

Thermal Processing Technologies for Biomass Conversion to Green Heat, Fuel and Power

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Abstract

Biomass is now accepted as having the potential to provide a major part of the projected renewable energy provisions of the future. There are three main routes to providing these bio-fuels, such as biological conversion, physical conversion, and thermal conversion. The pyrolysis of biomass is a promising route for the production of solid (charcoal), liquid (tar and other organics), and gaseous products. These products are of interest as they are possible alternate sources of fuels and chemicals. In the experimental study, fast pyrolysis of hazelnut cupula was investigated in a fixed-bed reactor under various conditions. Hazelnut cupula, an agricultural by-product, was selected as raw material for pyrolysis experiments. On the other hand, pyrolysis yields and conversion efficiencies depended mainly on pyrolysis temperatures. 600 °C was the most suitable temperature for decomposition of the hazelnut cupula to reach maximum oil yield.

Keywords: Biomass; thermal processing; pyrolysis; gasification; fuels; chemicals; renewables

1. Introduction

Bioenergy has several unique characteristics that distinguish it from other renewable energy sources (RES) that can be considered as either advantages or disadvantages [1]. But on the whole, biomass offers good potential as an important RES of the future [2]. Biomass already makes an important contribution to the global energy supply. Biomass is defined as any plant matter used directly as fuel or converted into other forms before combustion. Included are wood, vegetal waste, animal materials/wastes, black liquor,

and agricultural solid biomass [3]. On the other hand, biomass in the form of biofuels is the only RES that can directly replace fossil fuels, either fully or in blends of various percentages. In the latter case, the replacement can often be implemented without requiring any equipment modifications [4]. In the case of co-utilization with fossil fuels and subsequent carbon sequestration, bioenergy offers the only option to withdraw carbon from the environment [5-9]. Figure 1 shows the possibilities of biomass utilization.

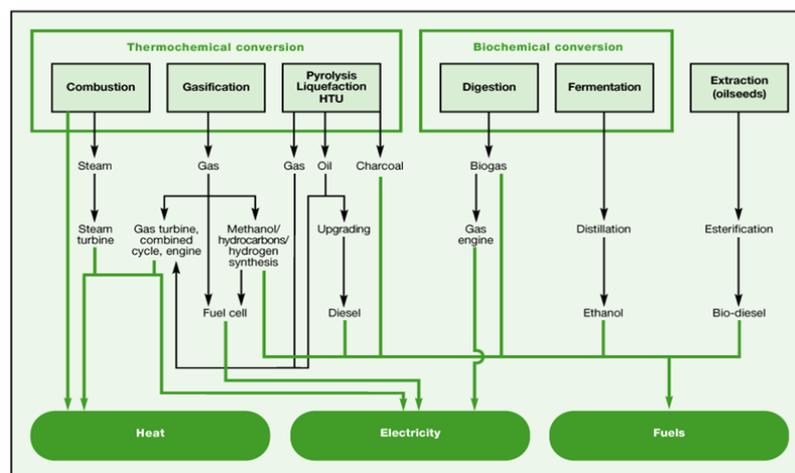


Figure 1. Possibilities of biomass utilization with high energy yield.

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2. Thermal Processing of Biomass

2.1. Combustion

Combustion of biomass and related materials is widely practiced commercially to provide heat and power [10-12]. The technology is commercially available and presents minimum risk to investors. The product is heat, which must be used immediately for heat and/or power generation as storage is not a viable option. Overall efficiencies to power tend to be rather low at typically 20% for small plants and up to 30% for larger and newer plants [12-14]. Costs are only currently competitive when wastes are used as feed material such as from pulp and paper and agriculture. Emissions and ash handling remain technical problems. The technology is widely available commercially and there are many successful working examples throughout North America and Europe utilizing forestry, agricultural, and industrial wastes [12].

