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Biomass to fuel gas conversion through a low Pyrrolysis temperature induced by Gamma radiation: an experimental and simulative study

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Abstract

Currently, 80% of the global energy is supplied by carbon-based fossil fuels which has led to concerns over the environmental impact of increasing atmospheric CO_2 levels and has sparked ever-growing interest in renewable energy sources. In line with, adding value to low or negative valued biomass feedstocks by converting them to marketable bio-fuel gases, to replace the current one, as a renewable resource for energy via the Pyrrolysis technology is the aim of this work. As a promising thermal conversion method in terms of high reliability, good flexibility through processing and the versatile range of products can be obtained, Pyrrolysis has been considered as an important process for the generation of sustainable energy and chemicals from biomass. Pyrrolysis process converts biomass carbon-containing materials into a combustible gas composed primarily of carbon monoxide, hydrogen, and methane. This is however the available literature over the last few decades reported that Pyrrolysis process should be carried out at elevated temperature which is at least 500 ^{o}C

The current research work has focused on the conversion of some of the biomass into a certain fuel gases at low operational temperatures assisted by γ radiation. At the first place, using raw untreated biomass, gas mixtures composed of different percentages of carbon dioxide and methane were obtained under different operating conditions of time and temperatures. In practical, maximum temperature and timing of 300 ^{o}C and four hours respectively were applied through this conversion process. A complete shift in the produced gas composition towards pure methane (natural gas) was obtained at the same operating conditions via introducing Gamma ray-treated biomass samples in the Pyrrolysis system. On the other hand, nano-carbon black particles were obtained as the by-product of the thermal conversion of the radiated biomass whilst an amorphous structured carbon was got when untreated biomass was applied. The gas composition determination analysis was done using GC equipped with TC detector and the carbon particles characteristics were carried out by both HR TEM and Raman spectroscopy.

Keywords: biomass to energy, pyrolysis, irradiated solid waste, methane and hydrogen production.

1. Introduction

Biomass is a promising eco-friendly alternative source of renewable energy in the context of current energy scenarios. Current global energy supply is to a large extent based on fossil fuels (oil, natural gas, coal), of which the reserves are finite. Given the growing world population, the increasing energy consumption per capital and the evidence of global warming, the necessity for long-term alternative energy sources is obvious. For these twin crises of fossil fuel depletion and environmental degradation, energy planning and technology improvement has become an important public agenda of most developed and developing countries.

Biomass energy is the one the earliest and now the third largest global source of energy, comprising up to 40%–50% of energy usage in many developing countries that have large agriculture and forest areas [1]. Biomass is used to meet a variety of energy needs, including generating electricity, heating homes and providing process heat for industrial facilities. Goyal et al. define biomass as any living matter on earth. More specifically, biomass can be defined as material derived from growing plants or from animal manure which mainly consists of carbon, hydrogen, oxygen, nitrogen and smaller portions of inorganic species [2]. Biomass can be directly or indirectly produced by green plants converting sunlight into plant material through photosynthesis [3]. The solar energy driving photosynthesis is stored in the chemical bonds of the structural components of biomass which is a natural process. During combustion, biomass releases this energy in the form of heat. For that reason, biomass species are considered as renewable sources of energy which do not add carbon dioxide to the environment, in contrast to non-renewable fossil fuels. In addition, the unique feature of biomass is that it is the only renewable energy source which can be converted into convenient solid, liquid and gaseous fuels [4].

Biomass can be converted to bio-fuel via different thermal, biological and physical processes. Nowadays there are mainly three ways frequently used to extract energy from biomass. These are: combustion (exothermic), gasification (exothermic) and pyrolysis (endothermic) [5]. Combustion is the oxidation of fuel in which biomass can be completely oxidized and transferred into heat. However, efficiency of this process is only about 10% and this manner of use is a source of substantial pollution [6, 7]. Gasification is a partly oxidizing process that converts a solid fuel into a gaseous fuel, while pyrolysis is the first stage of both combustion and gasification processes [8]. Therefore pyrolysis is not only an independent conversion technology, but also a part of gasification and combustion [9], which consists of a thermal degradation of the initial solid fuel into gases and liquids without an oxidizing agent.

Among the biomass to energy conversion processes, pyrolysis has attracted more interest in producing liquid fuel product because of its advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines, etc. Pyrolysis technology has the capability to produce bio-fuel with high fuel-to-feed ratios. In addition, solid biomass and waste are very difficult and costly to manage which also gives impetus to pyrolysis research. Some of these biomass species include beech wood [10], bagasse [11] woody biomass [12, 13], straws [141], seedcakes [15] and municipal solid waste (MSW) [16, 17].

