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Edited by

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Introduction

We are pleased to present a selection of papers presented at The Energy & Materials Research Conference (EMR2015), which was held in Madrid, Spain, from 25 to 27 February 2015.

The aims of this conference were to provide a forum for discussion of the latest developments and advances in materials and processes involving energy, and to create an opportunity for researchers and professionals from a broad set of science and engineering disciplines to meet and have the chance to find new research colleagues and partners for future research works. This edition gathered 260 participants, coming from 44 countries, and nearly 370 works were presented at the conference. Some of those research works are discussed in this book covering the topics: biomass and biofuels; solar energy; fuel cells; energy storage…

We specially thank the International Advisory Committee, a group of international experts who helped us in the development of the conference program. In addition, we also thank the authors for participating in the conference and sharing their work and findings.

This book acts as formal proceedings of the meeting. We hope that this set of papers is inspiring and stimulating enough for readers in their current research work. Finally, we would like to look forward to see another successful edition in 2017.

A. Méndez-Vilas
Editor
EMR2015 General Coordinator

Energy production from

Biomass – Biofuels

Bioenergy in Argentina: the first co-firing essay to national scale

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The co-firing (CF)- that is the biomass and coal combustion in power plants- may contribute to the simultaneous reduction of dependence on fossil fuels and emission of greenhouse gases (GHG). The purpose of this research was to provide information scientifically supported about the use of biomass in CF processes in Argentina. There is only one power plant that operates based on coal, the Saint Nicholas Thermal Station (SNTS), province of Buenos Aires, which was selected to study the behavior of lignocellulosic biomass (forest residues of *Pinus elliottii* and *Eucalyptus grandi*) in CF process. Different concentrations of biomass in coal (5-40 %) and formats (pellets, chips, sawdust) were tested. It was found that pelleted materials of *Pinus sp* are more suitable to CF considering physicochemical characteristics and response of mills. The optimum percentage of biomass is 12% in the mix. We studied possible sources of provision of biomass, availability and transport. The power plant kept its normal operating parameters during the CF and even showed reductions in the percentages of GHG emissions.

Keywords bioenergy; co-firing; lignocellulosic biomass; pellets; power plants

1. Introduction

Currently there is a major challenge with regard to supplying the energy needs of modern society, which are covered -worldwide- on more than 80% by fossil fuels, mainly oil, coal and gas. The high consumption of fossil fuels, entail mainly two problems: their depletion and a major impact on the atmosphere as a result of their intensive use. Moreover the global energy demand is increasing. It is estimated that this demand will grow 50% in the period 2007-2035 [1]. One possible alternative to address the energy and environmental challenge is the use of renewable energy such as biomass.

The co-firing (CF) - combustion of biomass and coal in the same combustion system in power plants- improves the advantage of large plants based only on coal (> 100 MWe) that are not suitable for only biomass burning due to limited availability and dispersion of this resource [2]. The CF is one of the most effective ways to reduce emissions of CO_2 because it means the partial substitution of coal which is the largest source of CO_2 per kWh of produced electricity. Mann and Spath [3] found that for a 5% and 15% of coal substitution with residual biomass, decrease GHG emission (CO_{2eq}) in 5.4% and 18.2% respectively.

In Argentina there is only one Thermoelectric Station where CF tests could be performed: the Saint Nicholas Thermal Station (SNTS), in San Nicolas locality, province of Buenos Aires. It covers part of the primary fuel demand with mineral coal from South-Africa and it has a total installed capacity of 650 MW. Promote the CF process could imply decrease the GHG emissions and drop the dependence of imported coal.

The purpose of this study was assessment the performance the SNTS with lignocellulosic resources from forest plantations in CF process. The specifics objectives were: evaluate the resources provenance for the supply; assess and define the forest specie and shape of biomass resources; typify the carbon and biomass resources; analyze the biomass optimum percentage in the mix; quantify the GHG reduction; optimize the power plant operation with the coal-biomass mix. This paper shows the first experience of co-firing in an operating power plant in Argentina.

2. Materials and Methods

2.1 Selection of the sampling location of mineral coal

The samples were taking from ships unloading area of SNTS. Three points were defined for the sampling in the unloading line following the recommendations of international standards (ASTM D 7256, 2006). The samples were stored in closed plastic bags to prevent humidity. It was collected 140 samples of approximately 1kg each (exceeding the theoretical calculated of 104 samples). These samples were subjected to a process of cracking, reduction, separated and analysed in the lab.

2.2 Selection of the sampling location of biomass

There were selected two forest-industrial centers: one in the province of Entre Rios (Concordia locality, for *Eucalyptus grandi* samples extraction) and another in the province of Corrientes (Esquina locality, for *Pinus elliottii* samples obtaining). The main reasons underlying this choice were: more convenient distances between the facilities and the SNTS; amount of waste generated; availability of the Enterprises to perform the studies of processes, traceability of resources that are manufactured, waste volumes and ability to extract samples; proximity of the complexes to routes or ports, which would allow to take out the forest residues production. For the samples extraction the CENT/TS 14778-1, 2005 regulation was followed. There were extracted samples of sectors with material in movement and of stockpiles. We collected 13 chip and 2 sawdust samples of *Eucalyptus grandi* and the following samples of *Pinus elliottii*: 7 chips, 2 sawdust, 3 pellets, 4 barks.

2.3 Processing and analysis of samples

We perform analysis of moisture, ash, volatile and fix carbon content, particle size analysis, bulk density, ultimate o elementary coal analysis and determination of higher and lower heat value (HHV and LHV, respectively), following the ASTM standards. For biomass, for the same analysis, there were considered the following standards: CEN 14778; CEN 14780; CEN 14774; CEN 14775; CEN 15148; CEN15149; CEN 15103; CEN 15104; CEN 164001.

2.4 Co-firing test in the Saint Nicolas Thermal Station:

It was decided to perform the test in unit N° 2 of 75 MW of capacity installed, as equipment are less vulnerable to the new materials for having a robust structure. If appears the need to take out of service this sector of the plant –as could happen during the test- this would not have a significant impact on the electrical system. The mills of unit 2 are of hammers even though, the others are of disc. The biomass powdered would work better in the hammers mills, because the breaking is made by impacts of their pieces and then, the reduced material is carried in a pneumatic circuit to the burners. It was chosen one of the four mills to receive and process the new fuel mixture, while the other worked with coal only, which would enable it to compare the performance parameters between the different mills.