2.2. Gasification

Fuel gas can be produced from biomass and related materials by either partial oxidation to give a mixture of CO, CO₂, H₂, and CH₄. Gasification occurs in several sequential steps [9]:

- Drying to evaporate moisture
- Pyrolysis to give gas, vaporized tars, or oils and a solid char residue
- Gasification or partial oxidation of the solid char, pyrolysis tars, and gases

When a solid fuel such as biomass was heated to 300°C-500°C in the absence of an oxidizing agent, pyrolysis to solid char, condensable hydrocarbons, and gases occurred. The relative yields of gas, liquid, and char depend mostly on the rate of heating and the final temperature. In gasification, pyrolysis proceeds at a much quicker rate than gasification and the latter is thus the rate-controlling step. The gas, liquid, and solid products of pyrolysis then react with the air to give permanent gases of CO, CO₂, H₂, and lesser quantities of hydrocarbon gases [15]. Char gasification is the interactive combination of several gas-solid and gas-gas reactions in which solid carbon is oxidized to carbon monoxide and carbon dioxide, and hydrogen is generated through the water gas shift reaction [16]. The gas-solid reactions of char oxidation are the slowest and limit the overall rate of the gasification process. Many of the reactions are catalyzed by the alkali metals present in wood ash, but still do not reach equilibrium. The gas composition is influenced by many factors such as feed composition, water content, reaction temperature, and the extent of oxidation of the pyrolysis products [6].

Not all of the liquid products from the pyrolysis step are completely converted due to the physical or geometrical limitations of the reactor and the chemical limitations of the reactions involved, and these give rise to contaminant tars in the final product gas. Due to the higher temperatures involved in gasification compared to pyrolysis, these tars tend to be refractory and are difficult to remove by thermal, catalytic, or physical processes. This aspect of tar cracking or removal in gas cleanup is one of the most important technical uncertainties in implementation of gasification technologies [16].

Atmospheric circulating fluidized bed gasifiers (Figure 2 and 3) have proven very reliable with a variety of feedstocks and are relatively easy to scale up from a few MW_{th} up to 100 MW_{th}. Even for capacities above 100 MW_{th}, there is confidence that the industry would be able to provide reliable gasifiers. This appears to be the preferred system for large-scale applications and is used by most industrial companies; these systems, therefore, have high market attractiveness and are technically well-proven.

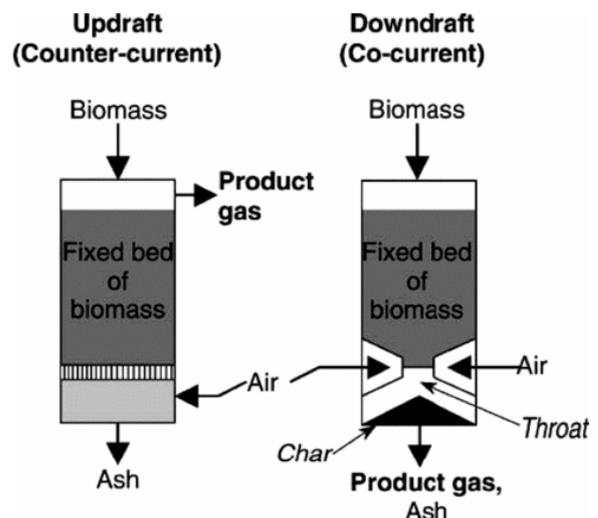


Figure 2. Fixed bed gasifiers.

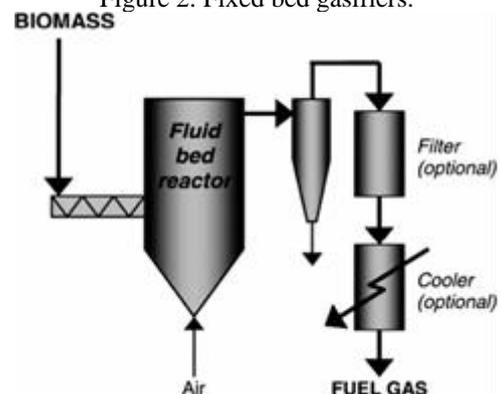


Figure 3. Fluid bed gasifier.

Atmospheric downdraft gasifiers are attractive for small-scale applications up to about 1.5 MW_{th} as there is a very big market in both developed and developing economies. However, the problem of efficient tar removal is still a major problem and a higher level of automation is needed especially for small-scale industrial applications. Nevertheless, recent progress in catalytic conversion of tar gives more credible options and these systems can therefore be considered to be average technical strength [7].