The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process; thermal decomposition of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C in the absence of air/oxygen [18]. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis) temperature; biomass heating rate; pressure; reactor configuration; feedstock; etc. Depending on the operating condition, pyrolysis can be classified into three main categories: conventional, fast and flash pyrolysis. These differ in process temperature, heating rate, solid residence time, biomass particle size, etc. However, relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters [19, 20]. Yield of products resulting from biomass pyrolysis can be maximized as follows: (1) charcoal—a low temperature, low heating rate process, (2) liquid

products—a low temperature, high heating rate, short gas residence time process, and (3) fuel gas—a high temperature, low heating rate, long gas residence time process. Products from pyrrolysis processes also strongly depend on the water content in the biomass which produces large quantities of condensate water in the liquid phase [21]. This contributes to the extraction of water-soluble compounds from the gaseous and tar phases, and thus a greater decrease in gaseous and solid products [22]. Similar to char, about 10% to 35% of bio-gas is produced in slow pyrrolysis processes. However, a higher syngas yield is possible in flash pyrrolysis with high temperatures [23]. For example, He et al. investigated syngas production from pyrrolysis of MSW in a bench-scale downstream fixed-bed reactor over a temperature range of 750°C–900°C using calcined dolomite as a catalyst [24]. Their study achieved 78.87% gas yield at 900 °C. Likewise, Tang and Huang produced up to 76.64% syngas in a radio frequency plasma pyrrolysis reactor [25]. However, syngas yield is strongly influenced by the pyrrolysis temperature.

1.1 Design of experiments

Design of Experiments (DOE), is an alternative experimentation approach that maximizes learning using the minimum of resources. DOE is widely used in many fields with broad application in particular to improve manufacturing processes by the maximization of yield and decreasing variability. In addition, it can be used to optimize processes where no scientific theory or principles are available. Experimental design techniques become extremely important in such circumstances to develop new products and processes in an economical and robust manner. DOE is able to identify the significant variables affecting a process in the most efficient way, with subsequent optimization of the levels of these variables to achieve an improved quality and an increased productivity [26]. The methodology of DOE ensures that all variables and their interactions are systematically examined. Thus, information obtained from a DOE analysis is much more reliable and complete than those of OFAT experiments that ignore interactions and may lead to misleading conclusions [27].

1.2 Factorial designs

Factorial experiments enable to test the effect of all factors included in the investigation and the possible interactions between them on a measured response(s). At the time of which all the possible treatment combinations whilst associated with the factors and their levels are tested, the design is called a Full Factorial Design (FFD). Due to the large number of trials required, most of the FFD test the factors at two levels (minimum/maximum) and are called as the two levels Full Factorial Design. The number of runs required to test all possible combinations is 2^n, where n is the number of tested variables. The obtained data from the FFD are reliable with the highest level of confidence (high confidence designs are usually called resolution-5 design) [28].

For a low number of variables a Full Factorial Design was found to be the most appropriate choice; however as the number of tested variables increases the design becomes impractical due to the large number of the requested experiments. The two levels Fractional Factorial design in such case is highly desirable in terms of reducing the number of trials [29]. A Fractional Factorial Design is derived from the full factorial matrices by substituting the higher order interactions with new factors leading to reduced number of runs. This type of a design is called a resolution-4 design with a level of confidence lower than that of FFD. Fractional Factorial Design is usually a fraction, most commonly ½ or ¼, of the FFD. This

type of design is able to measure the main effect, either the two way interactions or some of the three ways interactions that are not aliased with any other effect, while the higher level of interaction are usually neglected by the design.

The presented study in this manuscript is directed towards the controlled disposal of some of the biomass fractions namely cane bagasse and rice straw in order to produce highly advantageous products. Specifically, this work is focusing on the conversion of these biomass fractions into certain fuel gases, hydrogen and methane, via a novel technique based on the utilization of a low temperature pyrolysis route assisted by the gamma irradiation. The current work reports an original and entirely new and novel methodology since no approaches have been previously investigated through literature up till now.

2. Experimental

2.1 Methodology

Two types of biomass based wastes namely; sugarcane bagasse [labelled as material type A] and rice straw [labelled as material type B] are introduced through this research work in order to produce fuel gases via the pyrrolysis technique. The chemical composition, elemental analyses and the physical properties of the selected feedstocks in this study are next reported in table 1. The selection of these two feedstocks had been based on certain national environmental problematic issues. Specifically, such types of biomass based waste have been two of the major contributor for the environmental pollution in Egypt. This in fact is due to the plantation of these crops regularly and in large quantities at the different cities around the country.

