M, Wu GL, Li Y, Li CH, Jiang GM, 2010, Biomass energy utilization in rural areas may contribute to alleviating energy crisis and global warming: A case study in a typical agro-village of Shandong, China. *Renewable and Sustainable Energy Reviews*, 14, 3132-3139.
- Zygarlicke JC, Kurt EE, McCollar PD, Musich AM, Toman LD, 2000, Impacts of co-firing biomass with fossil fuels. In: *Proceedings of the 25th international technical conference on coal utilization and fuel systems*, Clearwater.



PUBLICATIONS

Reduction of Ash Sintering Precursor Components in Rice Straw by Water Washing

Noha Said,^{a,b,*} Mahmoud M. Abdel daiem,^b Angela García-Maraver,^a and Montserrat Zamorano^a

The thermal conversion of rice straw is an attractive option for recovering its energy, but the process requires exhaustive control because of ash-related problems. Straw washing is one method of reducing ash-related problems and improving combustion behaviour. In this study, the ash of washed and unwashed rice straw samples was chemically characterized, tested using thermogravimetric analysis and environmental scanning electron microscopy (ESEM), and subjected to higher combustion temperatures in a muffle furnace. Results showed that silicon was the most important component in the ash. Furthermore, a reduction in undesirable inorganic compounds related to ash problems, such as chlorine and potassium, was achieved by washing the straw samples. This practice could improve thermal behaviour and decrease the sintering formation of ash.

Keywords: Rice straw; Ash; Thermal analysis; Electron microscopy; Sintering

Contact information: a: Civil Engineering Department, Area of Environmental Technology, Granada University 18071, Granada, Spain; b: Environmental Engineering Department, Faculty of Engineering, Zagazig University 44519, Zagazig, Egypt; *Corresponding author: nsaid_2020@ugr.es

INTRODUCTION

Given the excessive use of fossil fuels and concerns over environmental protection, the utilization of biomass resources, including agricultural residues, has attracted increasing worldwide interest (Fu *et al.* 2009). Rice straw is one of the main agricultural residues in countries such as Egypt, Thailand, China, and especially Japan, where it comprises the largest amount of unused agricultural residue by far (Matsumura *et al.* 2005; Delivand *et al.* 2011; Liu *et al.* 2011; Said *et al.* 2013a). Its energy can be recovered directly through a combustion process, or it can be converted to a valuable energy product through indirect techniques such as gasification and biochemical conversion, after which the products can be burned (Ewida *et al.* 2006).

The combustion of rice straw to directly produce thermal energy not only saves energy, protects the environment, and reduces field-burning pollution; it also increases the income of farmers (Ewida *et al.* 2006; Yu *et al.* 2008). There are, however, some technical limitations involved in thermal conversion systems, such as high ash content, sintering, slag formation, and corrosion problems (Jenkins *et al.* 1996; Baxter *et al.* 1998; Fu *et al.* 2009; Said *et al.* 2013b). Washing rice straw with water is a feasible option for reducing these problems (Jenkins *et al.* 1996; Bakker *et al.* 2002). Previous work (Said *et al.* 2013b) describes the effects of water-washing on the chemical and thermal characteristics of rice straw, indicating enhanced thermal behaviour. This included a higher heating value and a reduction in ash content and sintering formation compared

with the unwashed samples. Also, an improvement in the alkali index value was observed for the washed samples.

Ash analysis based on thermogravimetric analysis and electron microscopy provides more details about its behaviour through combustion processes (Skrifvars *et al.* 2005; Fang and Jia 2012) and the effects of washing samples before combustion. Such studies are rare, however. Against this background, the main objective of the present study is to investigate the effect of washing rice straw on the chemical composition and thermal characteristics of its ash by using X-ray fluorescence (XRF), thermogravimetric analysis (TGA/DSC), and environmental scanning electron microscopy (ESEM).

EXPERIMENTAL

Materials

Sampling procedure

Samples of rice straw approximately 1 m tall were collected from El Sharkia Government, Egypt. They were cut to a size of 10 cm, washed with flushed tap water, and dried in air dry oven at 105 °C to a constant weight in the laboratory; the particle size for the dried washed and unwashed straw samples was reduced to less than 0.5 mm with a cutting mill. Finally, unwashed and washed samples of rice straw were subjected to combustion at 550 °C in a muffle furnace for 5 h to obtain ash samples used for this research, according to UNE-EN 14775 (2010). Moreover, the ash samples were subjected to temperatures of 700, 800, 900, and 1000 °C in a muffle furnace for 2 h to investigate changes in colour and in physical states.

Methods

Laboratory tests

To determine ash composition, ash samples of washed and unwashed straw were analysed using a Philips Magix Pro PW-2440 sequential spectrometer with a dispersive wavelength and an X-Ray generator of 4 KW. The ESEM analysis for the ash samples was performed using an FEI Quanta 400 ESEM (The Netherlands) equipped with a SAPPHERE Si(Li) SUTW detector operating at an accelerating voltage between 0.20 to 30 kV to obtain the image, particle size, and composition of the ash analysed in the selected spots. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on the ash of both types of straw samples using a Shimadzu TGA-50H thermo analyser (Japan) in an oxidative atmosphere. The initial mass of the ash samples was kept between 2 and 5 mg and heated from 30 °C to 1000 °C at a heating rate of 5 °C/min and a constant airflow rate of 50 mL/min.

RESULTS AND DISCUSSION

Ash Composition

The chemical composition of the ash obtained from the washed and unwashed straw samples is summarized in Table 1. For unwashed straw samples, the highest ash component was silica (SiO₂), which constituted 65.4% of the total content, followed by K₂O, Cl, Na₂O, MgO, CaO, SO₃, and P₂O₅. In washed samples the silica content was as high as 72.6%, followed in order by K₂O, CaO, Cl, Na₂O, MgO, P₂O₅, and SO₃. Washing

proved very efficient for removing over half the SO₃ and chlorine (respective removal ratios of 59.5% and 59.1%). For Na₂O, K₂O, MgO, and P₂O₅, the removal ratios were 35.7%, 26.1%, 21.9%, and 8.82%, respectively. Calcium oxide and SiO₂ removal were substantially higher, reaching 41.3% and 11%, respectively. Both SiO₂ and CaO appear to reside largely in the plant cell wall of rice straw (Miles *et al.* 1996; Soest 2006); therefore, the washing practice did not effectively remove them. However, washing the straw does serve to extract large amounts of alkali metals such as potassium, which dissolved very well in water, and chlorine, which is highly leached by water (Lee *et al.* 2005; Skrifvars *et al.* 2005). In addition, washing removes varying amounts of sulphur, phosphorus, and other elements caused by soil contamination of the straw (Jenkins *et al.* 1996; Bakker *et al.* 2002; Skrifvars *et al.* 2005); while their percentages are reduced, the relative contents of SiO₂ and CaO are seen to increase.

Table 1. Composition (%) of Ash Elements in Washed and Unwashed Samples

Samples	SiO ₂	K ₂ O	Cl	Na ₂ O	MgO	CaO	SO ₃	P ₂ O ₅	Others
Unwashed	65.43	13.01	5.40	3.11	2.24	2.13	1.26	0.68	6.74
Washed	72.59	9.61	2.21	2.00	1.75	3.01	0.51	0.62	7.70

Environmental Scanning Electron Microscopy Inspection

Figure 1 shows the ESEM results for ash of the unwashed straw samples and the chemical analysis of selected spots. Supporting the results expounded in the previous section, high amounts of chlorine and potassium were detected by ESEM. Additional elements such as Na and Mg were detected in spot 1, and similarly in spot 3, which were observed with a lighter appearance compared to surrounding area. Silica was the predominating element in spot 2, though similar constituents were observed at spot 4. These findings are in line with the results reported by Skrifvars *et al.* (2005) for rice straw ash samples.

Figure 2 shows the ESEM results for the ash of the washed straw sample and the chemical analysis of selected spots. While washing did not have a considerable effect on ash microstructure, it did cause changes in chemical composition. As shown in Fig. 2, all the selected spots consist primarily of silica. Small amounts of other elements including carbon, oxygen, magnesium, and sodium were also present. A considerably high amount of Ca was detected at spot 1. In turn, a considerable loss in chlorine and potassium from washing was observed by ESEM, supporting the results obtained for ash composition (higher SiO₂ and CaO). Meanwhile, markedly lower contents of Cl and K₂O were observed for the washed samples when compared with unwashed ones.

Qualitative Analysis of Ash

Unwashed samples

The ash obtained from the unwashed samples at 550 °C has a dark grey colouring (Fig. 3a). This colour could result from residual carbon compounds that require a higher temperature or longer time to completely burn the straw samples (Wattanasiriwech *et al.* 2010). The combustion of ash samples at 700 °C resulted in a grey colour, and they were easy to remove. Nevertheless, when the combustion temperature was increased to 800 °C, light ash sintering was observed, and the sintering increased with increasing combustion temperature (up to 900 °C). Severe sintering and slag formation of a dark brown colour was observed when the combustion temperature reached 1000 °C, making it impossible

to remove the ash from the crucibles (Fig. 3b). This may be caused by the fact that silica in combination with alkali and alkaline earth metals, especially potassium, can lead to the formation of compounds that readily slag and foul at normal furnace temperatures (Miles *et al.* 1996; Skrifvars *et al.* 2005). Moreover, chlorine could be an important facilitator in fouling and in the vaporization of alkali species, leading to the formation of more severe deposits (Miles *et al.* 1996).

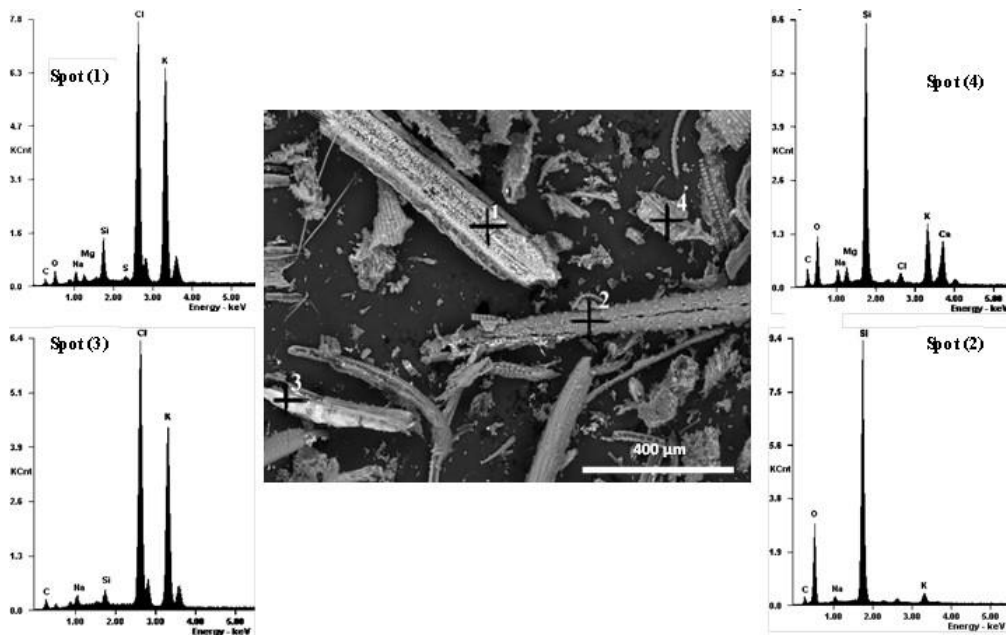


Fig. 1. ESEM analysis of ash (unwashed samples)

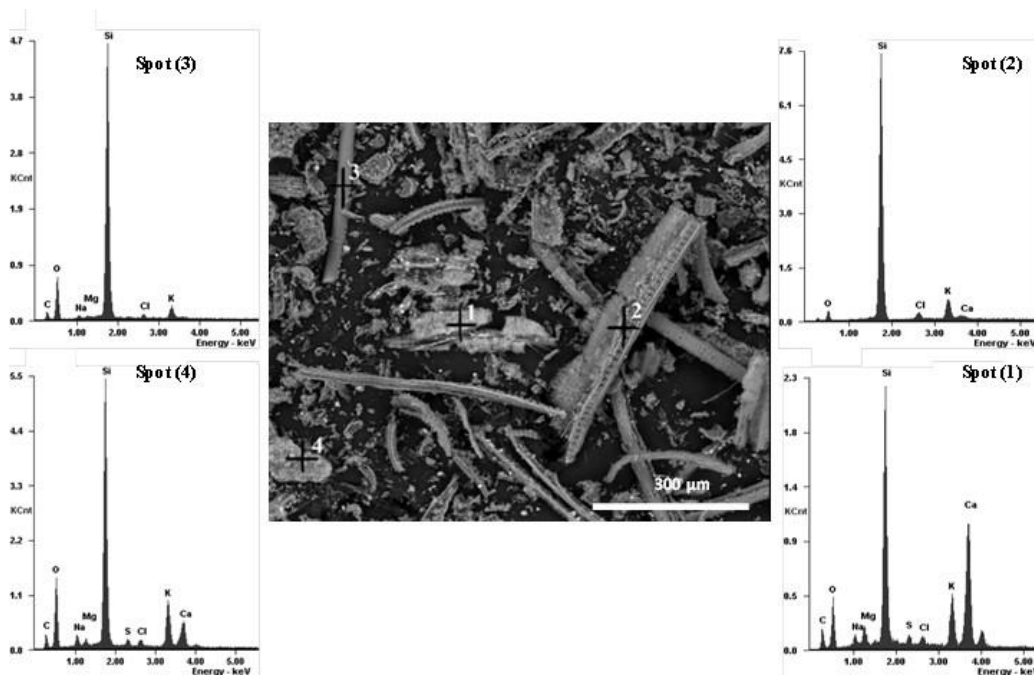


Fig. 2. ESEM analysis of ash (washed samples)

Washed samples

The ash of the washed samples at 550 °C was grey-coloured (Fig. 3c). With increasing combustion temperature (up to 700 °C), the ash had a lighter grey colour and became close to white when the furnace temperature was increased to 1000 °C (Fig. 3d). Unlike the unwashed samples, the ash of the washed samples was easy to remove and did not show sintering or slag formation. This could be explained by the reduction of undesirable compounds, especially potassium, after washing (Table 1). Moreover, the alkali index of rice straw is greatly decreased when washed, as indicated previously (Said *et al.* 2013a). Washing therefore leads to significant changes in inorganic composition and substantially improves combustion behaviour (Jenkins *et al.* 1996; Bakker *et al.* 2002; Lee *et al.* 2005).