The lab analysis of different types of materials (chips, bark, sawdust and pellets) showed that the pellets of Pinus had the best performance for the essays. The biomass - coal mixtures were held on the carbon storage area. The materials were mingling by using Caterpillar bulldozers and cranes, until getting a uniform appearance. The worked proportions of biomass in coal were 6%, 12%, 14%, 20%, 34% y 48% (in mill 3, temporary storage hopper, burner fed through the mill with the mixture, etc.) and from 3 to 12% in the boiler (which was loaded with two mills performing only coal and the third with the mixture coal-biomass). During the CF test different blend proportions of the mix were loaded into the moving hopper. Each load continued the following path (Fig.1): conveyor belt of the area, aircraft, they fell into the cement hopper, the short inclined belt and then passed through the crusher. Finally the load was rose up to 50 m in height through the long inclined belt and fell into the hopper located on the seventh floor. From this point was supply the hammer mill N° 3 for reducing to a very small size. Drafts of about 70 ° C transported the mixture to the burners. Because the versatility of the system was possible carry a line of belts with the mixture and the other line with just coal.

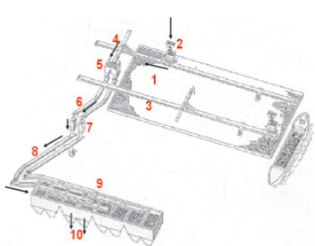

Fig. 1 Power circuit of the coal - biomass mixture (Plant Design, 1958). Where: 1) space of storage area where coal - biomass mixture was prepared, 2) loading crane mix, 3) steady belt load, 4) conveyor belt (aircraft), 5) concrete hopper with vibrators; 6) short inclined belt; 7) roller crushers, 8) long inclined belt; 9) hoppers on seventh floor at 50 m high of transient storage of the mixture; 10) coal fall to mills 1-2 and fall of coal-biomass to mill 3.

The mill 3 was subjected to the different mixtures mentioned (at different days). When there was no more mixture in the belts, it was assumed that the load was over. The time involved in the trial for each dosage was 19 hours. During the tests it was necessary to coordinate the availability of the operative staff in the site, external laboratories and laboratory technicians of the plant itself, considering that controls and measurements were also performed. We test: temperature, pressures, flows and streams mills. We assessed temperature in three areas: furnace, mill 3 and melting cone. Grinding samples were drawn for lab sieve analysis, in all cases of the same corner of the each boiler. The extraction of ash hoppers sampling was realized from the electric filter N°1. Also were measured emissions and gases compositions.

3. Results

3.1 Comparative analysis of coal and biomass

Table 1 shows the strengths and weaknesses of biomass compared to coal. The chips have significantly lower bulk density than coal, which implies more storage place. In general the volatile in the biomass are greater than those of coal and may cause explosions, while the ash and sulfur percentage in the biomass are lower than the coal which indicates environmental benefits.

Table 1 Chemical and thermochemical characterization of different materials. Where: LHV, lower heat value at 0% of water; H whole, humidity whole, S, sulphur.

Determined Parameter	Coal	*Pinus elliot*i			*Eucalyptus grandis*	
		Pellets	Sawdust	Chips	Sawdust	Chips
Bulk Density (kg/m^3)	945	780	279	267	235	216
LHV $_{0\%}$ (cal/g)	5966	4720	4007	4014	4536	4293
H whole $_{(bs)}$ (%)	7.94	7.89	118.48	67.74	39.83	31.18
Volatile (%)	25.13	74.92	70.94	65.76	82.78	81.38
Ash (%)	16.71	0.29	1.43	2.36	0.45	1.62
Fixed Coal (%)	58.16	24.79	27.63	31.88	16.78	16.7
S (%)	0.5	0.05	0.05	0.05	0.05	0.05

The Pinus pellet had the best performance for the high heat value, the highest bulk density, the lowest humidity content and percentage of ash also. Moreover it has the other advantages: availability in the market, the best performance of the machines (due to the homogeneous characteristics) and simple grinding structure. For using others heterogeneous materials (chips, bark, etc.) will be necessary the adaptation of the equipment. The processing of chips showed some difficulty especially in the milled because of the fibrous texture of the material. Moreover, the size of the chips (40x 40 mm) should be reduced by mechanical tasks, prior to mixing with the coal.

3.2 SNTS performance with co-firing processes

The control gas emission components with ORSAT and TESTO 350 considering the comparison of combustion conditions and CF, shows a decrease of the content of suspended particle concentration in the exhaust gases (26% lower) and CO_2 decreased (a 38,75% of reduction) when increasing dosage rates with biomass. The concentration of particles has changed from 109.3 mg/Nm^3 in the combustion process to 80.6 mg/Nm^3 for a 12.10% of substitution. For the same conditions, the CO_2 percentage of 8% in the combustion was reduced to 4.9%. In the combustion gases of the boiler it's observed a decrease in the values of NO_x and SO_2 with increasing dose rates of biomass into coal (Table 2).

Table 2 Control of components, combustion gases ORSAT and TESTO 350.

Test	% fuel mix		O_2 (%)	CO_2 (%)	CO (ppm)	NO_x (ppm)	SO_2 (ppm)
	Coal	Biomass					
Combustion	100	0	12.4	14.6	5	548	49
Co-firing	93.98	6.02	11.2	9.2	5	352	44
Co-firing	87.90	12.10	8.0	10.1	0	337	40

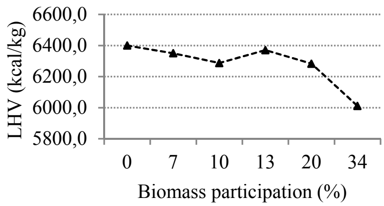

Figure 2 shows that the LHV in the samples after the combustion process decrease as the percentage of biomass in coal increases, reaching a plateau of stabilization of about 20% of biomass in coal content.

Fig. 2 LHV 0% variation with the dosage of biomass. The zero point corresponds to the historical average value of coal.

4. Discussion

4.1 Utilization opportunities of residual woody biomass in the SNTS

The feasibility of the pre- treatments to the studied forest residues is identical in both areas although cleaning, chipping, drying and compaction increase the cost. The pellet has physical characteristics and moisture content making it very suitable for CF processes, but it has a high cost. Other alternatives may be cheaper such as Eucalyptus and Pinus chips with earlier stages of reduction in size to small chips and dried to lower the moisture content to less than those recommended percentages by Rivero [4]. Although the first trials were performed with pellets by the skills found, it will be necessary to evaluate the possibility of combining this biomass format with another with a lower added cost and observe the performance of the SNTS.

4.2 Estimates for a continuing dosage in the studied plant

Considering as initial conditions a power of 50 MW with a consumption of 21.000 kg/h of coal, the amount of coal to be replaced is a 12.10% and the selected materials for replacement are Pinus pellets and Eucalyptus chips. For a LHV of coal of 5,810 $_{10\%}$ kcal/kg, the Pinus pellets of 4,568 $_{9\%}$ kcal/kg, and the Eucalyptus chips of 3,170 $_{26\%}$ kcal/kg [5] the estimations are showed in the Table 3.