Feedstock	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Density (Kg/m3)	Ash Content (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)
Sugarcane bagasse	23–32	19–24	32–48	1198	3.2–5.5	48.2	7.4	5.7
Rice straw	18	32.1	24	200	4.3	44.5	6.3	29.1

Table 1. Physical properties and chemical compositions of materials A & B

The as received materials [A&B] were left, at the first place, for about 24h to dry under sunlight. Both materials were then introduced for a cut stage using electrical mill in order to obtain uniformly sized particles of about 2000 microns. The obtained grains were then subjected to the pyrolysis process; using low temperature autoclave, under different operating conditions of temperatures and times of thermal conversion. In practical, the pyrolysis processes of both materials A and B were carried out inside the autoclave at two temperatures, namely 100 and 200 ^{o}C. The pyrolysis processes were run for 2 or 4 hours at each operational temperature. The criteria of using such low operational temperatures had been based on the avoidance of the formation of any liquid products since the main goal of this study has been the conversion of the solid waste into fuel gases. The probability of the liquid hydrocarbons formation could be increased by running the pyrolysis at over 250 ^{o}C. In addition, the choice of the operational times to be 2 and 4 hours had been meant to allow the maximum possible conversion of the biomass to take place. This selection of the operational time was also based on preliminary Lab investigations were imposed, by the authors of this study, on the thermal conversion of the solid waste at different timing. In these investigations

it was detected that 2h as time interval could significantly affect the rate of conversion while running the pyrrolysis for more than 4h did not add any value to the process.

At the beginning, the autoclave after it was fully set up via charging the raw material inside, was left at the desired temperature for about 1h in order to obtain a steady state of the operational temperature as well as to get rid of any adsorbed water in the sample. The gas samples and the carbon species that were collected at the end of each run were then analysed using the gas chromatography (GC), for the gas fractions, and transmission electron microscopy (TEM) and Raman spectroscopy for the carbon ones. Potions of the raw samples [A and B] were then exposed for a Gamma radiation with intensity of 30 Kev for a certain time of 2h. The radiated samples have been labelled as A* and B* for the cane bagasse and rice straw respectively. These samples were then subjected to the pyrrolysis stage at the same operational conditions, as described before, in order to study the impact of the exposure of materials A and B to the radiation on both the composition of the obtained gas and the rate of the biomass-to-gas conversion either. The data collected from the experimental work were then a subject for analysis using a design of experiments model as illustrated in the following section.

2.2 Resolution IV Fractional Factorial Design:

Using DOE approach, the tested variables could be screened for their main effect and tp explore any possible interaction which could affect the process. Four variables including, Temperature, Time, Cane bagasse and Rice straw materials were tested on two levels (minimum and maximum), as shown in Table 2.

Variables	Code	unit	Minimum level (-)	Maximum level (+)
Temperature	A	°C	100	200
Cane Bagasse	B	-	Un-treated	Irradiated
Time	C	(hrs)	2	4
Rice Straw	D	-	Un-treated	Irradiated

Table 2. Variables investigated for Methane production via 2-level fractional factorial design

A matrix was generated via using Minitab 16 software in order to test the different operatimg conditions and the different combinations between the tested variables within the selected ranges (Table 3). Both the content of the methane gas im the produced gas and the rate of biomass conversion into gases were used as responses to be next calculated and optimized. These experiments had allowed an objective comparison of the significance and the main effect of each factor on the amount of the produced methane due to the operated conditions. The main effects of each variable were calculated using equation 2.1

$$E_{(Xi)} = \frac{2[\sum Y_i^+ - \sum Y_i^-]}{N}$$ (2.1)

where $E_{(Xi)}$ is the effect of the tested variable and Y_i^+ and Y_i^- are the responses at maximum and minimum levels, respectively. The significance level (P-value) of each variable was determined using the Student's t test (equation 2.2)

$$t_{(Xi)} = \frac{E_{(Xi)}}{SE}$$ (2.2)

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where (SE), the standard error of variables; calculated as the square root of the variance of an effect. Any variable with P < 0.1 was considered to be significant at 90% level of confidence.

The relationship between the response and the significant variables within the fractional factorial design can be expressed using the following equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4$$

(2.3)

where Y is the response variable, β_0 is the model intercept, β_i is the regression coefficient for each corresponding variable and X_i is the corresponding variable [30].

3. Results and Discussion

The continuous dependence on the fossil fuel as a main source for energy, of which its combustion usually produces greenhouse and toxic gases (such as SO_2, NO_x and other pollutants), take part directly in causing the global warming and environmental pollution [31, 32]. In line with, the biomass based wastes can be harmful for the environment if unutilized.