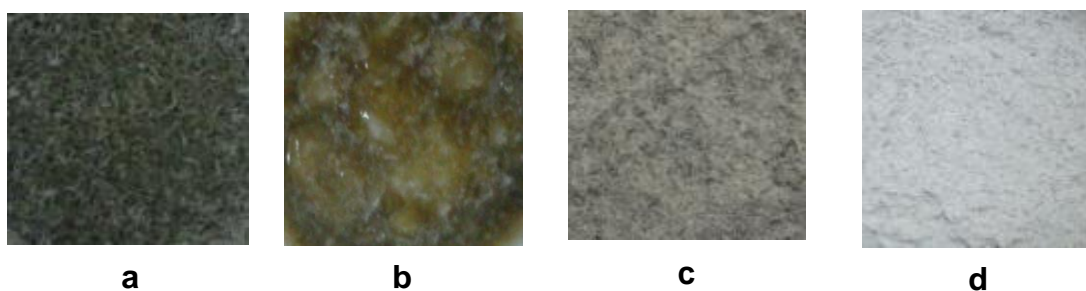


Fig. 3. Ash combusted in a muffle furnace. (a) unwashed sample at 550 °C; (b) unwashed sample at 1000 °C; (c) washed sample at 550 °C; and (d) washed sample at 1000 °C

Thermogravimetric Analysis and Differential Scanning Calorimetry

To consider the combustion behaviour of ash in detail, the thermogravimetric curves of the ash obtained at 550 °C for washed and unwashed straw samples were analysed (Fig. 4).

Thermogravimetric analysis

The TGA curves showed changes in the mass loss of the ash samples with increasing temperature, essentially in the same order as found in previous work (Fang and Jia 2012). An initial mass loss occurred at temperatures lower than 200 °C because of the evaporation of water, which was readily absorbed into the atmosphere by the much smaller ash particles before testing (Fang and Jia 2012). The mass loss at 200 °C in the unwashed samples was higher than that for the washed samples (2.80% versus 1.20%). It may be that the moisture in the unwashed samples was absorbed by components such as chlorine and potassium, which were present together in greater concentrations than in the washed samples (Lee *et al.* 2005; Skrifvars *et al.* 2005).

Because the ash samples tested were obtained at 550 °C, a very low rate of mass loss was observed from 200 up to 700 °C; only about a 3.60% loss in the ash mass of the unwashed sample. This loss may be attributed to the oxidation of some organic components that had not completely burned, as well as to the evaporation of some inorganic matter from the ash with further increases in temperature (Fang and Jia 2012). Above 700 °C and up to 850 °C, a markedly increase in mass loss (5.50% and 7.70% for washed and unwashed samples, respectively) was observed. This may be due to the higher deposition rate of char particles of unwashed straw during higher combustion temperatures (Bakker *et al.* 2002), and also to the removal and decomposition reaction of

inorganic components such as chlorine and potassium (Fang and Jia 2012) which are found together and in greater proportions in the unwashed samples, as indicated by the ash composition and ESEM analyses described above.

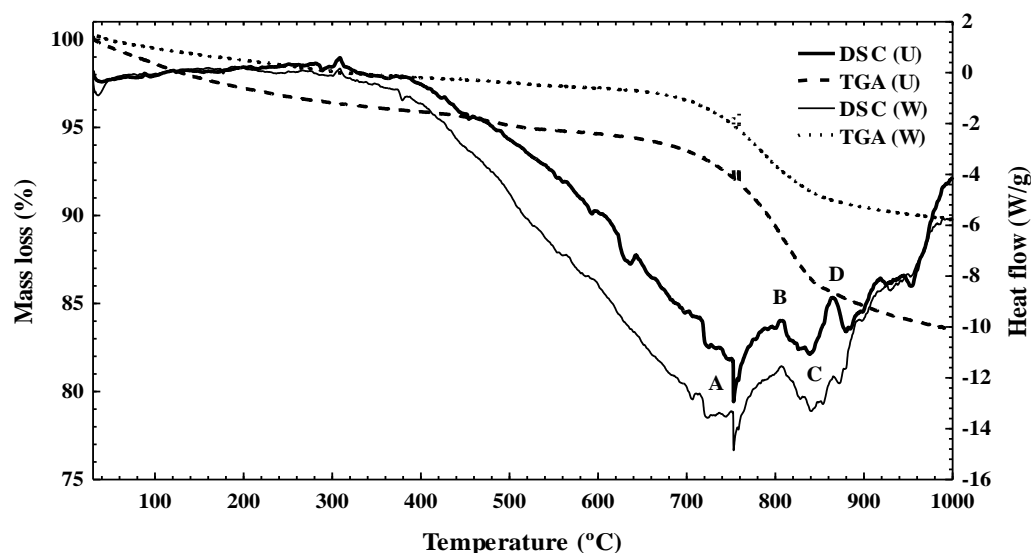


Fig. 4. TGA and DSC for ash of washed (W) and unwashed (U) samples

Potassium starts to be released at a low rate at very low temperatures, but is then more rapidly released as the temperature increases up to 800 °C (Knudsen *et al.* 2004; Skrifvars *et al.* 2005). The potassium absorbed from the soil mainly remains as ions in fresh plants; when the plants wither, the potassium may exist in simple salts such as KCl and K₂SO₄, which have high activity and strong migration characteristics at high temperatures (Yu *et al.* 2010). A high content of potassium salts is retained in ash after the completion of combustion, and at high temperatures these salts may evaporate and volatilise into gas or react with silicon, calcium, or other elements to form complex silicates after 800 °C (Baxter *et al.* 1998; Fang and Jia 2012). The minor mass loss observed from 850 °C up to 1000 °C (1.33% and 2.51% for washed and unwashed samples, respectively) can be attributed to the evaporation of KCl and the reaction between Si and KCO₃, which decomposes after 1000 °C (Masia *et al.* 2007; Szemmelveisz *et al.* 2009).

Differential scanning calorimetry

The DSC curves are important for studying the thermal behavior of ash, representing the melting point as a maximum of the endothermic peaks of DSC trace (Buzarovska *et al.* 2008). As can be seen in Fig. 4, the ash samples recorded a maximum endothermic peak in the range of 700 °C to 800 °C, represented as zone (A). In agreement with Wanger (2009) and as indicated in the figure, the melting peak was followed by an exothermic decomposition reaction represented in zone (B); then, the evaporation of the decomposition product represented at zone (C) was followed by a crystallization exothermic peak represented at (D), which was only observed for the unwashed sample and not detected in the washed one.

This crystallization peak could indicate sintering formation occurring with the ash of the unwashed sample, as discussed in the section on ash behaviour. No considerable

difference in melting temperature was observed between the washed and unwashed samples. However, the fact that the unwashed sample recorded a lower heat flow rate may be associated with the higher ash-related problems of the unwashed samples; this would result in low thermal conductivity, retarding the rate of heat transfer (Jenkins *et al.* 1996; Zbogar *et al.* 2009).

CONCLUSIONS

1. Chemical analysis and ESEM of rice straw ash samples revealed that silica was the foremost component (65.4%), followed by K₂O (13%), and that these two components are combined at high combustion temperatures and associated with ash sintering problems.
2. Thermogravimetric analysis provided valuable indications of component decomposition, which occurred in stages, and more detailed information about thermal behaviour and related reactions at high combustion temperatures.
3. The washing process resulted in a reduction of some sintering precursor components in the ash samples, such as K₂O and Cl. Lower ash mass losses at greater combustion temperatures and enhanced thermal behaviour were observed after washing.

ACKNOWLEDGMENTS

This research was funded by the Innovation and Science Division of the Andalusian Regional Government (Research Projects P08-RNM-03584 and TIC-02913), the Spanish Ministry of Science and Innovation (Research Project CTM2009-07199), and the Spanish Agency for International Development Cooperation (AECID) of the Ministry of Foreign Affairs and Cooperation (Project AP/045946/11).

REFERENCES CITED

- Bakker, R. R., Jenkins, B. M., and Williams, R. B. (2002). "Fluidized bed combustion of leached rice straw," *Energ. Fuel.* 16(2), 356-365. DOI: 10.1021/ef010197w
- Baxter, L. L., Miles, T. R., Miles Jr., T. R., Jenkins, B. M., Milne, T., Dayton, D., Bryers, R. W., and Oden, L. L. (1998). "The behavior of inorganic material in biomass-fired power boilers: Field and laboratory experiences," *Fuel Process. Technol.* 54(1-3), 47-78. DOI: 10.1016/S0378-3820(97)00060-X
- Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., Gentile, G., and Errico, M. (2008). "Potential use of rice straw as filler in eco-composite materials," *Aust. J. Crop Sci.* 2(1), 37-42.
- Delivand, K. M., Barz, M., and Gheewala, S. (2011). "Logistics cost analysis of rice straw for biomass power generation in Thailand," *Energy* 36(3), 1435-1441. DOI: 10.1016/j.energy.2011.01.026
- Ewida, K. T., El-Salmawy, H., Atta, N. N., and Mahmoud, M. M. (2006). "A sustainable approach to the recycling of rice straw through pelletization and controlled burning," *Clean Technol. Envir.* 8(3), 188-197. DOI: 10.1007/s10098-006-0043-x

- Fang, X., and Jia, L. (2012). "Experimental study on ash fusion characteristics of biomass," *Bioresour. Technol.* 104, 769-774. DOI: 10.1016/j.biortech.2011.11.055
- Fu, P., Hu, S., Xiang, J., Sun, L. S., Yang, T., Zhang, A. C., and Zhang, J. Y. (2009). "Mechanism study of rice straw pyrolysis by Fourier transform infrared technique," *Chinese J. Chem. Eng.* 17(3), 522-529. DOI: 10.1016/S1004-9541(08)60240-2
- Jenkins, B. M., Bakker, R. R., and Wei, J. B. (1996). "On the properties of washed straw," *Biomass Bioenerg.* 10(4), 177-200. DOI: 10.1016/0961-9534(95)00058-5
- Knudsen, J. N., Jensen, P. A., and Dam-Johansen, K. (2004). "Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass," *Energ. Fuel.* 18(5), 1385-1399. DOI: 10.1021/ef049944q
- Lee, K., Kang, B., Park, Y., and Kim, J. (2005). "Influence of reaction temperature, pretreatment, and a char removal system on the production of bio oil from rice straw by fast pyrolysis, using a fluidized bed," *Energ. Fuel.* 19(5), 2179-2184. DOI: 10.1021/ef050015o
- Liu, Z., Xu, A., and Zhao, T. (2011). "Energy from combustion of rice straw: Status and challenges to China," *Energy Power Eng.* 3, 325-331. DOI: 10.4236/epe.2011.33040
- Masia, A. A. T., Buhre, B. J. P., Gupta, R. P., and Wall, T. F. (2007). "Characterizing ash of biomass and waste," *Fuel Process. Technol.* 88(11-12), 1071-1081. DOI: 10.1016/j.fuproc.2007.06.011
- Matsumura, Y., Minowa, T., and Yamamoto, H. (2005). "Amount, availability, and potential use of rice straw (agricultural residue) biomass as an energy resource in Japan," *Biomass Bioenerg.* 29(5), 347-354. DOI: 10.1016/j.biombioe.2004.06.015
- Miles, T. R., Miles Jr., T. R., Baxter, L., Bryers, R., Jenkins, B., and Oden, L. (1996). "Alkali deposits, A summary report for the National Renewable Energy Laboratory, NREL," Subcontract No. TZ-2-11226-1.
- Skrifvars, B. J., Yrjas, P., Kinni, J., Siefen, P., and Hupa, M. (2005). "The fouling behavior of rice husk ash in fluidized-bed combustion. 1: Fuel characteristics," *Energ. Fuel.* 19(4), 1503-1511. DOI: 10.1021/ef049714b
- Said, N., El-Shatoury, S. A., Díaz, L. F., and Zamorano, M. (2013a). "Quantitative appraisal of biomass resources and their energy potential in Egypt," *Renew. Sust. Energ. Rev.* 24, 84-91. DOI: 10.1016/j.rser.2013.03.014
- Said, N., Bishara, T., García-Maraver, A., and Zamorano, M. (2013b). "Effect of water washing on the thermal behavior of rice straw," *Waste Manage.* 33(11), 2250-2256. DOI: 10.1016/j.wasman.2013.07.019
- Soest, P. J. V. (2006). "Rice straw, the role of silica and treatments to improve quality," *Anim. Feed. Sci. Tech.* 130(3-4), 137-171. DOI: 10.1016/j.anifeedsci.2006.01.023
- Szemmelveisz, K., Szucs, I., Palotas, A. B., Winkler, L., and Edings, E. G. (2009). "Examination of the combustion conditions of herbaceous biomass," *Fuel Process. Technol.* 90(6), 839-847. DOI: 10.1016/j.fuproc.2009.03.001
- UNE-EN 14775 (2010). "Solid biofuels - Determination of ash content," *Spanish Association for Standardisation and Certification (AENOR)*.
- Wanger, M. (2009). *Thermal Analysis in Practice-Collected Applications*, Mettler Toledo Application Handbook, http://cn.mt.com/cn/zh/home/applications/Application_Browse_Laboratory_Analytics/Application_Browse_thermal_analysis/TA_Appl_Handb/TA_in_Practice/_jcr_content/standardpar/1145/file/file.res/Thermal_Analysis_in_Practice.pdf.
- Wattanasiriwech, S., Wattanasiriwech, D., and Svasti, J. (2010). "Production of amorphous silica nanoparticles from rice straw with microbial hydrolysis

- pretreatment,” *J. Non-Cryst. Solids* 356(25-27), 1228-1232. DOI: 10.1016/j.jnoncrysol.2010.04.032
- Yu, Z. S., Ma, X. Q., and Ao, L. (2008). “Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis,” *Biomass Bioenerg.* 32(11), 1046-1055. DOI: 10.1016/j.biombioe.2008.02.001
- Yu, C. J., Qin, J. G., Xu, J., Nie, H., Luo, Z. Y., and Cen, K. F. (2010). “Straw combustion in circulating fluidized bed at low-temperature: Transformation and distribution of potassium,” *Can. J. Chem. Eng.* 88(5), 874-880. DOI: 10.1002/cjce.20321
- Zbogar, A., Frandsen, F., Jensen, P. A., and Glarborg, P. (2009). “Shedding of ash deposits,” *Prog. Energy Combust. Sci.* 35(1), 31-56. DOI: 10.1016/j.pecs.2008.07.001

Article submitted: July 10, 2014; Peer review completed: September 7, 2014; Revised version received and accepted: September 13, 2014; Published: September 23, 2014.