Table 3 Replacement values of coal for pellets and chips on the N°2 unit of the SNTS.

	Unit	Value
Percentage of coal replacement	%	12.10
Coal to be replaced	kg/h	2,541
Energy to be replaced	kcal/h	14,770,669
Amount of pellets required for the replacement	kg/h	3,234.40
	t/day	78
	load/year (in pockets of 600 kg)	45.260
Amount of chips required	(kg/h)	4,660.90
	t/day	112
	load/year (trucks of $83m^3$)	1,642

The required amounts of pellets could not be supplied at this time for the producing plant in Corrientes. The amounts of reduced Eucalyptus chips that would be needed could be covered by the investigated plants in Concordia (Entre Rios) with special production conditions such as: time extensions, affecting more than one of its production lines and ensuring the availability of forest residues. It is therefore important to consider the mixing of different formats of biomass or, in the case that in the future the cost of the pellets decrease or get more profitable, further the option of pelletized the forest residues at source.

4.3 Features of grinding mills

One of the parameters considered as critical for the use of other physical forms of biomass is their size, since the performance characteristics of the mills. The developed experience provided knowledge that will guide future research. For the use of chips it will be required to go into detail and experiment if mills produce their break to such a degree that the resulting material can be transported by the internal air circuit mill. By the installation of new mills or crushers in SNTS it could achieve a reduction of chips to smaller sizes transforming them into splinters. Otherwise, it could also assess the feasibility of performing such grinding in origin, considering the added value that this might represent. It was also found that the mills were not capable of crushing the biomass, since it contains fibers and that special mills are needed. Tests were performed with a small one and the results were satisfactory. By prior grinding of less than 11 mm of size has been achieved to 3% of substitution [6].

4.4 Project of a new supply system

Based on the experiences in Europe [2, 7-8] and knowledge acquired during the tests, it is concluded that it would be essential to have a new supply system for enable the plant to achieve a permanent and automatic dosage form of the unit under test as well, automatically achieve the planned mix proportion. The sector that was detected with higher skills is one that is very close to the normal system of coal transportation. The tasks required to be performed would be:

- Rebuild and adapt a supply belt running from one sector of the fuel area to the concrete hopper where the material coming from the coal belt falls, with a system that allows modifies their velocity for a dosage;
- The belt to be set up has its own metal hopper in its supply sector, which should be modified and equipped with vibrators to prevent biomass clogging;
- The possible storage sector would be modified, providing it of an enclosure to protect the biomass of the atmospheric agents. It was initially estimated a covered area of about 40 m x 40 m.
- There would be different possibilities to unload the biomass: trucks would be able to unload on the metal hopper or the biomass could temporarily stay stored under the protection mentioned above and then could be loaded according to the need of supply. For this a loading system for the pellets pockets should be installed, that could be a rotating crane or small portable belts when using chips as the material. In case of using biomass in chip format, it should be installed a crusher to reduce their size in the previously detailed sector.

5. Conclusion

This paper concludes that the Pinus pellet is the most appropriate biomass format to be used in the CF process, given its properties of easy ground and their physicochemical virtues (especially the low moisture content and an energy density higher than the other materials). The studied plant in Corrientes could partially provide a CF process in the SNTS with pellets for the 12% of substitution. To continue with the use of pellets, the current transport system (truck) should be reconsidered (ship), since it raises the price of the material. Furthermore, the results of the lab tests show that the chips, reduced in size and with prior dried could be another type of alternative material for use in a CF process. The production capacity of the investigated plants in Entre Ríos, would be sufficient to supply, in two of its units, the SNTS for the coal-biomass CF process, on the dosage tested values. Among its weaknesses it is noticed high moisture content when not having a proper repose and drying time and high percentages of volatiles; for this special care should be taken with the equipment to prevent auto ignitions or explosions. The CF tests showed a good performance of the SNTS facilities for new fuels and enable to develop new knowledge and experiences for the future applications of other types of biomass. Achieving continuous dosage of biomass involve carrying out the construction of new facilities to allow its supply and control. Any effort invested in improving the plant will allow the partial substitution of coal involving currencies added to the domestic market and not the foreign ones; and also the decrease of the GHG and the acid rain, with consequent environmental benefits.

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Effect of biomass type blended with rice production wastes in syngas produced by co-gasification

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Rice production is one of the major food sources in the world, it generates a great amount of wastes mainly straw and husk. The common solutions to deal with these wastes are not appropriate, thus it is important to search for more adequate solutions. These wastes energetic content encourages its use in thermochemical processes, like gasification. However, the high content of silica and alkali metals of biomass rice wastes bring some challenges, as the formation of solids with lower melting point may occur during gasification, which may cause reactor erosion and serious damage. To solve this problem and also the seasonability of these wastes, they were co-gasified with different types of biomass wastes to study the possibility of producing a gaseous bio-fuel to produce energy to be used in rice milling process. The promising results obtained so far, encourage further studies to fully understand the synergic effects that may occur during co-gasification of mixtures of rice biomass wastes with other types of biomass.

Keywords Co-gasification; biomass; rice husk; rice straw; energy crops; eucalyptus stumps

1. Introduction

Rice is one of the most consumed cereals in the world. The world annual production of rice is higher than 700.7 million tons. In Europe annual rice production is around 4.1x106 ton. Spain is the second highest producer in Europe and Portugal the forth, producing around $182x10^3$ ton per year [1, 2]. Rice production generates a great amount of wastes mainly straw and husk. Rice straw are incorporated and/or burned in the fields to integrate nutrients, but this last procedure discharges pollutants, like dioxins and poly aromatic hydrocarbons. Rice husk is used to produce animal food, but the low nutrient content and the high content of silica do not encourage this utilisation. The high energetic content of these wastes encourages their valorisation by thermochemical processes, like gasification.

However, as rice straw is seasonable the operation of gasification installation may be compromised. On the other hand, rice husks have a high content of silica and alkali metals that lead to the formation of solids with lower melting point. Thus, this may lead to bed agglomeration that causes reactor erosion and serious damage. Co-gasification of rice wastes with other types of biomass that have lower ash content and lower contents of silica and alkali metals may allow diluting the unsuitable features and solve the problems related to seasonability. In case there is lack of rice production wastes, the gasifier could continue to operate with blends of these wastes with other types of biomass. In the choice of the biomass to be blended with rice wastes should be considered the contents of undesirable components.