The unused biomass would otherwise be burned, land filled, degrade or accumulate in ecosystem and habitat. Biomass landfill leads to greenhouse gas emission, soil and water contamination, and depresses watershed and productivity [33-35]. Alternatively, the utilization of biomass and wastes as sources for energy production [36]; as proposed through this work can be considered as one of the promising renewable resources owing to their abundance, wide distribution worldwide as well as of being a cost effective solution.

3.1 Pyrrolysis of as received and irradiated feedstocks

Methane is a promising energy resource for transport applications in the medium term owing to abundant reserves in both conventional and unconventional resources, such as shale gas. Also, the relatively clean combustion products which are gained from methane can positively impact towards the environmental issues. The methane gas has been the dominant fraction in the composition of the produced gas out of the pyrolysis process which was carried out during this work using two different types of biomass stocks. The conversion rates of the two different types of biomass, used in this study, into gases as well as the compositions of the acquired gases are next illustrated in Tables 3 and 4.

Material Type	Temperature (°C)	Time (hrs)	Methane Gas Content %	Biomass Conversion %
A	100	2	97	35
A	100	4	98.5	42
A	200	2	99	47
A	200	4	100	55
A*	100	2	97	39
A*	100	4	99	45
A*	200	2	99.5	56
A*	200	4	100	62

Table 3. Operational conditions and conversion rates of Materials type A & A*

Material Type	Temperature (°C)	Time (hrs)	Methane Gas Content %	Biomass Conversion %
B	100	2	0	0
B	100	4	0	0
B	200	2	78	51
B	200	4	82	56
B*	100	2	0	0
B*	100	4	0	0
B*	200	2	95	61
B*	200	4	98	71

Table 4. Methane gas outcome and conversion rates acquired of Materials type B & B at different operational conditions.*

Table 3 shows the dependency of both the operational time and temperature to the rate of biomass conversion into gas, using material type A. In practical, the conversion rate has increased for about 30 % as the temperature increased to the double while the operational times remained the same. In line with, the rate of biomass conversion to gas had increased for about 20 %. when the time boosted from 2 to 4 hours at the same operational temperature. On the other hand, the composition of the produced gases out of the experiments in which material type A was utilized has not been remarkably influenced. In particular, the lowest methane content was 97% at a processing time of 2h and under operational temperature of 100 ^{o}C whilst the remains of the gained gas were approximately equal percentages of C_2 and C_3 gases. The CH_4 percentages had come up to 100% as both the operational temperature and time increased to 200°C and 4h respectively.

The domination of methane in the produced gas can be referred to the slight cracking that had taken place in the poly saccharides molecules (which are forming to the cane bagasse feedstock) due to the effect of the low pyrolysis temperatures, as utilized so far. These temperatures were highly likely just sufficient to break up the terminal C-H bonds in the poly saccharides molecules which are less strong than the C-O and O-H bonds which are highly polar and require much energy. The orientation of the thermal energy; that was provided during the pyrolysis, towards the cleavage of the C-H bonds can be obviously confirmed through the composition of the produced gas since it's mainly consisted of C_1 to C_3 fractions.

According to table 3, the irradiated cane bagasse (samples A*) have displayed the same trend as the un-treated ones in terms of the increment of the solid-to-gas conversion rate by increasing either the operational temperature or the time. In general, the conversion rates which were obtained via introducing A* in the pyrolysis system were higher at all testing conditions, compared to material type A. This can be explained as a result of the pre-treatment of the biomass based waste via using gamma ray before the pyrolysis stage. The exposure to the radiation for 2h had probably made some fragmentations of the high molecular weight structures within the biomass stock. The exposure to radiation had likely contributed in opening the external complicated structure of the cane bagasse which in turn might facilitate the conversion process. Nevertheless, a different tendency was detected by material A* in comparison to the type A. In particular, at the same operating temperature, when the time increased from 2 to 4 hours the conversion rate was decreased from 20 to 15% and from 17 to 10% respectively while the temperature was 100 and 200 in order. This can be referred to the open external structure acquired in type A* due to the radiation impact which had probably made the longer retention time of the sample inside the autoclave is not a highly effective parameter since the conversion to gas could take place rapidly.

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On the other hand, material type B had shown different attitude on both the levels of the solid-to-gas conversion and the produced gas composition. No conversion had occurred using an operating temperature of $100^{o}C$ either at the testing times of 2 or 4 hours. This might be explained due to the insufficient provided energy to crack up the highly complicated structure of the rice straws as a result of its swerved morphology at the external side. Similar conversion rate, to what was produced out from sample A, was then obtained via applying operational conditions of 4h and at 200 ^{o}C. However the material type B* (the irradiated rice straw) had shown a significant change in both the conversion percentages of the solid waste to gas and the composition of the produced gas. The conversion was obviously increased to about 26 % higher than in the case of material B while the methane content had reached 98% instead of 82, at the same operating conditions. This can reflect the remarkable influence of the gamma radiation on the pyrolysis behavior of material B*. The remains of the produced gas composition was mainly CO either using material b or B*. This can be referred to the high oxygen content in the raw rice straw, see table 1.