Effect of water washing on the thermal behavior of rice straw



N. Said^{a,b}, T. Bishara^a, A. García-Maraver^a, M. Zamorano^{a,*}

^a Civil Engineering Department, University of Granada, Campus de Fuentenueva, 18071 Granada, Spain

^b Environmental Engineering Department, Faculty of Engineering, Zagazig University, 44519 Zagazig, Egypt

ARTICLE INFO

Article history:

Received 1 March 2013

Accepted 12 July 2013

Available online 7 August 2013

Keywords:

Rice straw
Thermal behavior
Sintering
Water washing

ABSTRACT

Rice straw can be used as a renewable fuel for heat and power generation. It is a viable mean of replacing fossil fuels and preventing pollution caused by open burning, especially in the areas where this residual biomass is generated. Nevertheless, the thermal conversion of rice straw can cause some operating problems such as slag formation, which negatively affects thermal conversion systems. So, the main objective of this research is studying the combustion behavior of rice straw samples collected from various regions by applying thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In addition, the thermal behavior of ashes from rice straw was also analyzed in order to detect their melting points, and ash sintering was detected at different temperatures within the range between 550 and 1000 °C. Since washing rice straw with water could reduce the content of undesirable inorganic compounds related to the ash fusibility, samples of washed rice straw were analyzed under combustion conditions to investigate its differences regarding the thermal behavior of rice straw. The results showed that rice straw washing led to a significant improvement in its thermal behavior, since it reduced the ash contents and sintering formation.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass materials with high energy potential include agricultural residues and all of the agricultural residues are biological forms of renewable energy, rice straw is considered to be the most important of such residues and represents one of the major by-products from rice production process in most rice producing countries (Abou-Sekkina et al., 2010; Said et al., 2013; Werther et al., 2000). The rice collection harvest generates large amounts of straw, for each ton of grain harvested, about 1.35 tons of rice straw remain in the field (Kadam et al., 2000) making up approximately 50% of the dry weight of rice plants, with a significant variation of 40–60% depending on the crop and agricultural method. The annual production of rice straw is about 731 million tons which is distributed in Africa, Asia, Europe, America and Oceania as 20.9, 667.6, 3.9, 37.2 and 1.7 million tons, respectively (Balat et al., 2008; Sarkar et al., 2012).

During the rice harvest, the elimination of rice straw is frequently carried out by farmers by burning it in the fields because of the difficulty and high cost of removing it and because of its null use (Abril et al., 2009); the justification for this practice is the reincorporation

of part of the necessary nutrients for the crop (N, P, K and amorphous silica) (Datnoff et al., 1997). However, open burning after grain harvest results in emissions to air that have a deleterious effect on air quality and human health (Suramaythangkoor and Gheewala, 2010); these emissions show high concentrations of pollutants in form of particles (PM_{2.5} and PM₁₀), CO_x, hydrocarbons, NO_x, SO₂, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorated compounds, dioxins and furans, with the corresponding affectation to the environment and to human health (Abril et al., 2009; EEA, 2007). There are other elimination options such as crushing and mixing it with the soil, or removing it for its use. Since the alternative of burying the straw generates between 2.5 and 4.5 times more methane than burning it, this practice is not recommendable either (Fitzgerald et al., 2000); moreover, the abandoned rice straws in the field sometimes may flow into the drainage during the rainy season, causing an obstruction of the drainage, or providing the place for the propagation of the bacteria (Chou et al., 2009).

Rice straw as agricultural waste biomass could be a source of alternative energy that therefore substitutes fossil energy for reducing greenhouse gas emissions as well as avoids the local pollution problems from open burning (Suramaythangkoor and Gheewala, 2008). Because of the high price of crude oil, attention has been focused on rice straw as a potential renewable energy source (Lee et al., 2005); however it has not yet been commercially used as a feedstock for heat and energy because of insufficient

* Corresponding author. Tel.: +34 958249458; fax: +34 958246138.

E-mail addresses: nsaid_2020@ugr.es (N. Said), taniabishara@gmail.com (T. Bishara), agmaraver@ugr.es (A. García-Maraver), zamorano@ugr.es (M. Zamorano).

incentives or benefit for farmers to collect rice straw instead of field burning (Kargbo et al., 2009). Generating electricity by burning straw directly not only saves energy, protects the environment, and reduces field-burning pollution, but also increases the income of farmers (Zhaosheng et al., 2008). Due to low bulk density, rice straw is difficult to handle, transport, store, and utilize in its original form. It should be processed by densification techniques such as pelletizing or briquetting. The densified rice straw can be easily handled and can reduce the costs of transportation, handling and storage, moreover, the densification process also provides potential storage for off-season utilization (Ewida et al., 2006; Gilbert et al., 2009; Kaliyan and Morey, 2009).

Rice straw can also be converted into energy via processes including direct and indirect techniques. The direct techniques include standalone burning and co-firing it with other fuels, and the indirect technique includes gasification, pyrolysis, anaerobic digestion, thermo-chemical conversion and liquid fuel production, where these products can then be burned (Ewida et al., 2006). Burning rice straw either with other fuel or stand-alone has the advantage of high energy conversion efficiency compared with indirect techniques. On the other hand, it suffers from some technical limitations and causes operating problems in thermal conversion systems. These problems include high ash content, sintering, fouling, slag formation, and corrosion problems. This has the drawback of retarding the rate of heat transfer as a result of low thermal conductivity and high reflectivity (Jenkins et al., 1996; Zygarlicke et al., 2000). Sinters and slags problems are mainly related to a high relative content of alkaline compounds in straw ashes, during combustion in the furnace, K compounds evaporate to form KCl and K₂SO₄. These compounds and other mixtures of ash compounds have low melting point temperatures; straw ash melting point is 1000 °C or even less (Bryers, 1996; Picco, 2010). The high contents of salts, alkali oxides attributed to the use of fertilizers in agricultural farms, and low melting points can lead to various problems during combustion process (Bapat et al., 1997; Grubor et al., 1995).

For using rice straw to generate energy efficiently and obtain products with high added value, it is necessary to develop an industry of collection, transport and storage as well as solve the difficulties caused by the high content of silica (Abril et al., 2009) and other components. Using additives for rice straw such as kaolin or blending rice straw with other fuels such as coal may be suggested solutions to enhance combustion efficiency of boilers and to control fouling and slag formation (Picco, 2010). However, practical experiences with co-combustion of rice straw show a certain increase of slagging tendency in high temperature part of the boiler, comparing with coal combustion (Pronobis, 2005), meanwhile, co-combustion of rice straw with wood based fuel may be beneficial and may reduce fouling (Thy et al., 2004). Leaching rice straw with water is a possible way of reducing the content of the undesirable compounds which cause fouling and slag formation (Bakker et al., 2002; Jenkins et al., 1996).

The main objective of this research was to study the thermal behavior at different temperatures of washed and unwashed rice straw from different regions in Spain (Andalusia, Murcia and Valencia) and Egypt (El Sharkia province). The combustion behavior of the straw was studied using thermal analysis (TGA and DSC) as a complimentary method provides useful and valuable information about the nature and composition of the organic wastes, moreover, it is widely used to study the mechanisms of the thermal decomposition and combustion of biomass (Fernández et al., 2012; Zhaosheng et al., 2008). Furthermore, ash melting points, ash content, and ash sintering were investigated at different temperatures within the range between 550 and 1000 °C.

2. Material and methods

2.1. Sampling

The rice straw samples were collected from different provinces in Spain (Andalusia, Murcia, and Valencia), and Egypt (El Sharkia province). According to Deng et al. (2013), water washing appears to be a more controllable manner than natural rain washing and washing with tap water and distilled water makes no difference to element removal, washing the straw samples with tap water is used in this study as a simple and an effective method to remove a large part of troublesome elements from biomass fuels.

The straw samples were cut to 10 cm then washed with flushed tap water and dried at 105 °C to a constant weight. Elemental analysis for the dried washed and unwashed straw samples was performed according to UNE-EN 15104: 2011. Before the application of the experimental methods, the particle size for the unwashed and the dried washed samples was reduced to less than 0.5 mm to ensure the heat transfer rate within the kinetic regime of decomposition (Rath et al., 2002). Moreover, the initial mass of the sample was between 2–5 mg for the ash and between 6–8 mg for the rice straw to avoid any possible effect on mass and heat transfer during the process of biomass decomposition (Blasi et al., 2001; Calvo et al., 2004).

2.2. Analytical procedures

2.2.1. TGA and DSC

The TGA and DSC of the samples were performed using a SHIMADZU TGA-50H thermo analyzer in an oxidative atmosphere. The samples are heated from 30 to 1000 °C at heating rate of 5 °C/min for the ash and 10 °C/min for the rice straw, to maintain an oxidative atmosphere for thermal decomposition of the particles and this heating rate is generally considered capable of ensuring that there is no temperature gap between the sample and its surroundings, moreover, the low heating rate makes the chemical kinetic properties of the biomass sample clearer (Bilbao et al., 1997; Deng et al., 2013; Liu et al., 2002). According to Calvo et al. (2004) and Saddawi et al. (2012), an air atmosphere was passed continuously at a flow rate of 100 mL/min for the rice straw and 50 mL/min for the ash; moreover, higher flow rate was applied and did not give uniform and expressed relation for the thermograms. The oxygen in the air atmosphere enhances the decomposition of the material at low temperatures, and when the temperature becomes sufficiently high, oxygen is likely to cause the combustion of the char residue generated in the early stages of solid decomposition (Liu et al., 2002). The analysis for each sample was repeated to ensure that it follows the same trace for the same conditions.

2.2.2. Ash and volatile matter (VM) content

Ash contents of unwashed (U) and washed (W) rice straw samples were determined by igniting grinded straw samples in muffle furnace at 550 °C according to UNE-EN 14775:2010 and VM was determined at 900 °C according to UNE-EN 15148:2010. Three measurement series per sample were obtained and the average value was calculated.

Elemental composition of the ash obtained at 550 °C for the washed and unwashed straw samples was analyzed through X-ray Fluorescence according to UNE-EN 15290:2011.

2.2.3. Heating value

Higher heating value (HHV) at constant volume was determined by adiabatic bomb calorimeter according to UNE-EN

14918:2011. Three measurement series per sample were obtained and the average value was calculated.

2.2.4. Melting point, sintering and slagging tendencies

Melting points were detected from DSC thermograms of the different rice straw ash samples. The sintering of the unwashed and washed rice straw samples was detected by combusting the samples in a muffle furnace and observing the appearance at different temperatures (550–1000 °C) (Bakker et al., 2002; Jenkins et al., 1996). The prediction of slagging or fouling tendencies of the washed and unwashed straw samples has been determined using the alkali index that expresses the quantity of alkali oxide in the biomass per unit of fuel energy. It has been computed according to Eq. (1) where I is the alkali index, expressed as kg alkali/GJ or lb alkali MMBtu⁻¹, Q is the heating value (GJ/kg), Y_f is the mass fraction (dimensionless) of ash, Y_{K_2O} and Y_{N_2O} are the mass fractions (dimensionless) of K₂O and Na₂O in the ash (Jenkins et al., 1998; Skrifvars et al., 2005). Miles et al. (1995) suggested that above 0.17 kg alkali/GJ (0.4 lb alkali MMBtu⁻¹) fouling is probable, and above 0.34 kg/GJ (0.8 lb MMBtu⁻¹), fouling is virtually certain to occur.

$$I = (1/Q)Y_f(Y_{K_2O} + Y_{N_2O}) \quad (1)$$

3. Results and discussion

3.1. Straw composition and ash content

The harvesting time, soil, cultivation and storage conditions of the rice straw, such as its exposure to rain washing and soil contamination, are factors that may affect its properties (Bakker et al., 2002; Jenkins et al., 1996; Pronobis, 2005).

The composition of different straw samples is shown in Table 1. Carbon contents in the different samples ranged between 39.01% and 41.24%, hydrogen content were between 6.49% and 6.99% and nitrogen content in the range of 0.4% and 1.23%. Soil contamination may be high and may result in an increase in the percentage of some elements for the unwashed straw and due to washing this percentage decreases but also may increase for other main constituent components of the straw such as C and H, where the removing of the other surface elements by water washing result in an increase of their contents as a percentage of the whole straw. After washing the straw, almost all the washed straw samples showed an increase in carbon, hydrogen and VM content with ratio reached to 16.45%, 8.47% and 3.42%, respectively, in Valencia straw. A decrease in nitrogen content for most of the samples has been detected and reached to 59.38% in Egypt straw, see Table 2. Similar results were found with other authors (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Lee et al., 2005; Saddawi et al., 2012).

Ash contents of the washed and unwashed straw samples are indicated in Table 1. Valencia straw recorded the highest ash

Table 2

The variation in the parameters due to straw washing.