There is already some scientific knowledge about biomass gasification, including gasification of rice husk and straw [3-6]. It is possible to obtain high quality gas by gasification, though some bed agglomeration could happen, which could be avoided by the use of catalysts [4, 5]. Another option could be by diluting the negative characteristics of biomass rice wastes by blending it with other biomass types with suitable features for gasification. This was the objective of the work described in this paper. Thus, rice husk and straw were blended with different types of biomass, namely three types of energy crops: miscanthus, sweet sorghum and napier grass (elephant grass) and also with corn cob and eucalyptus stumps.

Cob growth needs soils with high moisture contents. Thus, in Portugal and Spain cob fields are located near big rivers basins, not very far from the places where rice culture happens. Hence wastes generated by these agriculture activities are not far from one another, which encourage the possibility of gasifying them in the same installation.

On the other hand, in Iberian Peninsula there is an intensive use of eucalyptus in the pulp and paper industry, because of its fast growth and high productivity. There are large areas of forest dedicated to its growth. After 2 or 3 harvesting cycles these tree stumps are removed from the fields and considered low value biomass wastes, but their energetic content encourages their valorisation by thermochemical conversion processes like gasification.

Hence, to solve the problems of biomass rice waste seasonability and some negative features, blends of biomass rice waste with different types of biomass wastes were co-gasified in a bench-scale installation.

Gasification gas yield and composition obtained with different biomass blends was analysed together with the performance of gasification installation to determine the best approach to produce gaseous bio-fuels that could be used for energy production for the rice milling processes.

2. Experimental Part

Gasification and co-gasification tests were done in a bench-scale fluidised bed gasification installation. The reactor was a bubbling fluidised bed gasifier made of a refractory steel pipe. The reactor was circular in cross-section with an inside diameter of 80 mm and with a height of 1 500 mm.

Mixtures of steam and air were introduced through a gas distributor at the base of the reactor to act as gasifying and fluidising agent. To avoid some clogging, that might be due to pyrolysis of the feedstock, prior to the entry into the gasifier, the feeding system was water cooled and a nitrogen flow was also used to help the waste feeding, to avoid the formation of a compact plug and to prevent gas back flow. Previous gasification studies with rice wastes lead to the selection of the following experimental conditions. Gasification temperature was around 800ºC, steam/fuel ratio was about 1.0 g/g daf (daf means dry and ash free) and feeding flow rates were adjusted to guarantee an equivalent ratio (ER) of around 0.2. ER is defined as the ratio between the amount of oxygen added and the stoichiometric oxygen needed for complete combustion of the feedstock.

The gasification gas formed passed through a cyclone to remove particulates. Tar and condensable liquids were removed in a quenching system. Next, the gas was filtered, before it was injected into CO and CO_2 on-line analysers. Gasification gas was sampled and collected in bags to be analysed by gas chromatography (GC) to determine the contents of CO, CO_2, H_2, CH_4, N_2, O_2 and other heavier gaseous hydrocarbons, referred as C_nH_m. Tar content in gasification gas was determined using CEN/TS 15439:2006 Standard. The solvent isopropanol (2-propanol or isopropylalcohol) was used for tar collection. The homogeneous liquid sampled was evaporated under well-defined conditions and the evaporation residue was weighed to calculate the amount of tar in g/Nm^3. After each experiment, solid bed residue, containing silica sand, ashes and unconverted carbon, was collected and analysed. Silica sand was separated from the remaining solids and char content was determined.

Each experiment lasted between 90 and 120 minutes, depending on the time to reach stabilised conditions and to collect all the samples. At least two sets of runs were repeated at the same experimental conditions and when deviations higher than 5% were observed, more tests were performed to assure the reproducibility of experimental results.

As rice husk and straw wastes are seasonal, to guarantee the availability of feedstock for gasification installation and to dilute the negative features of biomass rice wastes, these wastes were mixed with other biomass types, namely: three types of energy crops: miscanthus, sweet sorghum and napier grass (elephant grass) and also corn cob and eucalyptus stumps, as mentioned before.

Gas composition was presented on dry basis. Gas yield was calculated based on the production of inert-free gas per weight of dry-ash-free feedstock, excluding water from gas composition. Gas higher heating value (HHV) is defined as the gross calorific value of the inert-dry-free gas on a volumetric basis. Energy conversion was determined as the ratio between the energy present in the produced gas and the energy contained in the gasified feedstock.

3. Results and discussion

Previous studies about the gasification of rice husk and straw, as showed that the presence of steam promoted steam reforming reactions and thus favoured the conversion of gaseous hydrocarbons and tar, leading to the formation of higher H_2 contents in gasification gas. Thus, mixtures of air and steam were used in the present study as gasification and fluidisation agents. The rise of temperature also favoured cracking reaction and thus the conversion of tar into gaseous molecules and the overall gasification reactions, hence increasing gas yield and leading to a gasification gas richer in H_2 and with lower contents of hydrocarbons and tar. The rise of air favoured oxidation reactions, thus increasing the amount of both CO and CO_2, and reducing the contents of H_2, hydrocarbons and tar. The rise of air flow rate increased gas yields, but decreased gas HHV. Hence an ER of 0.2 and a temperature of 800ºC were selected for further studies.

The different biomass species selected for this study were first gasified alone at the experimental conditions selected. In Fig. 1 may be analysed the effect of biomass type on gasification gas composition. No great changes were observed when rice husk was substituted by straw; however straw led to higher CO_2 and to lower H_2 contents. Straw gasification also led to lower hydrocarbons release, both CH_4 and gaseous hydrocarbons with carbon atoms number higher than one (C_nH_m), being the total amount of hydrocarbons around 63% lower than the value obtained with husk for similar gasification conditions.

The gas obtained with eucalyptus was similar to those produced by rice straw, as similar CO_2 and total hydrocarbons contents were obtained. However, the gasification gas obtained by eucalyptus gasification was poorer in CO and richer in H_2.

Gasification of energy crops led to similar gas compositions. However, miscanthus led to the highest hydrocarbons content and to the lowest H_2. The gas produced by miscanthus was richer in CO and poorer in CO_2 than the gas obtained by the other energy crops studied: sweet sorghum and napier grass. However, the total amount of carbon oxides obtained by these three species remained constant and around 54% (v/v). Gasification gas obtained from corn cob was similar to that produced by miscanthus gasification, though corn cob led to lower release of hydrocarbons, including CH_4 and C_nH_m, than the contents obtained by miscanthus.

In Fig. 1 is presented gasification gas relative concentration to easier the comparison with gasification gases obtained with different experimental conditions, including different feedstocks. However, when the total concentration of each gaseous component is presented, for instance in Nl/g daf, similar tendencies to those described were observed.