Accordingly, the data given through table 4 can also display certain differences between the nature of the raw materials, A and B. The detected change in both the conversion rate of the solid waste to gas as well as the acquired gas composition can illustrate the different morphologies of both materials. In particular, materials type A has got a complicated firmly closed structure from both inside and outside. This might clarify the non-massive impact of exposing material A to the radiation, in reference to the results of material A*. Unlike material A, material type B was highly influenced via the exposure to the radiation, as prior discussed. This can be attributed to the morphology of material B in terms of having a highly gridlocked external structure while it has got a quite simpler and open one from the internal side.

3.2 Simulative model claimed trials

At the completion of the designed experiments (as described in section 2.1) as well as after the collection of all their results (as shown in section 3.1), all the data were subjected to the design of experiment module. Several trials were claimed by the simulation module to be carried out experimentally. The software generated a matrix of different combinations of the tested variables. Each trial contains the four tested variables either at its maximum or minimum (as displayed at Table 2), The details of the requested trials and the experimental results collected by the end of the eight trials are displayed in Table 5.

Trials	Variables				Responses	
	Temperature (°C)	Cane Bagasse	Time (hrs)	Rice Straw	Methane Gas Content (Vol %)	Biomass Conversion Rate Wt. %
1	200	A*	2	B	86	52.4
2	200	A*	4	B*	98.5	63.7
3	100	A*	4	B	48.2	23.8
4	100	A	4	B*	49	20.6
5	200	A	2	B*	96.3	55.5
6	100	A*	2	B*	48	20.2
7	100	A	2	B	48.8	17
8	200	A	4	B	89.9	54.7

Table 5. The generated matrix and the calculated responses for the Fractional Factorial Design for testing the main effect and the interactions of the variables under investigation. Four variables were tested including Temperature, Time and two different biomasses (Rice Straw and Cane Bagasse) which could be either untreated or irradiated.

According to the obtained results, the maximum amount of the produced Methane was approximately 98 (at trial number 2) when the temperature was 200°C, 4 hours as a retention time and irradiated Biomass (for both Rice straw and Cane bagasse). So, radiation, relatively high temperature and long running time lead to the maximum yield of productivity. All the acquired data were then a subject of investigation by the simulation module. All the results were then sent back to the module to find out about the simulation responses and also in order to attain the optimization to the best operational conditions.

The experimental runs were performed in a randomised order as indicated in Table 5 with different combinations between the different tested variables. Each value in the variable section represents the level at which the independent variable was present in the experiment, while each value in the response section shows the responses in terms of the gas composition and solid to gas conversion rate (%) for the experimental trial (represented by the rows). The experimental responses were subjected to multi-way analysis of variance (ANOVA) and the parameter estimates,-. Results are summarized in Table 6. The P-values designate statistical confidence of a factor estimate. A P-value of < 0.1 was used as a cut-off point indicating the statistical significance of a factor at 90% confidence level. Factor(s) with a P-value >1 was excluded from the model and was treated as noise. Table 6 shows the statistical analysis for the main effect and the interaction of the tested variables on the content of the Methane Gas in the produced gas as a calculated response.

Term	Effect	Coefficient	T-Value	P-Value
A: Temperature	44.175	22.0875	75.69	**0.000**
C: Time	1.6250	0.8125	2.78	0.108
D: Rice Straw	4.7250	2.3625	8.10	**0. 015**
AC: Temperature*Time	1.4250	0.7125	2.44	0.135
AD: Temperature*Rice Straw	4.7250	2.3625	8.10	**0.015**

Table 6. Estimated Effects and Coefficients for Methane Gas content (in coded units)