Parameter	Egypt	Murcia	Valencia	Andalusia
Ash content	-17.06	-10.66	-15.80	-19.77
HHV	+5.29	+1.84	+7.82	+7.89
VM	+1.81	+0.42	+3.42	+0.97
C	+3.59	-	+16.45	+3.83
H	+2.58	-1.62	+8.47	+2.72
N	-59.38	-10.00	-32.52	+23.81
Alkali index	-43.46	-55.43	-60.77	-63.24

–: No variation has been detected.

The negative values indicate reduction percentage in the parameter value due to washing.

The positive values indicate increasing percentage in the parameter value due to washing.

content followed by Egypt, Murcia and Andalusia straw. Reduction in ash contents has been observed for all the samples by washing the straw, however the reduction percentage in ash content due to washing depended on the type of sample; it reached from 10.66% in the case of sample from Murcia straw to about 19.77% in Andalusia straw, see Table 2. Ash content reduction was due to that washing the straw extracts large amounts of alkali metals, chlorine, in addition to variable amounts of sulfur, phosphorus and other elements caused by contamination of the straw with soil (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Kargbo et al., 2009; Skrifvars et al., 2005), see Table 3. This table shows that the washing was very efficient in chlorine removal and was significant in the other elements; the chlorine, magnesium and phosphorous removal ratios reached to about 87%, 39% and 35%, respectively in Valencia straw. About 60% sodium and sulfur removal were recorded in Andalusia and Egypt straw, respectively. Potassium removal ratio reached about 50% in Murcia, Valencia and Andalusia straw, where the potassium can be dissolved very well in water (Lee et al., 2005).

3.2. TGA and DSC for the straw samples

TGA and DSC thermograms in an air atmosphere for the different unwashed straw samples have been detected to determine the thermal nature as shown in Fig. 1. These thermograms showed slight difference for the different straw samples. TGA curve indicated the mass loss of the sample. It initially decreases below 100 °C because of drying and loss of the moisture that the samples contained owing to the hygroscopic nature of rice straw and there may be also loss of very light volatiles (Calvo et al., 2004; Singh, 1996). After 200 °C, straw devolatilization begins and high loss in the weight occurs due to decomposition and the emission of volatiles from cellulose and hemicelluloses, also small amounts of volatiles from the lignin component may also given off (Calvo et al., 2004; Koufopoulos and Maschio, 1989; Sun et al., 2002). After 300 °C, the weight loss is corresponding to lignin decomposition

Table 1

Analysis data of unwashed straw samples.

Parameter	Egypt			Murcia			Valencia			Andalusia		
	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
Ash content (%)	16.81	16.46	17.04	15.52	15.48	15.60	18.66	18.46	18.90	13.25	13.19	13.32
HHV (MJ/kg)	14.17	13.81	14.43	14.67	14.36	14.94	14.06	13.82	14.22	14.96	14.93	14.98
VM (%)	85.19	84.94	85.58	86.19	86.08	86.27	81.93	81.76	82.12	89.04	88.92	89.15
C ^a (%)	39.01			40.64			37.74			41.24		
H ^a (%)	6.59			6.80			6.49			6.99		
N ^a (%)	0.64			0.40			1.23			0.63		
Alkali index ^a (kg alkali/GJ)	1.91			1.75			2.09			1.85		

^a The variations of this parameter were imperceptible (about 0.01% in some of the samples tested), so the maximum and minimum values would fit in with the average value.

Table 3
Percentage of inorganic elements in ash and removal ratio due to washing.

Parameter ^a	Egypt		Murcia		Valencia		Andalusia	
	(%) Ash	% Removal	(%) Ash	% Removal	(%) Ash	% Removal	(%) Ash	% Removal
Na	2.30	35.65	0.73	40.08	1.61	52.86	2.02	59.95
K	10.80	26.14	12.92	49.48	11.25	49.38	15.06	49.09
Mg	1.35	21.98	1.36	–	2.93	38.80	2.03	17.97
P	0.30	7.80	0.42	–	0.78	34.83	0.45	–
S	0.50	59.44	0.69	30.26	1.43	55.24	0.82	25.46
Cl	5.40	59.04	4.18	80.82	4.70	86.96	7.54	82.90

–: No removal has been detected.

^a The variations of these parameters were imperceptible (about 0.01% in some of the samples tested), so the maximum and minimum values would fit in with the average value.

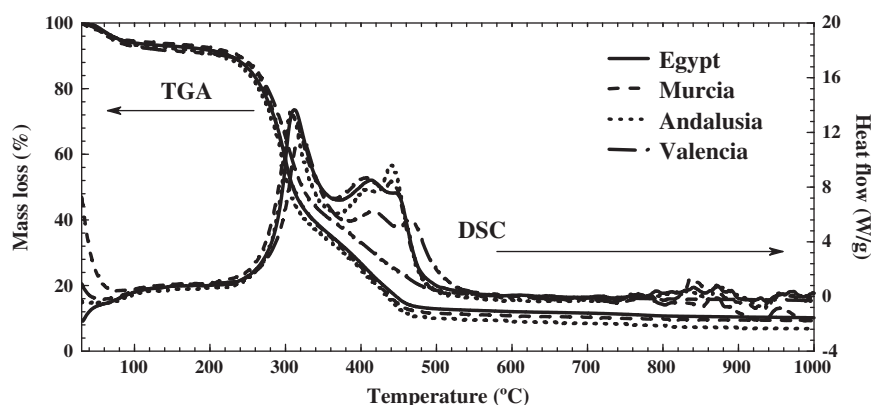


Fig. 1. TGA and DSC thermograms of the different straw samples.

and the decomposition rate becomes very low after 460 °C and becomes negligible at around 600 °C, similar results found by Jung et al. (2008). The maximum mass loss has been occurred in the range between 200 and 500 °C for the different straw samples. DSC thermograms show that the overall thermal degradation of rice straw is an exothermic process and the large exothermic peaks were observed at around 300 °C, which is attributed to the decomposition of hemicelluloses and cellulose (Chakraverty et al., 1987; Sun et al., 2002). Andalusia straw recorded the highest mass loss rate and lowest char residue in TGA profile and the highest exothermic peak in DSC profile compared to the others. It may be related to its lowest ash content and highest volatiles among the different straw samples (Table 1). In the other hand, Valencia straw recorded the lowest mass loss rate, highest char residue and the lowest exothermic peak, meanwhile, the TGA and DSC curves for Egypt and Murcia straw are nearly close.

As one example of the different rice straws, Fig. 2 shows TGA and DSC thermograms of washed and unwashed Andalusian rice straw. TGA profiles showed lower degradation residues, namely char, in the washed straw compared to the unwashed straw. This may be due to the lower metals content in the washed straw that acts as a catalyst in the formation of char (Raveendran et al., 1995). In contrast, the DSC profile for the washed straw recorded higher exothermic peak than the unwashed straw. This may be due to increase volatiles content in the washed straw (Table 2) compared to the unwashed straw (Lee et al., 2005).

3.3. Heating value

The HHV of the unwashed straw reached values between 14.06 and 14.96 MJ/kg (Table 1), similar to other studies (Bakker et al., 2002; Calvo et al., 2004; Deng et al., 2013; Jenkins et al., 1998; Jung et al., 2008; Skrifvars et al., 2005), and differences between the samples has not been detected.

After washing, the heating value increases with a percentage varied from 1.84% in the case of the sample from Murcia to 7.89% in Andalusia straw. The increase in HHV may be correlated to the decrease in the ash content of the washed straws (Jenkins et al., 1996). Table 2 shows that the highest reduction in ash content with the highest increase in HHV were occurred in Andalusia straw, whenever, Murcia straw recorded the lowest ash reduction and lowest increase in HHV due to washing. Moreover, the compositional changes after washing such as the increase of carbon values of the washed straw, as shown in Table 2, lead to modest increases in heating value (Bakker et al., 2002).

3.4. Melting point, sintering and slagging tendencies

3.4.1. Ash melting point

Since the fuel ash consists of a mixture of different inorganic compounds, the ash has no well defined melting point and the melting process takes place over a wide temperature range starting with the initial deformation temperature (where sintering begins), continuing with the hemisphere temperature and ending with the flow temperature (Picco, 2010; Saddawi et al., 2012). The DSC curves for the different unwashed rice straw ashes were detected in order to ascertain the melting point. Fig. 3 shows the DSC curves for the different rice straw ash samples. It was possible to represent the melting points as maximum of the endothermic peaks of the DSC traces (Buzarovska et al., 2008). The maximum endothermic peaks for the different samples were in the range between 700 and 800 °C.

3.4.2. Sintering and slagging tendencies

The appearance of unwashed and washed straw samples was observed by combustion at different temperature (550–1000 °C). The unwashed straw samples showed light ash sintering at temperature 700–800 °C, Fig. 4b, whereas severely sintering and

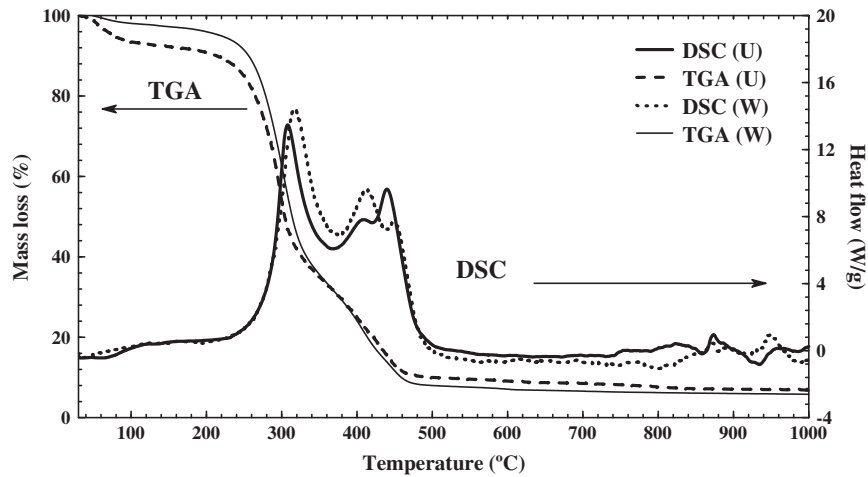


Fig. 2. TGA and DSC thermograms of washed and unwashed Andalusia straw.

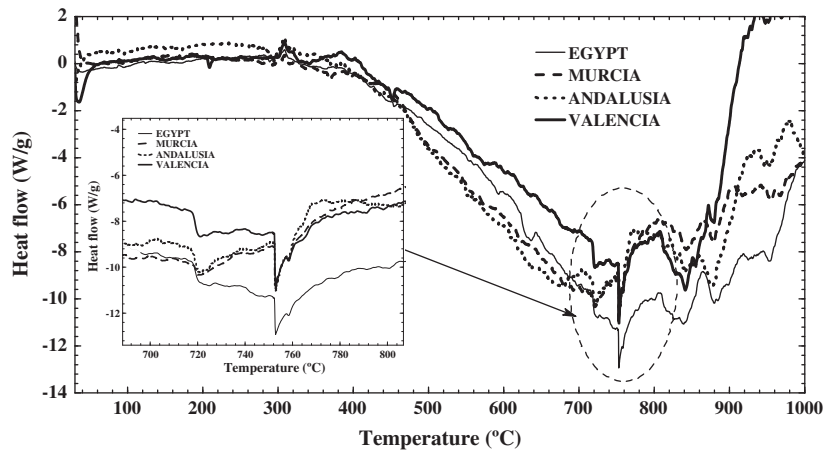


Fig. 3. DSC thermograms for the different straw ash samples.

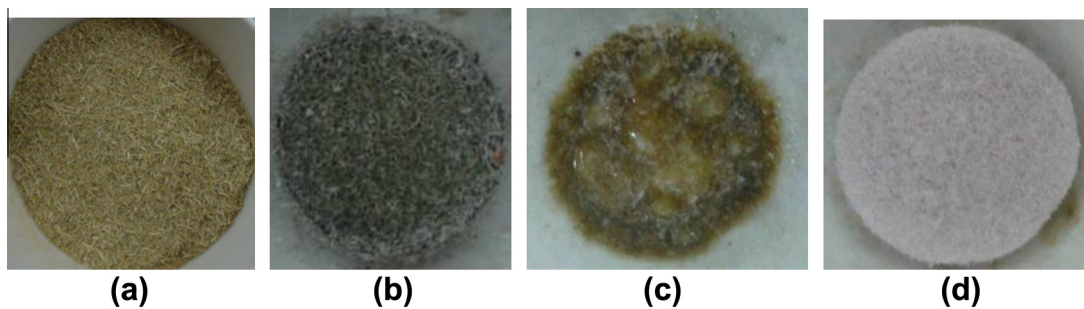


Fig. 4. Rice straw: (a) before combustion; (b) unwashed straw at (700–800 °C); (c) unwashed straw at (900–1000 °C); (d) washed straw at (900–1000 °C).

crystallized appearance was observed at 900–1000 °C, as shown in Fig. 4c. After washing, the washed straw samples were combusted at the same temperature range and the ash sintering of the unwashed samples was not observed in the washed samples, see Fig. 4d. Bakker et al. (2002) studied the evaluation of the ash from the muffle furnace experiments and revealed that the ash from rice straw severely sintered at 900 °C, while leached straw exhibited only light sintering at 1000 °C. Jenkins et al. (1996) found that the ash, which sintered at temperatures of 900–1000 °C for rice straw, was not observed in well washed samples though some sintering occurred at temperatures higher than 1100 °C.

Table 1 lists the alkali index values for the unwashed rice straw which are computed according to Eq. (1). Although all alkali index values exceed the probable value of 0.17 kg alkali/GJ as well as the critical value of 0.34 kg/GJ, which indicates that the samples will slag or foul, an improvement in alkali index values was observed for the washed samples, especially for Andalusian straw, for which the ratio improved by approximately 63.24%, see Table 2.