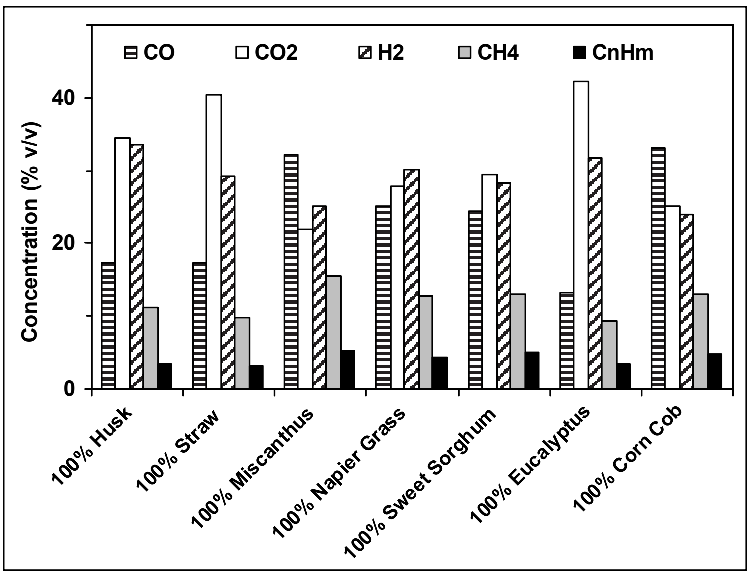

Fig. 1 Effect of biomass type on gasification gas composition. Gas composition is shown in dry basis and without N_2. Experimental conditions: Temperature - 800 ºC, ER – 0.2 (air), steam/feedstock ratio – 1.0.

Next it was study the possibility of replacing one biomass type by the other, by blending rice husk with 50% (w/w) of all the other biomass types presented in Fig. 1. It was decided to used rice husk and not rice straw, because straw is more seasonal, as it only exists during rice harvesting time at late Summer and Autumn, while rice husk may exist during a longer period of time, as rice production plants also deal with imported rice that needs to be peeled and prepared.

In Fig. 2 is shown the gasification gas relative concentration obtained by co-gasification of blends of different biomass wastes. Co-gasification of husk and straw led to a gas with contents between those obtained with only husk or only straw. The same tendency was obtained for the blend of rice husk with 50% (w/w) of miscanthus. In fact, for both of these mixtures the contents of each gaseous component laid between the values obtained by the gasification of each blend component. The same was observed when instead of only miscanthus; a mixture of the three energy crops in equal amounts was blended with rice husk. The main aim of using such a mixture was to test the possibility of substituting one energy crop species by another in case of lack of one of them. However, the co-gasification of the blend of rice husk with 50% (w/w) of napier grass led to a gas mixture with a composition similar to that obtained for the gasification of only napier grass. The same was obtained for the co-gasification of rice husk blended with 50% (w/w) of corn cob, whose composition was quite similar to those obtained by corn cob gasification. On the other hand, the gas obtained by co-gasification of rice husk mixed with 50% (w/w) of eucalyptus was quite different of those produced by gasification of only rice husk or only eucalyptus. The blend led to around more 55% of total hydrocarbons and to less 20% of H_2 than the gasification of each of these biomass species. Though the total content of carbon oxides was similar, the gasification of each single biomass led to a gas poorer in CO and richer in CO_2, while with the blend identical CO and CO_2 contents were obtained.

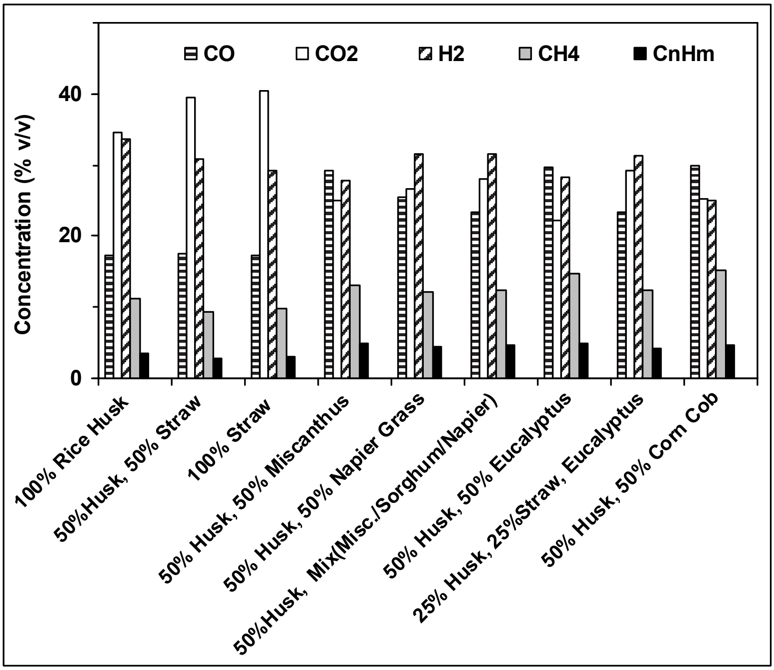

Fig. 2 Effect of biomass mixtures composition on co-gasification gas content. Gas composition is shown in dry basis and without N_2. Experimental conditions: Temperature - 800 ºC, ER – 0.2 (air), steam/feedstock ratio – 1.0.

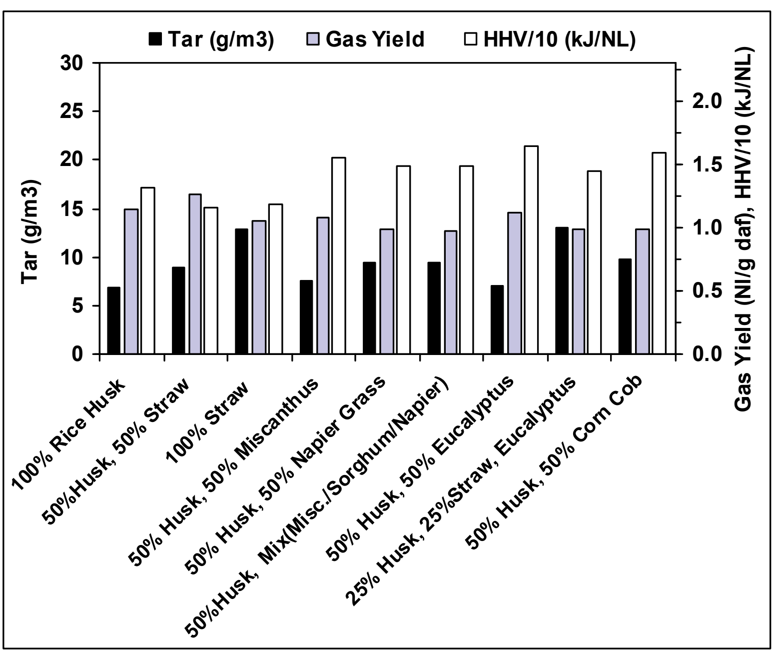

Fig. 3 Effect of biomass type on tar content, gas yield and HHV. Gas composition is shown in dry basis and without N_2. Experimental conditions: Temperature - 800 ºC, ER – 0.2 (air), steam/feedstock ratio – 1.0.