The Pareto chart plot (Fig 1) with the displayed P-values and effects illustrate the order of significance of the variables affecting the methane production.
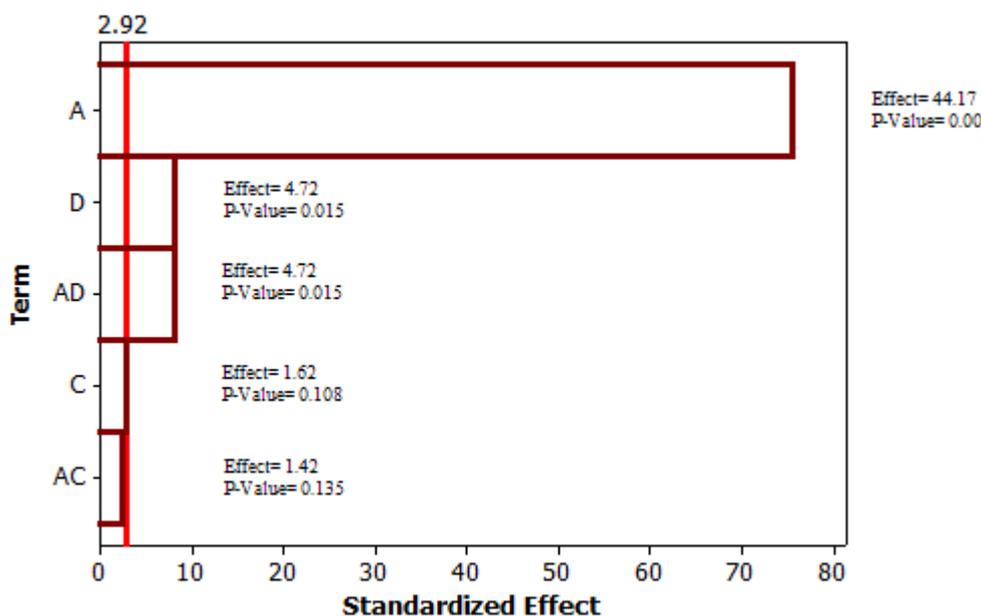
Figure 1. Pareto Chart for the Fractional Factorial Design to study the main effect and the two way interactions of the tested variables on the Gas Composition where, any factor cross the line will be considered significant. Factors are coded as follows: A is Temperature, C is Time and D is Rice Straw.

The statistical analysis of the variables and their effect on gas composition response revealed that the temperature was the most significant factor with 200°C as the preferred value. In order to attain the best gas composition, it was obvious that the irradiated rice straw was preferred. In addition, the interaction between the temperature and rice straw was found to be strongly significant as well. This interaction had indicated that the higher is the operational temperature, the more efficient is the pyrrolysis process when the irradiated biomass was used.

DOE is much more efficient than One Factor At a Time (OFAT) experiments, since it can detect the effect of interaction among several variables which is completely ignored when performing the OFAT experiment. Generally, in many processes; the interaction could be more significant than the main effect of each variable individually, which was obviously detected in the designed process throughout this work. In particular, it is due the significant effect of the interaction between temperature and the rice straw as well as the effect of time and the cane bagasse; however the first had deeply impacted.

The statistical analysis also showed that the long operational time is preferred. On the other hand, it was obvious that the utilization of either pre-treated or untreated cane bagasse has no strong influence on the produced gas composition. The relation between the variables, their interactions and response could be modeled as following:

$$\text{Gas Composition} = 8.3 + 0.39\ A - 1.325\ C - 4.72\ D + 0.014\ AC + 0.047\ AD$$

As previously done, the obtained results of the rate of the biomass conversion-to-gas was exposed to a multi-way ANOVA to determine the statistical significance of the effect of each variable individually and any possible interaction (as shown at Table 7).

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Term	Effect	Coefficient	T-Value	P-Value
A: Temperature	36.175	18.0875	289.40	**0.002**
B: Cane Bagasse	3.075	1.5375	24.60	**0.026**
C: Time	4.425	2.2125	35.40	**0.018**
D: Rice Straw	3.025	1.5125	24.20	**0.026**
AC: Temperature*Time	0.825	0.4125	6.60	**0.096**
AD: Temperature*Rice Straw	3.025	1.5125	24.20	**0.026**

Table 7. Estimated Effects and Coefficients for Rate of biomass Conversion (coded units)