Sinters and slags of rice straw ash are related to the presence of potassium, chlorine, and silicon in the straw and mainly related to the high relative content of alkaline compounds in straw ashes (Baxter et al., 1998; Peng et al., 2009; Picco, 2010; Werther et al.,

2000). Washing rice straw with water is reducing the content of these undesirable compounds because it extracts large amounts of chlorine and alkali metals, especially potassium, which can be dissolved very well in water. Therefore, it leads to significant changes in inorganic composition and substantially improves combustion behavior (Bakker et al., 2002; Jenkins et al., 1996; Lee et al., 2005).

4. Conclusions

Rice straw could be used as a renewable fuel for heat and power generation, replacing fossil fuels and preventing pollution from rice straw open burning. Thermal conversion of rice straw to energy is attractive option but it causes operating problems that affect thermal conversion systems such as sinter and slag formation due to the presence of potassium, chlorine and silicon in the straw. Washing rice straw with water is a feasible option to reduce the content of troublesome compounds.

Significant improvement in the thermal behavior and reduction in the ash contents, chlorine, alkali metals, and sintering formation were observed in the washed straw in comparison to the unwashed straw. After washing, chlorine and potassium removal ratio reached to about 87% and 50%, respectively. Reduction in ash content and increasing in HHV reached to about 19.77% and 7.89%, respectively. Ash melting point for the different straw samples was in the range between 700 and 800 °C. Light ash sintering was observed for the unwashed straw samples at 700–800 °C and strongly sintering at 900–1000 °C. Ash sintering of the washed samples was not observed for the washed samples at the same temperature range. Moreover, improvement in the alkali index value was observed for the washed samples, the ratio improved by approximately 63.2.

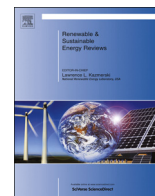
Acknowledgements

This research was funded by the Innovation and Science Division of the Andalusian Regional Government (Research Projects P08-RNM-03584 and TIC-02913), the Spanish Ministry of Science and Innovation (Research Project CTM2009-07199) and the Spanish Agency for International Development Cooperation (AECID) of the Ministry of Foreign Affairs and Cooperation (Project AP/045946/11).

References

- Abou-Sekkina, M.M., Issa, R.M., Bastawisy, A.E.M., El-Helece, W.A., 2010. Characterization and evaluation of the thermodynamic parameters for Egyptian heap fired Rice Straw Ash (RSA). *Int. J. Chem.* 2, 1.
- Abril, D., Navarro, E., Abril, A., 2009. Rice straw. Consequences of its management and use alternatives. *Agron* 17, 69–79.
- Bakker, R.R., Jenkins, B.M., Williams, R.B., 2002. Fluidized bed combustion of leached rice straw. *Energy Fuel* 16, 356–365.
- Balat, M., Balat, H., Oz, C., 2008. Progress in bioethanol processing. *Prog. Energy Combust.* 34, 551–573.
- Bapat, D.W., Kulkarni, S.V., Bhandarkar, V.P., 1997. Design and operating experience on fluidized bed boiler burning biomass fuels with high alkali ash. In: Preto, F.D.S. (Ed.), *Proceedings of the 14th International Conference on Fluidized Bed Combustion*, ASME, Vancouver, New York, NY, pp. 165–174.
- Baxter, L.L., Miles, T.R., Miles Jr, T.R., Jenkins, B.M., Milne, T., Dayton, D., Bryers, R.W., Oden, L.L., 1998. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Process. Technol.* 54, 47–78.
- Bilbao, R., Mastral, J.F., Aldea, M.E., Ceamons, J., 1997. Kinetic study for the thermal decomposition of cellulose and pine sawdust in an air atmosphere. *J. Anal. Appl. Pyrol.* 39, 53–64.
- Blasi, C.D., Branca, C., Santoro, A., Hernandez, E.G., 2001. Pyrolytic behavior and products of some wood varieties. *Combust. Flame* 124, 165–177.
- Bryers, R.W., 1996. Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Prog. Energy Combust.* 22, 20–120.
- Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., Gentile, G., Errico, M., 2008. Potential use of rice straw as filler in eco-composite materials. *Aust. J. Crop Sci.* 2, 37–42.
- Calvo, L.F., Otero, M., Jenkins, B.M., Morán, A., García, A.I., 2004. Heating process characteristics and kinetics of rice straw in different atmospheres. *Fuel Process. Technol.* 85, 279–291.
- Chakraverty, A., Banerjee, H.D., Pandey, S.K., 1987. Studies on thermal decomposition of rice straw. *Thermochim. Acta* 120, 241–255.
- Chou, C., Lin, S., Peng, C., Lu, W., 2009. The optimum conditions for preparing solid fuel briquette of rice straw by a piston-mold process using the Taguchi method. *Fuel Process. Technol.* 90, 1041–1046.
- Datnoff, L.E., Deren, C.W., Snyder, G.H., 1997. Silicon fertilization for disease management in Florida. *Crop Prot.* 16, 525–531.
- Deng, L., Zhang, T., Che, D., 2013. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. *Fuel Process. Technol.* 106, 712–720.
- European Environment Agency (EEA), 2007. Greenhouse gas emission trends and projections in Europe. Tracking Progress towards Kyoto Targets, EEA Report No. 5/2007, EEA, Copenhagen.
- Ewida, K.T., El-Salmawy, H., Atta, N.N., Mahmoud, M.M., 2006. A sustainable approach to the recycling of rice straw through pelletization and controlled burning. *Clean Technol. Environ. Policy* 8, 188–197.
- Fernández, J.M., Plaza, C., Polo, S.B., Plante, A.F., 2012. Use of thermal analysis techniques (TG–DSC) for the characterization of diverse organic municipal waste streams to predict biological stability prior to land application. *Waste Manage. (Oxford)* 32, 158–164.
- Fitzgerald, G.J., Scow, K.M., Hill, J.E., 2000. Fallow season straw and water management effects on methane emissions in California rice. *Global Biogeochem. Cy.* 14, 767–776.
- Gilbert, P., Ryu, C., Sharifi, V., Swithenbank, J., 2009. Effect of process parameters on pelletisation of herbaceous crops. *Fuel* 88, 1491–1497.
- Grubor, B.D., Oka, S.N., Ilic, M.S., Dakic, D.V., Arsic, B.T., 1995. Biomass FBC combustion-bed agglomeration problems. In: Heinschel, K.J. (Ed.), *Proceedings of the 13th International Conference on Fluidized Bed Combustion*, ASME, Orlando, FL, New York, NY, pp. 515–522.
- Jenkins, B.M., Bakker, R.R., Wei, J.B., 1996. On the properties of washed straw. *Biomass Bioenerg.* 10, 177–200.
- Jenkins, B.M., Baxter, L.L., Miles Jr, T.R., Miles, T.R., 1998. Combustion properties of biomass. *Fuel Process. Technol.* 54, 17–46.
- Jung, S., Kang, B., Kim, J., 2008. Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *J. Anal. Appl. Pyrol.* 82, 240–247.
- Kadam, K.L., Forrestb, L.H., Jacobson, W.A., 2000. Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. *Biomass Bioenerg.* 18, 369–389.
- Kaliyan, N., Morey, R.V., 2009. Factors affecting strength and durability of densified biomass products. *Biomass Bioenerg.* 33, 337–359.
- Kargbo, F.R., Xing, J., Zhang, Y., 2009. Pretreatment for energy use of rice straw: a review. *Afr. J. Agr. Res.* 4, 1560–1565.
- Koufopoulos, C.A., Maschio, G.A., 1989. Luchesi, kinetic modelling of the pyrolysis of biomass and biomass components. *Can. J. Chem. Eng.* 67, 75–84.
- Lee, K., Kang, B., Park, Y., Kim, J., 2005. Influence of reaction temperature, pretreatment, and a char removal system on the production of bio oil from rice straw by fast pyrolysis, using a fluidized bed. *Energy Fuel* 19, 2179–2184.
- Liu, N.A., Fan, W., Dobashi, R., Huang, L., 2002. Kinetic modeling of thermal decomposition of natural cellulosic materials in air atmosphere. *J. Anal. Appl. Pyrol.* 63, 303–325.
- Miles, T.R., Miles, T.R., Jr., Baxter, L., Bryers, R., Jenkins, B., Oden, L., 1995. Alkali deposits, A Summary Report for National Renewable Energy Laboratory, NREL Subcontract No. TZ-2-11226-1, p. 73.
- Peng, F., Song, H., Jun, X., Lushi, S., Tao, Y., Anchao, Z., Junying, Z., 2009. Mechanism study of rice straw pyrolysis by fourier transform infrared technique. *Chin. J. Chem. Eng.* 17, 522–529.
- Picco, D., 2010. Thermal efficiency report, TENBIORE PROJECT (Ref. No. 1206.011A-09).
- Pronobis, M., 2005. Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass Bioenerg.* 28, 375–383.
- Raveendran, K., Ganesh, A., Khilar, K.C., 1995. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* 74, 1812–1822.
- Rath, J., Steiner, G., Wolfinger, M.G., Staudinger, G., 2002. Tar cracking from fast pyrolysis of large beech wood particles. *J. Anal. Appl. Pyrol.* 62, 83–92.
- Saddawi, A., Jones, J.M., Williams, A., Coeur, C.L., 2012. Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel, characteristics and quality. *Energy Fuel* 26, 6466–6474.
- Said, N., El-Shatoury, S.A., Diaz, L.F., Zamorano, M., 2013. Quantitative appraisal of biomass resources and their energy potential in Egypt. *Renew. Sust. Energy Rev.* 24, 84–91.
- Sarkar, N., Ghosh, S.K., Bannerjee, S., Aikat, K., 2012. Bioethanol production from agricultural wastes: an overview. *Renew. Energy* 37, 19–27.
- Singh, A., 1996. A Study of Reaction Kinetics for Thermochemical Conversion of Rice Straw. University of California, Davis.
- Skrifvars, B.J., Yrjas, P., Kinni, J., Siefen, P., Hupa, M., 2005. The fouling behavior of rice husk ash in fluidized-bed combustion. 1. Fuel characteristics. *Energy Fuel* 19, 1503–1511.
- Sun, X.F., Sun, R., Sun, J.X., 2002. Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup. *J. Agric. Food Chem.* 50, 6428–6433.

- Suramaythangkoor, T., Gheewala, S.H., 2008. Potential of practical implementation of rice straw-based power generation in Thailand. *Energy Policy* 36, 3183–3187.
- Suramaythangkoor, T., Gheewala, S.H., 2010. Potential alternatives of heat and power technology application using rice straw in Thailand. *Appl. Energy* 87, 128–133.
- Thy, P., Jenkins, B.M., Williams, R.B., Leshner, C.E., 2004. Slag formation and potassium volatilization from rice straw blended wood fuel. *Prepr. Pap.-Am. Chem. Soc. Div. Fuel Chem.* 49 (1), 89–91.
- UNE-EN 14775:2010, Solide biofuels, Determination of ash content.
- UNE-EN 14918:2011, Solide biofuels, Determination of calorific value.
- UNE-EN 15290:2011, Solide biofuels, Determination of major elements.
- UNE-EN 15104:2011, Solide biofuels, Determination of total content of carbon, hydrogen and nitrogen, Instrumental methods.
- UNE-EN 15148:2010, Solide biofuels, Determination of the content of volatile matter.
- Werther, J., Saenger, M., Hartge, E.U., Ogada, T., Siagi, Z., 2000. Combustion of agricultural residues. *Prog. Energy. Combust.* 26, 1–27.
- Zhaosheng, Y., Xiaoqian, M., Ao, L., 2008. Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis. *Biomass bioenerg.* 32, 1046–1055.
- Zygarlicke, J.C., Kurt, E.E., McCollar, P.D., Musich, A.M., Toman, L.D., 2000. Impacts of co-firing biomass with fossil fuels. In: *Proceedings of the 25th International Technical Conference on Coal Utilization and Fuel Systems*, Clearwater.



Quantitative appraisal of biomass resources and their energy potential in Egypt

N. Said^{a,b,*}, S.A. El-Shatoury^c, L.F. Díaz^d, M. Zamorano^a

^a Civil Engineering Department, University of Granada, Campus de Fuentenueva, 18071 Granada, Spain

^b Environmental Engineering Department, Faculty of Engineering, Zagazig University, 44519 Zagazig, Egypt

^c Botany Department, Faculty of Science, Suez Canal University, 41522 Ismailia, Egypt

^d CalRecovery, Inc. 2454 Stanwell Drive, Concord, CA 94520, USA

ARTICLE INFO

Available online 11 April 2013

Keywords:

Biomass residues

Egypt

Potential energy generation

Renewable energy

ABSTRACT

The utilization of biomass as a renewable source of energy is important from the energetic as well as the environmental viewpoint. It can reduce the rate of fossil fuel depletion caused by the rapid increase in energy consumption. This paper presents an estimation of the biomass and its potential energy in Egypt. Four main types of biomass energy sources are included: agricultural residues (dedicated bioenergy crop residues), municipal solid wastes, animal wastes, and sewage sludge. The potential biomass quantity and its theoretical energy content were computed according to statistical reports, literature reviews, and personal investigations. The results show that Egypt produces a considerable amount of biomass with a total theoretical energy content of 416.9×10^{15} J. The dry biomass produced from bioenergy crop residue sources has been estimated at about 12.33 million tons/year, of which 63.75% is produced from rice straw. This source represents the highest percentage (44.6%) of the total theoretical potential energy in Egypt, followed by municipal solid wastes, which could produce 41.7% from an annual amount of 34.6 million tons. Meanwhile, the rest of the total theoretical potential energy could be produced from animal and sewage wastes. The estimated biomass with its considerable potential energy content represents an important renewable energy source in Egypt.