2.3. Pyrolysis of Biomass

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Lower process temperature and longer vapor residence times favor the production of charcoal [10]. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapor residence time are optimum for producing liquids. Table 1 shows the product distribution obtained from different modes of the pyrolysis process. Fast pyrolysis for liquid production is of particular interest currently.

Table 1. Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood [17]

		Liquid (%)	Char (%)	Gas (%)
Fast pyrolysis	Moderate temperature, short residence time	75	12	13
Carbonization	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence times	5	10	85

Fast pyrolysis occurs in a time of a few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. The critical issue is to bring the reacting biomass particle to the optimum process temperature and minimize its exposure to the intermediate (lower) temperatures that favor formation of charcoal [10]. One way this objective can be achieved is by using small particles, for example in the fluidized bed processes that are described later. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source [12]. On the other hand, in fast pyrolysis, biomass decomposes to generate mostly vapors and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid [10-15].

The main product, bio-oil, is obtained in yields of up to 75 wt% on dry feed basis, together with by-product char and gas which are used within the process so there are no waste streams other than flue gas and ash [8]. On the other hand, a fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimize the water in the product

liquid oil, grinding the feed to give sufficiently small particles to ensure rapid reaction, pyrolysis reaction, separation of solids (char), and collection of the liquid product (bio-oil) [21]. Any form of biomass can be considered for fast pyrolysis [12]. Table 2 shows some biomass energy technology pathways.

In wood-derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts [1-6]. A current comprehensive review focuses on the recent developments in wood/biomass pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of fast wood pyrolysis [6]. Sufficient hydrogen added to the synthesis gas to convert all of the biomass carbon into methanol carbon would more than double the methanol produced from the same biomass base [5].

Rapid heating and rapid quenching produced the intermediate pyrolysis liquid products, which condense before further reactions break down higher-molecular-weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher, fast pyrolysis temperatures, the major product is gas. Many researchers have attempted to exploit the complex degradation mechanisms by conducting pyrolysis in unusual environments [8-16]. The main pyrolysis variants are listed in Table 3.

Table 2. Some biomass energy conversion technology pathways [11]

Electricity	
All systems include biomass feedstock plus Generator set; some may provide low to medium temperature heat (cogeneration)	-combustion boiler + steam turbine -thermal gasification: gasifier + gas turbine or gas engine -external combustion engine + generator -anaerobic fermentation: biogas digester – gas engine
Transport fuels	
Sugar and starch crops (sugarcane)	-fermentation + distillation – ethanol
Lignocellulosic biomass	-hydrolysis + fermentation – ethanol -gasification + gas processing – methanol, hydrogen -gasification + Fischer-Tropsch synthesis – synthetic gasoline
Oil seed crops	-esterification-biodiesel
Cooking energy	
Wood, woody residues	-charcoal
Wood wastes, residues	-briquettes, pellets
Sugar and starch crops	-ethanol (+ gel)
Prepared biomass	-gasifier-producer gas (+ methanol)
Biomass & animal wastes	-biogas digester – biogas
Process heat	
Any biomass	-direct combustion
Prepared biomass	-gasifier-producer gas
Pyrolysis oils	-substitute for fuel oil

Table 3. Pyrolysis methods and their variants [36]

Pyrolysis technology	Residence time	Heating rate	Temperature (°C)	Products
carbonization	Days	Very low	400	charcoal
conventional	5-30 min	Low	600	oil, gas, char
Fast	0.5-5.0 s	very high	650	bio-oil
flash-liquid	< 1 s	High	< 650	bio-oil
Flash-gas	< 1 s	High	< 650	chemicals, gas
Ultra	< 0.5 s	very high	1000	chemicals, gas
Vacuum	2-30 s	medium	400	bio-oil
Hydro-pyrolysis	< 10 s	high	< 500	bio-oil
Methanol-pyrolysis	< 10 s	high	> 700	chemicals

Pyrolysis is the simplest and, almost certainly, the oldest method of processing one fuel in order to produce a better one [20]. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (gasification), water (steam gasification), or hydrogen (hydrogenation). One of the most useful products is methane, which is a suitable fuel for electricity generation using high-efficiency gas turbines [10]. On the other hand, the biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing [6].