The Pareto chart plot (Fig 2), with the displayed P-values and effects, illustrate the order of significance of the variables affecting the rate of biomass-to-gas conversion.
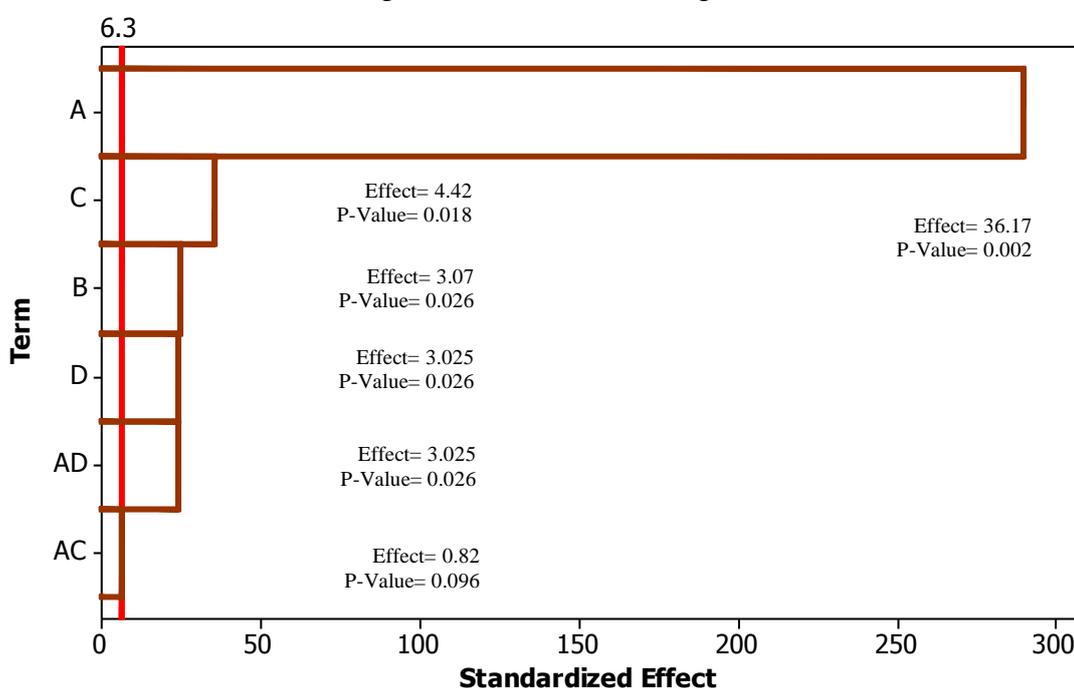
Figure 2. Pareto Chart for the Fractional Factorial Design to study the main effect and the two way interactions of the tested variables on the rate of biomass conversion where, any factor cross the line will be considered significant. Factors are coded as follows: A is Temperature, B is Cane Bagasse, C is Time and D is Rice Straw.

With regard to the rate of conversion as it was responded by the model, temperature was found to be the most significant factor affecting the process of solid-to-gas conversion. The effect of the other variables on both the rate of conversion and the composition of the obtained gas was the same, according to the model response. In reference to the cane bagasse type of biomass, the irradiated feedstock was rather preferred than the untreated one since no remarkable influences on the outcomes of the thermal process were detected.

The used first order polynomial models, in terms of the coded factors, were as follows:

Rate of Conversion= -18.7+ 0.33 A+ 1.53 B+ 0.98 C- 3.02 D+ 0.008 AC+ 0.03 AD

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3.3 Carbon black characterization

The by-products which were obtained at the end of the pyrrolysis experiments; attained at the highest conversion rate of the solid biomass (A* and B*) to gas, were then subjected to characterization using Raman spectroscopy and TEM. These by-products, as they were visually inspected, had come as black species which are commonly known as carbon black. The characteristics of these species are given in figures 3 and 4.
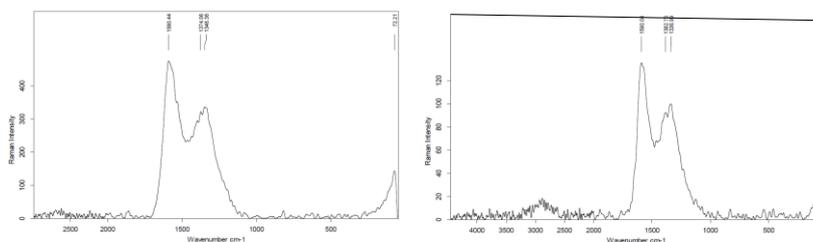
Figure 3. Raman spectrum for carbon black samples obtained at 200 ^{o}C out of (a) material type A (b) material type B*.*
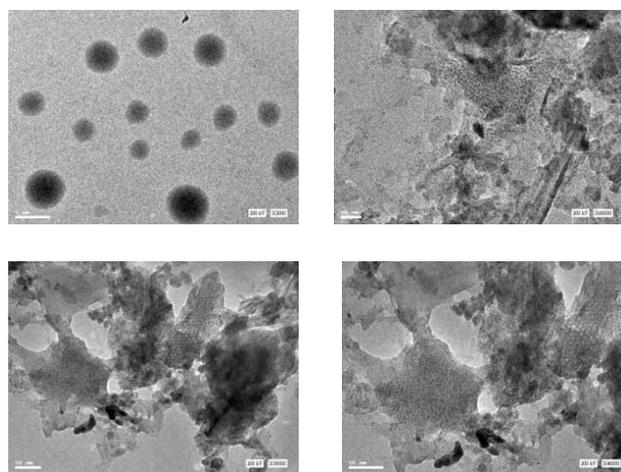
Figure 4. TEM images at different magnifications of material type B* given in figure 3b