Again, similar tendencies were observed when instead of gas relative concentration, the total concentration of each gaseous component in Nl/g daf was analysed.

Tar content in gasification gas was greatly affected by the type of biomass gasified. The highest values were obtained for sorghum and corn cob, which more than doubled the lowest value obtained by rice husk gasification. On the other hand, the range of variation between the highest and the lowest gas yield was only 20%. Higher changes were observed for gas HHV, whose values changed between 11.6 and 16.8 kJ/NL.

Co-gasification of husk and straw led to a gas with higher gas yield and lower tar content than that obtained with only straw. No many changes were observed when husk was co-gasified with other biomass wastes. In average there was an increase in tar of around 35% and a decrease in gas yield of about 15%. This was followed by an increase in HHV of around 20%. Thus, similar CGE (Cold gas efficiency) were obtained. Thus, it is possible to substitute one biomass waste by the other, without main changes in the gas produced.

In general, gasification and co-gasification results are in good agreement with others obtained in the same experimental installation with other feedstocks [7]

The results obtained so far showed that some synergic effects might have occurred during co-gasification of mixtures of rice biomass wastes with other biomass types, which need to be further studied and understood to allow substituting one biomass species by another. As no great changes in gas relative concentration were observed when husk was replaced by other biomass types, it is possible to substitute one biomass by the other, without main changes in gasifier operation; small adjustments in gasification conditions would allow smooth operation. However, this subject needs to be further studied and longer operation times need to be tested.

4. Main conclusions

No major operational problems were observed and no great adjustments in the gasification installation were needed when rice biomass wastes were blended with other types of biomass.

No great changes were observed in gas composition and yield when husk was substituted by straw, or by other biomass type, the changes in gas composition and yield may be overtaken by some adjustment in operation conditions.

Co-gasification of biomass rice wastes blended with other biomass wastes is a possible technology to originate a valuable gaseous bio-fuel from low cost renewable energy sources.

The substitution of rice and straw by another biomass type may help to solve bed agglomeration problems that may occur during long operation time, due to rice and straw contents in Na, K, Ca, etc. by the diluting effect of cleaner biomass. However, the synergic effects during co-gasification of mixtures of rice biomass wastes with other types of biomass need to be further studied

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Estimation of cold flow performance and oxidation stability of fatty acid ethyl esters obtained from *Escherichia coli*

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The increase in energy demand and the decrease in oil reserves encourage the search for alternative energy resources. Biodiesel composed of fatty acid ethyl esters (FAEEs) is a promising alternative fuel. The more extended use of fatty acid methyl esters (FAMEs) over FAEEs comes from the higher cost of ethanol compared to methanol. But the genetic development of microorganisms able to produce bioethanol in extensive quantities or directly FAEEs omitting the transesterification process can diminish the cost of FAEEs and make them competitive. This work shows how to predict the cold flow properties and the oxidation stability of biodiesel composed of FAEEs using only some milligrams of the sample. Prediction of the cloud point (CP), the pour point (PP) and the cold filter plugging point (CFPP) has been made with a multiple linear correlation using the total percentage of unsaturated compounds and the average length of the carbon chains. The oxidation stability assessed through the induction time (IT) was correlated with a multiple linear regression using as parameters the total percentage of monounsaturated esters and the bis-allylic position equivalents index (BAPE).

Keywords biodiesel; fatty acid ethyl esters (FAEEs); cold flow peformance; oxidation stability; *Escherichia coli*

1. Introduction

Biodiesel, besides being a renewable energy, has important advantages compared to ordinary diesel: contains significantly lower sulfur and no aromatic hydrocarbons, has higher cetane number and oxygen content, showing better combustion performance, has higher flash point and is considered a biodegradable, non-toxic and harmless substance. The main disadvantages concerning the properties of the biodiesel are its cold flow performance and its oxidation stability. However, the key factor for the economic feasibility of biodiesel is the reduction of the cost of biodiesel fuel. It has been found that feedstock alone represents 75 % of the overall biodiesel production cost [1]. Therefore, selecting the best feedstock is vital to ensure low biodiesel cost. The option lies in considering non-edible oils as a feedstock for biodiesel. In fact some studies point out that biodiesel from microorganisms (bacteria, yeast, fungi or microalgae) seems to be the only renewable biofuel that would have the potential to displace petroleum-derived transport fuels without adversely affecting the problem of land occupation and food supply [2,3]. Moreover, these microorganisms can produce biofuels derived from lignocellulosic or waste feedstocks [4].

From this point, two alternatives seem to be the most viable: first, the improvement through genetic modification of microorganisms to be able to accept lignocellulosic feedstocks and produce triglycerides with a good efficiency, for later carrying out the transesterification process [5, 6]. Second, make the microorganisms produce directly FAEEs from lignocellulosic materials [5]. This second way could reduce cost due to the elimination of the transesterification stage. From the second process mainly FAEEs are produced because the toxicity of methanol for many life forms makes the production of FAMEs more difficult. From the first process both FAMEs and FAEEs can be obtained. But methanol is currently produced from natural gas, it is a highly toxic and hazardous compound, and its use requires special precautions. Thus, FAME-based biodiesel is not an entirely renewable product since the alcohol component is of fossil origin and only the use of bioethanol for production of FAEE-based biodiesel would result in a fully sustainable fuel [7, 8]. Therefore, from both processes and considering environmental and health issues, the most feasible compound for biodiesel formulation is FAEE.

Escherichia coli (*E. coli*) seems to be the most promising host for these studies. *E. coli* is able to use both pentose and hexose sugars, and is highly amenable to metabolic engineering for fuel production. Additionally, while the genetic engineering is greatly facilitated by the tractability of *E. coli*, the approaches described can be readily adapted for other microorganisms for use in a consolidated bioprocess to generate advanced biofuels from biomass [5]. A crucial challenge is the characterization of the fuel produced by bacteria. The concentration obtained in FAEEs from *E. coli* reaches by now only 1 g/L [9, 10]. This amount makes difficult to test the biodiesel to know its physical properties.

The purpose of this paper is, first, to have a fast, easy and non-expensive way to assess the cold flow performance and oxidation stability of FAEEs produced via classical transesterification process and second to be able to assess the properties of FAEEs produced in minimum amounts through genetic studies.