© 2013 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	85
2. Energy situation in Egypt	85
2.1. Geography, climate, and energy balance in Egypt	85
2.2. Electrical energy in Egypt	86
3. Biomass resources in Egypt	86
3.1. Agricultural residues	86
3.2. Animal wastes	87
3.3. Sewage waste	87
3.4. Municipal solid wastes	87
4. Theoretical energy potential from biomass in Egypt	88
4.1. Theoretical energy from agricultural crop residues	88
4.1.1. The potential energy content	88
4.1.2. Potential energy of some residues in different forms	88
4.2. Theoretical energy from animal waste	89
4.3. Theoretical energy from sewage sludge	89
4.4. Theoretical energy from municipal solid waste	89

* Corresponding author at: University of Granada, Civil Engineering Department, Campus de Fuentenueva, 18071 Granada, Spain. Tel.: +34 958249458; fax: +34 958246138.

E-mail addresses: nsaid_2020@ugr.es (N. Said), sahar_hassan@science.suez.edu, eg (S.A. El-Shatoury), Ludiaz@aol.com (L.F. Díaz), zamorano@ugr.es (M. Zamorano).

4.4.1. Theoretical energy from thermo-chemical conversion by incineration..... 89
 4.4.2. Theoretical energy from bio-chemical conversion through anaerobic digestion 89
 4.5. Theoretical potential energy from biomass 90
 5. Conclusions 90
 Acknowledgments..... 90
 References 90

1. Introduction

Widespread and massive consumption of fossil fuels has led to rapid economic growth in advanced industrial societies but has also increased carbon dioxide in the atmosphere and consequently caused global warming and climate change. Renewable energy sources should replace fossil fuels fundamentally and structurally; they are receiving worldwide attention and will play an important role in meeting the future needs of the world [1,2]. Renewable energy sources are natural resources such as sunlight, wind, biomass, and geothermal heat, which are naturally replenished. Based on factors such as the availability and choice of technologies in Egypt, Khalil et al. [3] positioned wind energy and solar water heating as leading renewable energy technologies in power generation, followed by biomass technology.

Biomass represents an important source of energy which includes a large variety of different fuels with different chemical compositions and combustion characteristics. Its utilization as a source of energy is important from an energetic as well as an environmental viewpoint [4,5]. Unlike coal, CO₂ emissions from biomass are negated by the photosynthetic contribution during the growth cycle of biomass, resulting in a net zero impact on the environment [6,7]. Moreover, biomass reduces the rate of fossil fuel depletion and has the theoretical potential to supply 100% of the world's energy needs [2,8].

Due to the vital role played by the energy sector, energy demand is increasing in direct proportion to the increase in population and industrial development to satisfy technological needs and the development of lifestyles in Egypt. Primary energy demand has grown at an average annual rate of 4.64% during the last years [9]. Securing energy supply on a continuous basis is a vital element for sustained development plans, and Egypt, as a country of limited fossil fuel resources as well as growing demand for electrical energy, has given due consideration to the diversification of its energy portfolio by utilization of its renewable energy resources [10].

In Africa, about half of the energy used originates from biomass or agricultural residues [11]. A study by Smeets et al. [12] projected that Africa has the largest potential for bioenergy production by 2050 in the world: 317 exajoules (EJ) per year, which could constitute a quarter of the projected total world potential (1272 EJ per year). In this sense, during the last decade, Egypt has been one of the developing countries following successful programs for the development of renewable energy resources [13]. It produces millions of tons of biomass waste every year, which could contribute more than 151 PJ (petajoules) of primary energy [14], but nowadays these wastes are causing pollution and health problems [2]; in consequence, the incorporation of biomass with other renewable energy sources will increase the potential for solving energy and environmental problems.

However, there have been insufficient investigations regarding the production of biomass in Egypt and an analysis of existing and potential biomass sources will be required well before the start-up of large-scale production of bioenergy from this renewable fuel. As a consequence, a quantitative appraisal of biomass resources and their energy potential in Egypt represents the main objective of this study.

2. Energy situation in Egypt

2.1. Geography, climate, and energy balance in Egypt

Egypt forms the northeast corner of Africa and covers a total area of almost one million Km² (Fig. 1) [15]. It has hot and dry weather in summer and a warm winter with average rainfall of 50 mm/year. The inhabited part of Egypt is the 1000 km valley from Aswan to Alexandria, flanked by desert [16]. According to the Central Agency for Public Mobilization and Statistics (CAPMS) [17], Egypt has an estimated population of about 83 million in 2013.

The energy sector plays a major role in Egypt's economic development. The primary energy resources and production in Egypt are shown in Fig. 2. It is clear that crude oil is the most important, representing 53.11% of the total resources. Electricity from the High Dam in Aswan accounts for a share of about 5% and natural gas accounts for 41.89% of the total resources. On the other hand, primary production of coal accounts for only 1.6 PJ, and Egypt has to import coal. The sectoral energy consumption in Egypt is summarized in Fig. 3. The industrial sector accounts for about 46% of consumption, representing the highest value of energy consumption among the sectors [18].

Production of crude oil continues to decline despite new discoveries and improvements in oil recovery techniques at mature fields. Its production had fallen from 740 thousand barrels per day (bbl/day) in 2004 to 680 thousand bbl/day in 2009. On the



Fig. 1. Map of Egypt [15].

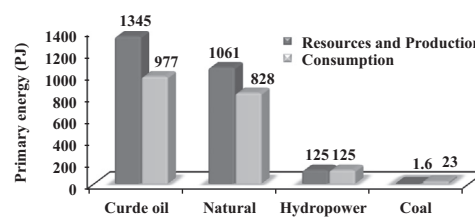


Fig. 2. Primary energy resources production and consumption in Egypt [18].

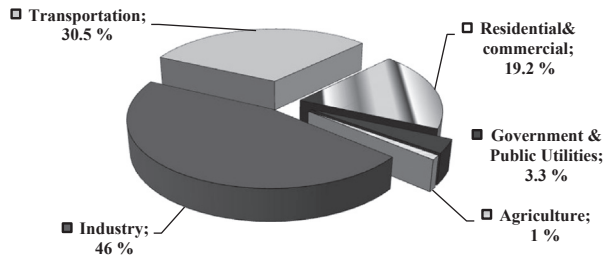


Fig. 3. Sectoral consumption of primary energy in Egypt [18].

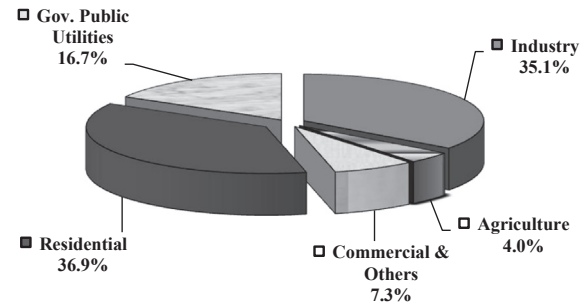


Fig. 5. Electrical energy consumption by sector in the year 2007 [22].

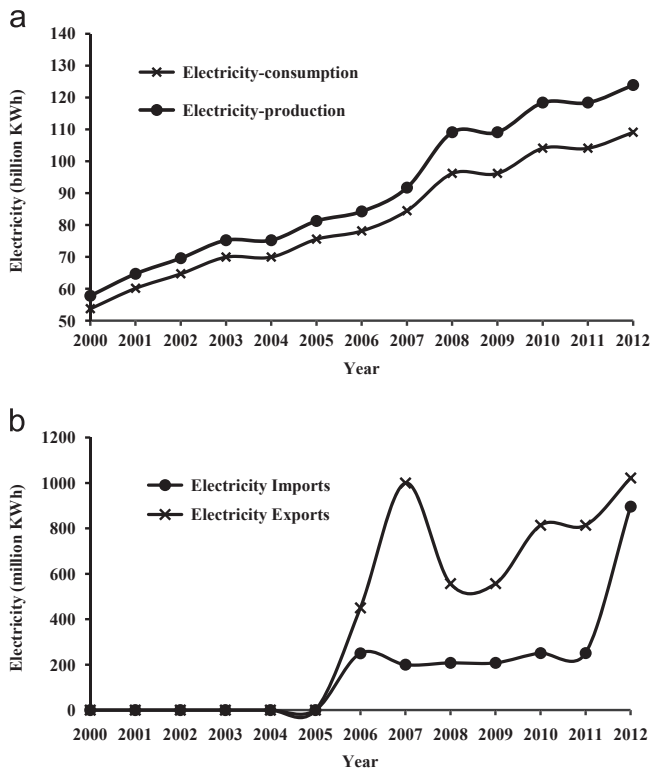


Fig. 4. Electrical energy production and consumption (a), and imports and exports by year (b) [19].

other hand, its consumption increased from 590 thousand to 683 thousand bbl/day over the same years, making the country a net importer of oil. In contrast, natural gas production continued to rise from 32.56 billion m^3 in 2004 to 62.69 billion m^3 in 2009 while its consumption increased from 31.46 to 44.37 billion m^3 over the same years, and the country became a major exporter, with its natural gas exports being estimated at 18.3 billion m^3 in 2009. The proven reserves of natural gas in 2011 were 2.2 trillion m^3 and there is growing concern among some experts that Egypt's gas reserves could be depleted as early as 2020, after which the country could face a deficit between consumption and production [19].

2.2. Electrical energy in Egypt

Electrical demand and consumption are growing rapidly in Egypt. As new industrial/residential cities and tourist complexes are built and the standard of living improves, demand for electricity is increasing at a faster rate than overall economic growth [20]. Fig. 4a shows electrical energy production and consumption from 2000 to 2012, while imports and exports of electrical energy are shown in Fig. 4b. The rapidly increasing rates

of electrical energy consumption and production, whose values doubled over the last decade, can be clearly observed. The large increase in demand across all sectors is leading to high electricity generation growth rates. It has been forecast that electricity consumption will reach 250 TWh by 2020 [21].

Fig. 5 presents the electrical energy consumption by sector for the year 2007 as a percentage of the total electrical energy consumption in Egypt [22]. The data in the figure show that the residential and industrial sectors account for the major parts of electrical energy consumption in Egypt: about 36.9% and 35.1% of electrical energy consumption, respectively. Together, the rest of the sectors account for only about 28% of total electrical energy consumption.

3. Biomass resources in Egypt

There is good potential for the utilization of biomass energy resources in Egypt. Biomass resources are currently used inefficiently, particularly agricultural residues, which are combusted in open fire stoves in villages [13]. However, real environmental benefits of biomass utilization can be achieved through large-scale application of biomass-based fuel to generate energy [23]. Consequently, Egypt has recently adopted an ambitious plan to produce 20% of its generated electricity using renewable energy resources by 2020 [10]. Biomass resources have been estimated in this study based on agricultural residues, animal wastes, sewage wastes, and solid wastes. The results are summarized in the subsections presented below.

3.1. Agricultural residues

Agricultural residues are the amount of crop that remains after the collection of the main product. Residues depend upon a wide range of local conditions and the primary factors influencing the amount of crop residue are the type and variety of crops planted and their yields [24]. The effective total cultivated area is around 6.09 million ha annually [25] and approximately 3.444 million ha of land are cultivated in Egypt, yielding crops two or three times a year. Therefore, Egypt produces millions of tons of agricultural wastes every year [2,26,27], contributing to about 50% of the total biomass potential [28].

Over 27 million tons of crop residues were generated in 2003 [29]. Types of crop residues and their estimated quantities and percentages in relation to the total residue generation are listed in Table 1. Wheat straw is the most abundant residue, followed by maize, rice straw, and sugar cane residues, respectively. Actual crop residue generation may vary by 10–15% or more in any given year. Table 1 lists the quantity and percentage of each crop residue utilized during the year 2004. At least 77.8% of the crop residues are reutilized for various purposes other than for energy generation, as shown in Table 2.

Nationally, unutilized crop residues are estimated to amount between 4.422 and 5.684 million tons. The largest amount of unused crop residue is rice straw, by a wide margin [29], followed by cotton stalks. Hamdy [30] mentioned that about 52% of agricultural residues are burnt directly on the fields or in inefficient burners (with less than 10% efficiency) in small villages. Both methods result in loss of energy as well as negative impacts on the environment. Moreover, traditional storage in farms and on roofs provides a large opportunity for insects and other disease carriers to grow and attack humans, animals, or new crops [5]. The burning of crop residues is, however, practiced by farmers, despite legal requirements [29].

3.2. Animal wastes

Animal wastes are another form of biomass used for energy generation. The amount of animal waste residue depends on the animal type, size, and population density for each location [24].

Large amounts of animal wastes are produced in Egypt. The total cattle herd (including domesticated buffalo) in 2009 was estimated at about 6.248 million head [31]. Table 3 shows that the total amount of cattle (buffalo and cow) manure is about 10.5 million tons/year [5,30], representing the majority of animal waste.

The uncontrolled handling and storage of manure causes loss of organic matter and also pollution problems. Hamdy [30] mentioned that about 60% of cattle waste is used as fuel by direct burning in low efficiency burners (less than 10%); another 20% of the animal waste is used as organic fertilizer, and the rest is lost in handling. From the overview given in Table 3, it can be concluded that cattle manure has the greatest potential to be used as a source of clean energy and organic fertilizer. It can also be concluded that sustainable treatment of such resources is of vital concern for Egypt [5].

Table 1
Estimated crop residue generation and utilization in Egypt during the year 2004 [29].

Types of residues	Residue generation (per year)		Total utilization (per year)	
	(1000 t)	Percentage (%)	(1000 t)	Percentage (%)
Wheat straw	8212	30	8130	99
Rice straw	4968	18.2	1900	38.2
Maize residue	6655	24.3	5657–6322	85–95
Sorghum stalks	1272	4.6	1208	95
Barley straw	212	0.8	196	92.5
Cotton stalks	1252	4.6	626	50
Sugar cane residue	4793	17.5	3830	80
Total	27,364	100	21,284–21,949	77.8–80.2

Table 2
Major uses of crop residues [29].

Crop residue	Use
Wheat straw	Animal feed
Rice straw	Composting, animal bedding, vegetable storage, animal feed following treatment with urea or ammonia, and manufacture of construction products
Maize residues	Animal feed and fuel
Sorghum stalks	Animal feed and fuel
Barley straw	Animal feed
Cotton stalks	Fuel
Sugar cane residues	Animal feed, building material, industrial fuel, and paper manufacture

Table 3
Total production of animal wastes in Egypt [5,30].