The Raman spectrums given in figure 3 had shown different structures of the carbon species obtained out from both A* and B*. in particular, figure 3a showed two broad peaks located between 1300 and 1600 cm^{-1} which are indicative for carbon species while two intense peaks was detected at the same range in figure 3b. Unlike figure 3a, figure 3b had displayed the presence of some non-intense peaks in the range of 500-1000 cm^{-1} which indicate the formation of some nano-carbon species. The two different morphological structures of the acquired carbons can clarify the differences in the structure of both raw biomass feedstocks. This also can confirm the dissimilar behaviour of both material A and B as well as their derivatives (A* and B*) during the pyrrolysis procedures as previously illustrated.

Figure 4, exhibited the TEM micrographs of the carbon black species that had been illustrated before in figure 3b. The given images show spheres of carbon ranged in size between ca 300 and 900 nm. At higher magnifications, the TEM showed a highly porous nature of the obtained carbon. The shown pores throughout the images can be classified into two different categories; namely macro and micro pores. This porous structure might have played an important role in the amount of gas released during the pyrrolysis since they could get a part of the gases molecules caged inside them via the adsorption mechanism.

3.4 Hydrogen production

The structure of the obtained carbon species as detected through the TEM images (figure 4), had suggested a high probability of capturing some gases within their structure owing to their porous nature. Methane, CO and hydrogen are the common gases which are normally produced from the pyrrolysis of biomass based wastes. So, an expectation for the presence of some hydrogen (if there any gas is adsorbed within the carbon structure) had been aroused by the authors of this study. A reasonable percentage of hydrogen was produced throughout this study using the material type B* and at an operational conditions of 300 ^{o}C and 4h. The selection of material type B* as well as the processing time had based on achieving the highest conversion rate; as prior discussed in section 3.1, at such operating conditions. The composition of the produced gas at these conditions was 70% methane and 30% hydrogen. In 2001, Cheng and his co-workers had reported that the carbon structures have got the ability to adsorb hydrogen and to get hydrogen storage at temperatures between 25 and about 225 ^{o}C. They also stated that desorption of the hydrogen molecules from the carbon structures; especially the nano-carbon ones, is usually starting to take place at temperatures above 250 ^{o}C [37]. In line with, in another investigation it was found that the hydrogen desorption starts at 175 ^{o}C for the Nobel metals such as Pt however for the carbon based structures it occurs at much elevated temperatures, Miller and his co-authors reported in 1993 [38]. This in fact can explain the criteria of selecting the operational temperature to be as high as 300 ^{o}C during the investigation on any adsorbed gases in the carbon species.

On the other hand, the solid waste-to-gas conversion had remained nearly constant, particularly 72%. The detection of the same conversion rate while obtaining hydrogen gas might be referred to the capture of the hydrogen gas into the porous structure of the carbon species at the lower temperatures, due to the carbon high adsorb-ability characteristics. This low operational temperature might be not enough [low de-binding energy] to release the H_2 out of the carbon pores via the desorption technique.

This finding could indicate that a strongly electrostatic and adsorption interaction took place between the H_2 molecules and the carbon surface as well as within its internal pores. The population of the produced hydrogen at elevated temperature can significantly reflect the adsorption behavior and the storage of hydrogen at the lower temperatures. This in turn might show that the hydrogen adduct is highly related to the intra-molecular bonding of H_2 and the relative geometric properties of the carbon species that is formed during the pyrrolysis.

4. Conclusion

The current research work has reported an innovative methodology for the thermal conversion of the biomass based waste into a certain types of fuel gases via the pyrrolysis technique and assisted by a pre-treatment of the feedstocks using Gamma radiation. Two types of the biomass based wastes had been selected for the presented investigation. The selection of these two types had based on being two of the major pollutants nationally. The chemical and elemental characteristics of the selected wastes were determined before executing the pyrolysis process. The experimental data had shown promising results on both the levels of the solid waste conversion to gas as well as on the composition of the produced gas; namely orientated towards the natural gas fraction. Both the experimental work and the simulative model have been matched together in the effect of the operating temperature on both the rate of conversion and the produced gas composition. In particular, temperature showed the most significant parameter on the percentage of methane in the produced gas as well as on the solid-to-gas conversion ratio. On the other hand, the simulative model had concluded that the effect of all the other variables was neutral on the rate of conversion and the gas composition, as responded via the claimed trials. Unlike in the case of using rice straw, the model had reported that the samples of the cane bagasse either irradiated or untreated did not show remarkable influences on the outcomes of the pyrolysis process; namely on the gas composition however it had slightly affected the conversion rate of biomass to gas.

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