Correlations between composition and properties have been generated. Gas chromatography with flame ionization detector (GC-FID) is used to know the fatty acid composition, where only some milligrams are needed. There are some studies concerning these correlations between composition and properties [11,12] but there is a huge scope in the development of accurate models to predict the properties of biodiesel [13] and no correlation between composition and CP, PP, CFPP and IT has been found concerning FAEEs.

2. Materials and methods

2.1 Materials

All the reagents and oils or fats were of commercial grade and were used without further purification. The *E. Coli* BL21 (DE3) strain was provided generously by the Centre for Plant Biotechnology and Genomics (GBGP), the LB medium was made through their components: Bacto Tryptone Peptone purchased from Becton Dickinson (BD), Yeast Extract purchased also from BD and sodium chloride purchased from Merck (PhEur).

2.2 Production of biodiesel

The process followed to make biodiesel from the oils and fats was previously described in the literature [14, 15] but slight changes were made due to the change in the final product from FAMEs to FAEEs.

E. coli BL21 (DE3) strain was cultivated in baffled flasks at 37 °C, rotating at 150 rpm for 16 h. Ampicillin was added for plasmid selection (100 mg/L) and LB medium for growth. The extraction of the fatty acids was done as described in the literature [16]. Once the extraction was completed the derivatization to FAEEs was done using thionyl chloride dissolved in ethanol [17].

EN 14103 Method was used for quantification of ester content in biodiesel. A Hewlett Packard 5890 Series II gas chromatograph equipped with FID detector and split/splitless injector was used for the analysis and an HP-Wax column (30 m x 0.32 mm id x 0.15 µm) of polyethylene glycol was used for separation.

2.3 Cold flow properties and oxidation stability tests

Both the CP and PP were determined with the Automatic Cloud and Pour Point Analyzer CPP 97-6. The CFPP was measured with the CFPP analyser TLF (ISL-ATPEM). The Rancimat method described in UNE-EN 15751 was used to assess the oxidation stability. This method is listed as the oxidative stability specification in ASTM D6751 and EN 14214.

3. Results and discussion

3.1 Experimental results of cold flow properties

The results of the cold properties tests of the biodiesel fuels are reported in Table 1. Camelina, linseed and rapeseed biodiesel fuels, with the highest percentage of unsaturated FAEEs (over 85 wt %), present the lowest values for CP, PP and CFPP. Nevertheless cold flow properties not only depend on the amount of unsaturated FAEEs, but also on the length of the carbon chain of the esters. This effect is clearly shown in the coconut biodiesel that, despite having the lowest percentage of unsaturated FAEEs (10.68 wt %), it has low cold flow temperatures, similar to soybean biodiesel, because of the high amount of short chain esters .These two properties, percentage of unsaturated FAEEs (U_{FAEE}) and average length of carbon chain (N_c), have been used to correlate composition and cold properties. The three multiple linear correlations found are:

$$CP = -81.62 - 0.45 \times U_{FAEE} + 5.87 \times N_c \qquad R^2 = 0.89 \qquad Eq.1$$

$$PP = -125.04 - 0.62 \times U_{FAEE} + 8.61 \times N_c \qquad R^2 = 0.76 \qquad Eq.2$$

$$CFPP = -103.47 - 0.59 \times U_{FAEE} + 7.30 \times N_c \qquad R^2 = 0.86 \qquad Eq.3$$

The assessment of the significance of the parameters was done through the Student's t-test for the individual parameters and with the F-test for the whole model. Both tests show significant results (p-value < 0.05).

Table 1 Results of the cold flow performance and oxidation stability with the main composition data

Biodiesel	CP (°C)	PP (°C)	CFPP (°C)	IT (h)	[a]C16:1	C18:1	C18:2	C18:3	N_c
Rapeseed	-5	-16	-11	4.12	0.00	59.55	17.74	6.59	19.92
Palm	9	9	10	7.73	0.00	33.53	9.14	0.00	19.03
Soybean	-1	-5	-5	0.71	0.00	29.37	46.06	4.92	19.73
Coconut	-2	-9	-5	8.60	0.00	8.31	2.37	0.00	14.44
Linseed	-7	-11	-15	0.58	0.00	21.34	17.27	49.08	19.87
Sesame	0	-3	-6	2.33	0.00	40.27	43.13	0.34	19.87
Camelina	-4	-6	-12	0.65	0.00	17.37	33.47	26.03	19.89
Sea-buckthorn	-	-	-	5.40	27.66	28.74	7.84	3.92	18.77
Animal fat	9	10	4	7.30	3.16	43.89	7.87	0.63	19.37
Waste frying oil	-1	-3	-2	5.00	2.37	66.40	10.33	0.77	19.72

[a]The content of the FAEEs are shown in weight percentage

3.2 Estimation of oxidation stability

Table 1 shows the IT of the biodiesel fuels obtained with the Rancimat procedure. Coconut, palm and animal fat biodiesel have the highest values of IT, all of them above 7 h and therefore acceptable considering standard ASTM D6751. On the contrary soybean, linseed and camelina biodiesel fuels have the lowest values of IT (all below 1 h). It can be noticed that these biodiesel fuels with low values of IT have high values of unsaturated esters (all above 80 % w/w) while the biodiesel fuels with high values of IT have lower values of unsaturated esters. A challenge that had to be addressed before doing the correlation is to find at least one oil with a significant content of palmitoleic acid (C16:1) because the bacteria *E. coli* has much more of this acid than any other common oil. That is the reason why sea-buckthorn berry oil was studied, since it has a content of this particular acid of 27.66 %. The main conclusions of the statistical analysis were: 1) Monounsaturated esters affected IT mainly when the amount of linolenic acid ethyl esters was low. 2) The effect of the palmitoleic ester is similar to the effect of the oleic ester so an appropriate parameter for the correlation is the sum of the monounsaturated palmitoleic and oleic ethyl esters (MU_{FAEE}). 3) The effect of polyunsatured esters can be measured with accuracy with the index proposed previously by Knothe [18] that takes into account the bis-allylic positions of the esters (BAPE = C18:2+2×C18:3). As a result of this analysis two equations are proposed to correlate the composition with the IT.

First, an equation for values of linolenic ester lower than 10 %:

$$IT = 9.50 - 0.03 \times MU_{FAEE} - 0.14 \times BAPE \qquad R^2 = 0.97 \qquad Eq.4$$

The p-values of the Student's t-test and Fischer test are lower than 0.05 so the parameters are statistically significant. An R-squared of 0.97 shows that the chosen parameters approximate with a good accuracy the IT. If the coefficients affecting variables MU_{FAEE} and BAPE are compared, the presence of polyunsaturated compounds is observed to affect the final IT result about four times more than that of the monounsaturated ones.