Animal	Total waste (1000 t/year)
Cows	5403
Buffaloes	5097
Horses, asses, mules, and camels	2348
Sheep and goats	729
Chickens, ducks, and turkeys	<1
Total	13,578

3.3. Sewage waste

The sludge waste from urban and industrial sewage treatment plants comprises residuals that have serious effects on the environment. Due to the increasing population density and the currently low capacity for wastewater treatment prevailing in Egypt, a future increase in the number and capacity of wastewater treatment plants (WWTPs) can be expected. As a consequence, the amount of sewage sludge produced is also expected to increase.

Based on population studies and rates of water consumption, the total wastewater flows generated by all governorates in Egypt, assuming full coverage by wastewater facilities, were estimated by Lasheen and Ammar [32] at about 3.5 billion m³/year. Approximately 1.6 billion m³/year is treated, and additional treatment plant capacity equivalent to 1.7 billion m³ is planned by the year 2017. Depending on the currently applied treatment technology, the amount of sewage sludge produced in Egypt was estimated at around 2 million tons/year of dry sludge in 2008 [33].

For many years, the methods and technologies implemented for sewage sludge treatment in Egypt were very limited. Recently, the application of anaerobic digestion technology for sludge stabilization and power generation was applied in Al Gabel Asfer WWTP. Windrow composting of dried sewage sludge is another type of sludge treatment that has been recently applied in Egypt, having been already applied in the Al Berka WWTP in Cairo and the (9N) site in Alexandria. These WWTPs are the largest centralized wastewater treatment plants in Egypt and produce more than 50% of the total dry sewage sludge produced in all of Egypt's WWTPs. The dried sludge from these plants is mainly reused in agriculture. About 0.66 million tons of the dried sewage sludge were sold to farmers in 2007, representing more than 85% of the total sewage sludge produced by all WWTPs in Egypt [33].

3.4. Municipal solid wastes

Municipal solid wastes, which comprise garbage, originate from residential, commercial, and institutional sources as well as construction, demolition, and municipal services [34]. In general, the more urbanized the area is, the higher the amount of waste generation per capita [35]. A positive correlation exists between increased welfare and generation of municipal waste [24].

Egypt generated an estimated 15.3 million tons of municipal solid waste in 2001, of which approximately 75% was generated in urban centers [36]. According to the Central Agency for Public Mobilization and Statistics, the estimated municipal solid waste generated in Egypt reached about 34.6 million tons in 2007.

The typical composition of municipal solid waste in Egyptian cities is shown in Table 4, where organic waste is the main component, representing 60% of the waste produced [16,25,35]. Eleven percent of the material is denoted as “other” and mainly includes construction and demolition debris and hazardous waste.

Between 30% and 50% of the municipal solid waste generated in developing countries is usually left unattended on the streets or vacant land plots [37,38]. In this sense the quantity of uncollected solid wastes in different governorates in Egypt reached a total of

25 million m³ by 2004 [39]. Landfilling and incineration have recently been introduced in Egypt as more environmentally sound solid waste treatment techniques [25]. Sanitary landfilling is usually the lowest-cost option, as long as the required landfill area is available. There are no landfill regulations or standards that provide a basis for compliance and monitoring; however national guidelines for these standards are being prepared by the EEA. The practice of sanitary landfilling is still in its infancy in Egypt [16].

4. Theoretical energy potential from biomass in Egypt

The information presented in the previous section has shown the high biomass production in Egypt, based on agricultural residues, animal waste, sewage waste, and solid waste. These could be used to produce bioenergy, reducing fossil fuel consumption and also improving the environment as a safe method of waste disposal. The theoretical energy potential from biomass in Egypt has been analyzed in this study. The results are summarized in the subsections below.

4.1. Theoretical energy from agricultural crop residues

To estimate the theoretical energy potential of crop residues, according to Klass [40], several parameters are necessary: theoretical annual crop production, annual theoretical residue production, availability, and dry weight. The collectible dry residue or dry biomass (D_b) is the theoretical biomass production in terms of weight. It is determined by Eq. (1) for a given crop. In this mathematical expression, A_{cp} is the theoretical annual crop production in tons, r is the residual factor that gives the total mass of residue when multiplied by the total country yield for that crop generated, a is the availability factor or availability of collectible crop residues as waste biomass, and w is the dry weight factor expressed as a percentage.

$$D_b = A_{cp} \times r \times a \times w \quad (1)$$

Table 5 shows agricultural crop production and dry biomass according to Eq. (1) based on agricultural crop production in Egypt for the year 2007 according to CAPMS [17]. The residue factor (r)

and availability factor (a) have been considered following Klass [40]. The highest theoretical dry biomass production corresponded to rice (7.86 million tons/year).

4.1.1. The potential energy content

The potential energy content of the collectible dry residue (P_e) has been calculated using Eq. (2) [40], where D_b is the amount of residue, O_c its organic content expressed as a percentage, and HHV the higher heating value of the organic material.

$$P_e = D_b \times O_c \times HHV \quad (2)$$

Table 5 also shows the potential energy from biomass according to Eq. (2); the organic content (%) and HHV (18.6 GJ/dry tons) have been determined according to Klass [40].

Although wheat straw represents the highest amount among the crop residues and has considerable biomass and energy content, it was excluded from the mathematical analysis because 99% of it is used as animal feed. Barley straw was also excluded from the analysis because it is generated in low quantities and is mainly used as animal feed (Tables 1 and 2). So in this study, wheat and barley straw have not been included as suitable candidates for crop energy production in Egypt.

The analysis indicates that a total of 12.33 million tons/year of dry biomass could produce a theoretical energy of 185.75 PJ/year. The biomass that could give the highest theoretical energy production is rice (113.99 PJ/year). The rest of the crops include biomass with considerably lower potential energy content.

4.1.2. Potential energy of some residues in different forms

Considering the important role of biomass for energy production and its increasing importance in the transport sector, studies on biomass utilization and the production of bioenergy and biofuels should be undertaken. In Egypt, transportation fuels represent around 30.5% of the total fuel energy consumption. The availability of high energy materials in Egypt suggests that biofuel (especially ethanol) is highly feasible if there is access to proper low-cost conversion and fermentation technologies [41]. The use of lignocellulosic biomass residues as feedstocks (i.e. starting material) allows a substantial increase in the fuel ethanol production capacity and a reduction in the cost of ethanol production to a competitive level [42]. Rice straw, maize residues and sugar cane residues are the most abundant lignocellulosic agriculture wastes produced in Egypt and the most suitable candidates for biofuel production [41].

Table 6 shows the theoretical ethanol yield and energy content from rice straw, maize residues, and sugar cane residues; the theoretical ethanol yield and the energy content of bioethanol (19.6 MJ/L) have been calculated according to Aly and Megeed [41]. The total theoretical energy content of ethanol from these residues is about 94.8 PJ/year. Rice straw represents the highest value among these residues, accounting for about 67.5% of the total energy content. So, it is considered the most important of such residues and can be used as a clean fuel to decrease the dependence on crude

Table 4
Typical composition of municipal solid wastes in Egyptian cities [16,35].

Waste composition	Percentage (%)
Organic waste	60
Paper	10
Plastic	12
Glass	3
Metals	2
Textiles	2
Other	11

Table 5

Theoretical agricultural crop production, dry biomass, and potential energy in Egypt, calculated according to estimated crop production in 2007.

Crop	Production (A_{cp}) (1000 t/year)	Residue factor (r)	Available factor (a)	Dry weight % (w)	Dry biomass (D_b) (million tons/year)	Organic content (O_c)%	Energy content (P_e) (PJ/year)
Sugar cane	16,656	0.52	1.00	20	1.73	84	27.06
Rice	6868	1.43	1.00	80	7.86	78	113.99
Maize	5572	1.10	0.60	53	1.95	90	32.63
Sorghum	827	1.57	0.64	40	0.33	84	5.19
Cotton	621	2.45	0.60	50	0.46	81	6.88
Total					12.33		185.75

oil in the transportation sector and to provide an environmentally safe technology for the straw disposal. Not only ethanol but also other different forms of bioenergy can be recovered by biochemical conversion of rice straw through different available techniques, such as biogas from anaerobic digestion, syngas through gasification, or bio-oil from pyrolysis [43–45].

The potential energy based on the estimated amount of rice straw biomass has been estimated in the forms of bio-oil, syngas, and biogas. The bio-oil yield (68% of straw weight) and its heating value (19 MJ/kg oil) have been taken from Jung et al. [43], while the syngas yield (1.84 m³/kg straw) and its heating value (6.01 MJ/m³ gas) have been found according to Lyang et al. [44]. The heating value for biogas (6.81 MJ/Kg straw) was estimated according to Summers [45]. The estimated values of potential energy from bio-oil, syngas, and biogas were 101.55, 86.92, and 53.53 PJ/y, respectively. So, pyrolysis is the best technique for recovering energy from rice straw, followed by gasification, biochemical conversion, and finally anaerobic digestion.

4.2. Theoretical energy from animal waste

Animal waste has been mainly used as fertilizer [46–48]; however the anaerobic digestion of manure is known to have the potential to produce energy [49]. This technology has the potential to solve waste-handling problems while producing renewable gas, electricity, heat, and also fertilizer [50].

Using Xuereb's conversion factor of 130 MJ/gal [51] moreover, Cooper and Laing [52] estimated that the energy (biogas) produced annually from a single head of cattle is equal to 50 gallons of gasoline, and taking into account the total cattle population in Egypt as indicated above (6.248 million head of cattle), the theoretical total potential is 40.61 PJ of energy, which equals approximately half the amount of bioethanol energy that would be produced from lignocellulosic residues in Egypt.

4.3. Theoretical energy from sewage sludge

With improved control and treatment of industrial wastewater, sewage sludge can be utilized as a valuable fertilizer and soil conditioner as well as for energy production by collecting methane from sludge digestion, which can generate electricity in a secondary step [32,53].

In this study, theoretical electrical generation from 1 kg of dry sewage sludge has been calculated as 0.78 kWh/kg of dry sludge, assuming that the quantity of digested gas obtained during the anaerobic digestion is 1 m³/kg of volatile solids destroyed and the lower heating value of the digested gas is approximately 6.22 kWh/m³ [33].

Considering the theoretical sewage sludge production explained in Section 3.3 (2 million tons of dry sludge), the estimated annual theoretical electrical energy generated from 0.78 kWh/kg of dry sludge is about 1560 GWh. The average calorific value used in the energy calculation for sewage sludge is 2000 Kcal/ kg dry matter [14]. The potential energy from sewage

sludge in Egypt can be estimated as about 16.74 PJ based on the indicated amount of sewage sludge and its average calorific value. Despite its minor energy content, it may contribute to an observed amount of the energy used to operate the WWTP that produces this sludge.

Energy production from sewage sludge is fairly well developed in Egypt. For example Al-Gabel Al-Asfer WWTP is the biggest wastewater treatment plant in Egypt, having a current sewage treatment capacity of 1.8 million m³/day, which will be increased to 3 million m³/day in 2020. The application of anaerobic digestion technology for sludge stabilization and power generation in Al-Gabel Al-Asfer WWTP has achieved good results and considerable experience of operation and maintenance has been gained. A large portion of the biogas produced is currently used for the operation of hot water boilers, which are used to heat the raw sewage sludge in the primary digesters. Dual fuel generators use the excess digested gas to generate electricity, representing about 37–68% of the power consumed by the WWTP. The digested sludge is dewatered, dried, and then reused in agriculture. Thus, there is an interest in using such technology on a large scale in Egypt, especially in big wastewater treatment plants in major cities [33].

4.4. Theoretical energy from municipal solid waste

Energy can be recovered from the organic fraction of waste through two methods: (i) thermo-chemical conversion by incineration and (ii) bio-chemical conversion by anaerobic digestion in which only the biodegradable fraction of the organic matter can contribute to the energy output.

4.4.1. Theoretical energy from thermo-chemical conversion by incineration

In thermo-chemical conversion all of the organic matter, biodegradable as well as non-biodegradable, contributes to the energy output. The power generation potential (P_{gp}) and the net power generation potential (NP_{gp}) from waste, both expressed in kilowatt hours, have been estimated using Eqs (3) and (4) [54], where W is the total quantity of waste (tons), NCV is the net calorific value (k-cal/kg), and CE is the conversion efficiency.

$$P_{gp} = \left(\frac{1000}{860} \right) \times W \times NCV \quad (3)$$

$$NP_{gp} = P_{gp} \times CE \quad (4)$$

In this study NCV has been considered as 1200 k-cal/kg when CE is 25% [54]. Taking into account the estimated amount of solid waste available in Egypt in 2007, the power generation potential becomes 48,279 GWh (173.8 PJ) and net power generation potential becomes 12069.8 GWh.

4.4.2. Theoretical energy from bio-chemical conversion through anaerobic digestion

In bio-chemical conversion, only the biodegradable fraction of the organic matter can contribute to the energy output. In this case P_{gp} and NP_{gp} from waste, both expressed in kilowatt hours, can be estimated by Eqs. (4) and (5) [54], where W is the total quantity of waste (tons), VS is the total organic/volatile solids (say 50%), OBF is the organic bio-degradable fraction (approx. 66% of VS), DE is the typical digestion efficiency (60%), BY is the biogas yield (0.80 m³/kg of VS destroyed), CV is the typical calorific value of bio-gas (5000 kcal/m³), and CE is the typical conversion efficiency (30%).

$$P_{gp} = \left(\frac{1000}{860} \right) W \times VS \times OBF \times DE \times BY \times CV \quad (5)$$

Table 6

Ethanol production and its energy content from lignocellulosic biomass in Egypt.

Lignocellulosic biomass waste	Dry biomass (million ton/year)	Ethanol yield (L/dry ton)	Ethanol production (million L/year)	Energy content (PJ/year)
Rice straw	7.86	416	3269.76	64.0
Sugar cane residues	1.73	424	733.52	14.4
Maize residues	1.95	428	834.60	16.4
Total	11.54		4837.88	94.8

For 34.6 million tons of solid waste, the power generation potential is equal to 31864.2 GWh (114.7 PJ) and net power generation potential is 9559.3 GWh.