Second, an equation for values of linolenic ester higher than 10 %:

$$IT = 4.45 - 0.04 \times BAPE \qquad R^2 = 0.94 \qquad Eq.5$$

In this case the statistical analysis shows that the parameter MU_{FAEE} is not significant so an equation with only the variable BAPE is proposed. The y-intercept and the coefficient of the BAPE show statistical significance with p-values of the Student's t-test lower than 0.05. F-test confirms also the significance of the model.

3.3 Estimation of properties of FAEE obtained from *E. coli*

The correlations described in this article allowed to estimate the cold flow properties and the oxidation stability of samples of FAEE obtained from an *E. coli* culture. The results of the correlation between composition and properties are shown in Table 2. The lack of polyunsaturated compounds and the presence of a high percentage of monounsaturated compounds (C16:1 and C18:1) causes a good oxidation stability but moderate cold flow behavior. From these initial results, and using the equations proposed, an optimum composition can be searched using genetic techniques. For example, the modification of the fatty acid synthesis of *E. coli* has been done successfully with the use of thioesterases [19], achieving changes in the final fatty acid composition. Cold flow properties of biodiesel from *E. coli* can be improved in future works using these techniques that allow modifying the ester composition.

Table 2. Prediction of properties of biodiesel from *E. coli*

FAEE	CP (°C)	PP (°C)	CFPP (°C)	IT (h)
E. coli	3.0	0.9	0.5	8.18

4. Conclusions

Rapeseed, camelina, soybean, palm kernel, coconut, linseed, sesame, sea-buckthorn, waste frying oils and animal fat have been transesterified with ethanol to produce biodiesel of ethyl esters. The composition of biodiesel fuels was measured using GC-FID. The cold properties (CP, PP and CFPP) were measured following the corresponding ASTM and EN standards. The oxidation stability was assessed through the IT measured with the Rancimat test. A multiple linear regression model was applied to find the correlation between total percentage of unsaturated FAEEs and length of the average carbon chain with the CP, PP and CFPP. Considering the difficulty in the prediction of these properties using only the composition the results were successful. The prediction of the oxidation stability was done using as parameters the percentage of monounsaturated compounds and the bis-allylic position equivalents index which contains the information of the polyunsaturated compounds. A multiple linear regression was necessary for values of C18:3 lower than 10 % using MU_{FAEE} and BAPE as variables. On the other hand for values of C18:3 higher than 10 % the parameter MU_{FAEE} was not significant and a simple linear regression was done.

An inexpensive and rapid way to predict the cold flow properties and the oxidation stability of the FAEE biodiesel using a minimum amount of substance is proposed. Researchers of biodiesel that work with microorganisms can use these equations to know these two crucial properties using milligrams of the sample. As an application of the equations an amount of *E. coli* BL21 (DE3) was produced following the method above described and the composition was used to predict the properties of *E. coli* biodiesel using the equations proposed. Biodiesel from unmodified *E. coli* presents a good oxidation stability and moderate cold flow behavior because of the presence of a high percentage of monounsaturated compounds (C16:1 and C18:1) and lack of polyunsaturated compounds.

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Parametric investigation of rapid heating fast pyrolysis of *Jatropha curcas* waste for bio-oil production

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In this research, rapid heating fast pyrolysis of *Jatropha curcas* for optimum quantity and quality of bio-oil production is investigated. The results show that both reaction temperature and nitrogen (N_2) velocity have strongly influenced the yield and quality of bio-oil. By developing valid empirical correlations and using normalisation, the optimum quantity and quality of bio-oil is found to be at a reaction temperature of 747.17 K and a N_2 linear velocity of 0.0078 cm/s. At this optimum point, 40.93 wt% of biomass is transformed into bio-oil with a gross calorific value of 16.92 MJ/kg, a water content of 28.02 wt% and a pH of 7.01. These properties demonstrate that this bio-oil can be used in burners without any modifications provided that other specifications of this fuel match those within ASTM D7554-10 bio-fuel standard.

Keywords bio-oil; fast pyrolysis; *Jatropha curcas*

1. Introduction

Over the last hundred years, a seventeen-fold increase in energy consumption has resulted in increasing use of fossil fuels and depletion of fossil fuels reserves worldwide [1–2]. Based on the International Energy Agency report in 2011 [3], more than 75% of the world's total primary energy supply originates from non-renewable fossil fuels such as coal, oil and natural gas. However, the political and economic instability of many of the fossil fuels producing countries have caused fuel price fluctuation and an overall increase in fuel cost with time. The usage of fossil fuels as the main source of energy has resulted in the accumulation of greenhouse gases especially carbon dioxide (CO_2) in the atmosphere. The current energy scenario coupled with the increasing amount of greenhouse gases, particularly CO_2, and pollutant emissions from the combustion of fossil fuels have led to intense research on sustainable and environmentally-friendly alternative fuels such as biodiesel, bio-ethanol and biomass. Amongst the many varied ways to utilise biomass as a source of energy is pyrolysis, a thermochemical decomposition process that can utilise biomass waste. Conventional pyrolysis is the foundation upon which all other pyrolysis methods are based on whereas fast pyrolysis targets the production of bio-oil, a liquid fuel that has zero net CO_2 emission when it is being combusted. Conventional and fast pyrolysis processes in two designed fixed-bed and rapid heating reactors to produce bio-oil has been investigated. The purposes of using a fixed-bed reactor were twofold. First, the pyrolysis process can be modelled by using a TGA unit operating at the same heating rate as the designed fixed-bed reactor [4]. Second, experiments on this reactor setup enable a baseline for comparing conventional and fast pyrolysis processes in terms of the effect of heating rate. Design of Experiment (DoE) was performed in order to study the effects of reaction temperature, N_2 linear velocity and heating rate on bio-oil yield, calorific value, water content and acidity. A full factorial experimental test matrix was introduced to create a proper baseline for a reliable model to be developed. A reliable method for modelling of experimental results is linear and non-linear regression, which is used in this work. After validation of the model, by using normalisation, the optimum quality and quantity test points were located. In view of potential future commercialisation, physicochemical properties of bio-oil produced from pyrolysis processes were measured. The optimum bio-oil products from both pyrolysis processes were tested and compared against the ASTM D7544-10 standard for burner biofuels [5].

2. Methodology

2.1 Feedstock, pyrolysis rig and Design of Experiment (DoE)

The biomass feedstock used in the pyrolysis experiments was *Jatropha curcas* pressed cake and its pre-treatment prior to pyrolysis has been described in [4]. A fixed-bed and a rapid heating pyrolysis rig both made out of stainless steel were used for conventional and fast pyrolysis processes, respectively. The details of the