From the previous results it can be noticed that the power generation potential value obtained from solid waste using thermo-chemical conversion is greater than that obtained using biochemical conversion. This is because all of the organic matter, biodegradable as well as non-biodegradable, contributes to the energy output in thermo-chemical conversion. Meanwhile, in bio-chemical conversion only the biodegradable fraction of the organic matter can contribute to the energy output.

4.5. Theoretical potential energy from biomass

Table 7 summarizes the maximum theoretical potential energy that could be obtained from biomass wastes in Egypt, considering biomass from agricultural crops, sewage sludge, municipal solids, and animal waste. It is possible to conclude that the total theoretical energy production from biomass is 416.9 PJ, representing 92.6% of the total production in all installed power plants in Egypt nowadays.

Because of the large amount of residual biomass from agricultural crops and its considerable energy content, it represents the major part of the total theoretical energy (44.6%), followed by municipal solid waste (41.7%); on the other hand, animal waste accounts for about 9.7% and sewage sludge for only 4.0% of the total amount. Due to the increase in crude oil consumption and decrease in its production over the years, the potential energy of agricultural crop residues and solid waste may contribute to decreasing the consumption of crude oil by approximately 19% and 17.8%, respectively, based on its consumption amount, which is indicated in Fig. 2.

Finally, rice straw represents the most important agricultural biomass residue due to its large amount and high energy potential, accounting for about 61.5% of the potential energy of crop residues, and its energy can be recovered in different forms such as bioethanol, bio-oil, biogas, and syngas.

Table 7
Theoretical potential energy from biomass residues in Egypt.

Biomass type	Theoretical potential energy (PJ)	Percentage of total energy (%)
Agricultural crop residues	185.75	44.6
Animal wastes (cows and buffalo)	40.61	9.7
Sewage waste (sewage sludge)	16.74	4.0
Municipal solid waste	173.80	41.7
Total	416.9	100

5. Conclusions

The main sources of biomass waste in Egypt are agricultural waste (crop residues), followed by municipal solid waste, animal waste, and sewage waste. The amount of dry biomass produced from agricultural crop residues is about 12.33 million tons/year, and 63.75% of this amount is produced from rice straw.

According to the quantity of biomass waste calculated in this study and its energy content, agricultural crop residues represent the highest value of theoretical potential energy from the main biomass sources in Egypt; this source could produce 44.6% of the total theoretical energy potential. Agricultural crop residues are followed by municipal solid waste, which could produce 41.7% of

the total theoretical energy potential from an annual amount of 34.6 million tons. Ethanol production from agricultural crop residues is a feasible option for second generation biofuel production in Egypt. Lignocellulosic agricultural wastes are cheap renewable resources and allow a substantial increase in fuel ethanol production capacity. Rice straw, maize residues and sugar cane residues are the most abundant lignocellulosic agricultural biomasses produced in Egypt, and represent the most suitable candidates for ethanol production. In this study, the total theoretical ethanol yield from these wastes is estimated at about 4837.88 million L/year, with an energy content of 94.8 PJ/year, of which 67.5% of the energy is represented by rice straw. As a consequence, crop residues, especially rice straw, would represent a good candidate as a renewable energy source in Egypt which could be used as a clean fuel and would decrease the dependence on fossil fuel; its energy can be recovered in other different forms such as bio-oil, biogas, and syngas.

Finally, buffalo and cow manure represent the major part of animal waste in Egypt. About 6.248 million head of buffalo and cows could produce 9.7% of the total theoretical energy. On the other hand, 2 million tons/year of dry sewage sludge accounts for only 4.0% of total theoretical energy production.

Acknowledgments

This research has been funded by the Innovation and Science Division of the Andalusian Regional Government (Research Project nos. P08-RNM-03584 and TIC-02913) and the Spanish Ministry of Science and Innovation (Research Project no. CTM2009-07199).

References

- [1] Vojdani F. Biomass and waste characterization as a potential energy sources in Iran. In: Proceedings of the third international symposium on energy from biomass and waste. Venice, Italy; 2010. p. 8–11.
- [2] Youssef MA, Wahid SS, Mohamed MA, Askalany AA. Experimental study in Egyptian biomass combustion in circulating fluidized bed. *Applied Energy* 2009;86:2644–50.
- [3] Khalil A, Mubarak A, Kaseb S. Road map for renewable energy research and development in Egypt. *Journal of Advanced Research* 2010;1:29–38.
- [4] Sun Z, Jin Bao-Sheng J, Ming-Yao Z, Ren-Ping L, Yong Z. Experimental study on cotton stalk combustion in a circulating fluidized bed. *Applied Energy* 2008;85:1027–40.
- [5] El-Mashad HM, van Loon WKP, Zeeman G, Bot GPA, Lettinga G. Reuse potential of agricultural wastes in semi-arid regions: Egypt as a case study. *Reviews in Environmental Science and Biotechnology* 2003;1:53–66.
- [6] Murphy ML. Retrofit of coal-fired power boilers using fluidized bed biomass gasification. Energy products of IDAHO. Coeur d'Alene, Idaho, USA, 208; 2001. p. 765–1611.
- [7] Ren J, Li F, Li Q, Wu J. Experiment study on the combustion characteristics of maize stalk biomass fuel. In: Proceedings of the 9th asia-pacific international symposium on combustion and energy utilization, China; 2008.
- [8] Baird MS, Eng MA. Energy fact sheet. The energy educators of Ontario; 1993.
- [9] Maiga AS, Chen GM, Wang Q, Xu JY. Renewable energy options for a Sahel country: Mali. *Renewable & Sustainable Energy Reviews* 2008;12:564–74.
- [10] El-Khayat MM, Ameen EE. Renewable energy in Egypt—challenges and prospects. *Thermal Issues in Emerging Technologies*. ThETA 3. Cairo, Egypt; December 19–22, 2010. p. 277–80.
- [11] Amigun B, Sigamoney R, Von Blottnitz H. Commercialisation of biofuel industry in Africa: a review. *Renewable & Sustainable Energy Reviews* 2008;12:53–68.
- [12] Smeets EMW, Faaij APC, Lewandowski IM, Turkenburg WC. A bottom-up assessment and review of global bio-energy potentials to 2050. *Progress in Energy and Combustion Science* 2007;33:56–106.
- [13] Zannoun MS. Egypt's renewable energy strategy, achievements and programs. New & Renewable Energy Authority (NREA), Egypt; 2009.
- [14] NREA. Implementation of renewable energy technologies—opportunities and barriers. Egypt country study; 2002.
- [15] EL-Shimy M. Viability analysis of PV power plants in Egypt. *Renewable Energy* 2009;34:2187–96.
- [16] Bushra M. Regional study on policies and institutional assessment of solid waste management in Egypt. Blue Plan. Regional Activity Centre, Sophia Antipolis; 2000.
- [17] CAPMAS. Central Agency for Public Mobilization and Statistics, (http://www.capmas.gov.eg/pages_ar.aspx)? pageid=708; 2013 [accessed 02.13].

- [18] El Saeidy E. Renewable energy in agriculture in Egypt. Technological Fundamentals of Briquetting Cotton Stalks as a Biofuel. Doctoral thesis. Berlin University; 2004.
- [19] IndexMundi. Egypt Electricity, (http://www.indexmundi.com/egypt/electricity_production.html); 2012.
- [20] Elmassy I. Sunny outlook in Egypt: potential and opportunities for cogeneration. Cogeneration and On-site Power Production. (<http://www.powergenworldwide.com/index/display/articledisplay/273399/articles/cogeneration-and-on-site-power-production/volume-7/issue-5/features/sunny-outlook-in-egypt-potential-and-opportunities-for-cogeneration.html>); 2006 [accessed 01.09.06].
- [21] GTZ. Integration of large amounts of renewable electricity in the Egyptian energy grid – capacity building for management and engineer – technical level (Egypt-RE-Grid); 2010.
- [22] Mahmoud SA. Electricity sector in Egypt. Egyptian Electricity Holding Company. DSM & EE workshop; 2009.
- [23] Mat SB. Biomass energy utilization & environment protection—commercial reality and outlook. Transtherm Engineering & Construction Sdn Bhd. Malaysia; 2003.
- [24] Karaj Sh T, Leis H, Müller J. Analysis of biomass residues potential for electrical energy generation in Albania. *Renewable & Sustainable Energy Reviews* 2010;14:493–9.
- [25] EQI. Environmental Quality International. Alternative methods for solid waste management and treatment and disposal of wastewater. Environmental Services for Improving Water Quality Management. Ministry of Water Resources & Irrigation, United States Agency for International Development; 2005.
- [26] Aref AA. Combustion characteristics of biomass fuels. *Bulletin of Faculty of Engineering, Minia University* 1995;126–38.
- [27] Shehata AM. Effect of particle size and firing load on characteristics of heat transfer in square fluidized bed combustor. MSc. Cairo University, Egypt; 2002.
- [28] NREA. Implementation of renewable energy technologies (RETs)—project opportunities and barriers. Egypt Country Study. Final Report to UNEP Collaborating Centre on Energy and Environment. Denmark: Risø National Laboratory; 2000.
- [29] GTZ. International Services. Technical/policy note on agricultural waste management in Egypt; 2006.
- [30] Hamdy YA. The current situation of Egyptian agricultural wastes. In: Proceedings of the anaerobic treatment of solid wastes workshop, Mansoura University, Egypt; 1998, p. 1–5.
- [31] Maldonado J, Sherif S. Egypt livestock and products annual. GAIN Report. USDA Foreign Agriculture Service. Global Agriculture Information Network; 2010.
- [32] Lasheen MR, Ammar NS. Assessment of metals speciation in sewage sludge and stabilized sludge from different wastewater treatment plants, Greater Cairo, Egypt. *Journal of Hazardous Materials* 2009;164:740–9.
- [33] Ghazy M, Dockhorn T, Dichtl N. Sewage sludge management in Egypt: current status and perspectives towards a sustainable agricultural use. *World Academy of Science Engineering and Technology* 2009;57:299–307.
- [34] Tchobanoglous G, Theisen H, Vigil S. Integrated solid waste management. New York: McGraw-Hill; 1993.
- [35] Badran MF, El-Haggar SM. Optimization of municipal solid waste management in Port Said – Egypt. *Waste Management* 2006;26:534–45.
- [36] CEA. Country Environmental Analysis (1992–2002). Arab Republic of Egypt, Water and Environment Department, the Middle East and North Africa Region. A World Bank Document; 2002.
- [37] UNEP. United Nations Environment Programme. Global environment outlook, vol. 3. London: Earthscan Publications; 2003.
- [38] Abdrabo MA. Assessment of economic viability of solid waste service provision in small settlements in developing countries: case study Rosetta, Egypt. *Waste Management* 2008;28:2503–11.
- [39] EEA. Egyptian Environmental Affairs Agency. Egypt state of the environment in 2004. Cairo, Egypt; 2005.
- [40] Klass DL. Waste biomass resource abundance, energy potential, and availability. Biomass for renewable energy fuels and chemicals. USA: E-Publishing Inc; 1998 p. 137–58.
- [41] Aly HF, Megeed EM. Lignocellulosic biomass conversion technologies to biofuels, potentials in Egypt. Report submitted to UNIDO. Cairo, Egypt: IMC; 2008.
- [42] Reith JH, Uil H, et al. Co-production of bio-ethanol electricity and heat from biomass residues. In: Proceedings of the 12th european conference on technology exhibition on biomass for energy, industry and climate protection. Amsterdam, Netherlands; 2002.
- [43] Jung S, Kang B, Kim J. Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *Journal of Analytical and Applied Pyrolysis* 2008;82:240–7.
- [44] Liang C, Yi S, Yi C, Yong-hao L, Fang L, Wen-Guang W. Effect of equivalence ratio on gasification characteristics in a rice straw two stage gasifier. School of Mechanical Engineering, Shanghai Jiao Tong University, China; 2009.
- [45] Summers DM. Using rice straw for energy production: economics, energetics and emissions. Department of Biological and Agricultural Engineering, University of California, USA; 2001.
- [46] Basso B, Ritchie JT. Impact of compost, manure and inorganic fertilizer on nitrate leaching and yield for a 6-year maize–alfalfa rotation in Michigan. *Agriculture, Ecosystems & Environment* 2005;108:329–41.
- [47] Schröder J. Revisiting the agronomic benefits of manure: a correct assessment and exploitation of its fertilizer value spares the environment. *Bioresource Technology* 2005;96:253–61.
- [48] Kuligowski K, Poulsen TG, Rubæk GH, Sørensen P. Plant-availability to barley of phosphorus in ash from thermally treated animal manure in comparison to other manure based materials and commercial fertilizer. *European Journal of Agronomy* 2010;33:293–303.
- [49] Wilkie AC, Castro HF, Cubinski KR, Owens JM, Yan SC. Fixed-film anaerobic digestion of flushed manure after primary treatment: wastewater production and characterisation. *Biosystems Engineering* 2004;89:457–71.
- [50] Oregon EC. Dairy manure anaerobic digester feasibility study report. Albany; 2009.
- [51] Xuereb P. Biogas—a fuel produced from waste. Available from: (<http://www.synapse.net.mt/miwm/newsletter/3836.asp>); 1997.
- [52] Cooper CJ, Laing CA. A macro analysis of crop residue and animal wastes as a potential energy source in Africa. *Journal of Energy in Southern Africa* 2007;18:10–9.
- [53] EIB. European Investment Bank. Cairo sludge disposal study. Mediterranean technical assistance programme for the execution of the Greater Cairo wastewater project; 1999.
- [54] CPH & EEOC. Central Public Health and Environmental Engineering Organization. Manual on municipal solid waste management. Energy recovery from municipal solid waste. Ministry of Urban Development, Government of India; 2000.