The pyrolysis of biomass is a thermal treatment that results in the production of charcoal, liquid, and gaseous products. Among the liquid products, methanol is one of the most valuable products [9, 10, 13]. The liquid fraction of the pyrolysis products consists of 2 phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase were higher than those of the non-aqueous phase. The point where the cost of producing energy from fossil fuels exceeds the cost of biomass fuels has been reached. With a few

exceptions, energy from fossil fuels will cost more money than the same amount of energy supplied through biomass conversion [15].

The bio-oil formed at 450 °C contained high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, and 2-Cyclopenten-1-one, etc. A significant characteristic of the bio-oils was the high percentage of alkylated compounds, especially methyl derivatives. As the temperature increased, some of these compounds were transformed via hydrolysis [38]. The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways such as dehydration, cyclization, Diels-Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexandione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% [4-8].

2.3.1. Reaction Mechanism of Pyrolysis

Thermal depolymerization and degradation of biomass, cellulose, hemicelluloses, and products were formed as well as a solid residue of charcoal. The mechanism of the pyrolytic degradation of structural components of the biomass samples was separately studied. If wood is completely pyrolyzed, hemicelluloses break down first at temperatures of 197 °C to 257 °C and cellulose follows in the temperature range of 237 to 347 °C, with lignin being the last component to pyrolyze at temperatures of 277 to 497 °C. The general changes that occur during pyrolysis are enumerated below [1-13]:

- Heat transfer from a heat source, to increase the temperature inside the fuel;
- The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char;
- The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel;
- Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar;
- Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and
- Further thermal decomposition, reforming, water gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the process's residence time/temperature/pressure profile.

A comparison of pyrolysis, ignition, and combustion of coal and biomass particles reveals the following [5-8]:

- Pyrolysis starts earlier for biomass compared with coal.
- The volatility matter (VM) content of biomass is higher compared with that of coal.
- The fractional heat contribution by VM in biomass is on the order of 70% compared with 36% for coal.
- Biomass char has more O₂ compared with coal. The fractional heat contribution by biomass is on the order of 30% compared with 70% for coal.
- The heating value of volatiles is lower for biomass compared with that of coal.
- Pyrolysis of biomass chars mostly releases CO, CO₂, and H₂O.
- Biomass has ash that is more alkaline in nature, which may aggravate fouling problems.

The organic compounds from biomass pyrolysis are the following groups [3-6]:

- A gas fraction containing CO, CO₂, some hydrocarbons, and H₂.
- A condensable fraction containing H₂O and low molecular weight organic compounds (aldehydes, acids, ketones, and alcohols).
- A tar fraction containing higher molecular weight sugar residues, furan derivatives, phenolic compounds, and airborne particles of tar and charred material that form the smoke.

Destructive reaction of cellulose is started at temperatures lower than 52 °C and is characterized by a decreasing polymerization degree [20]. Thermal degradation of cellulose proceeds through a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The glucose chains in cellulose are first cleaved to glucose and, in the second stage, glucosan is formed by the splitting off of one molecule of water. Initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation [19]. Dehydration reactions around 200 °C are primarily responsible for thermal degradation of lignin. Between 150 °C and 300 °C, cleavage of α - and β -aryl-alkyl-ether linkages occurs. Around 300 °C, aliphatic side chains start splitting off from the aromatic ring. Finally, carbon-carbon linkage between lignin structural units is cleaved at 370-400 °C. Degradation reaction of lignin

is an exothermic reaction, with peaks occurring between 226 °C and 450 °C; the temperatures and amplitudes of these peaks depend on whether samples were pyrolyzed under nitrogen or air [1-12].

The mechanism of pyrolysis reactions of biomass was extensively discussed in an earlier study [13]. Water is formed by dehydration. In the pyrolysis reactions, methanol arises from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Methanol also arises from methoxyl groups of uronic acid. Acetic acid is formed in the thermal decomposition of all three main components of wood. When the yield of acetic acid originating from the cellulose, hemicelluloses, and lignin is taken into account, the total is considerably less than the yield from the wood itself [2, 3, 5, 7].

3. Experimental Study of Biomass Pyrolysis

3.1. Materials and Method

Tea bush, walnut shell, and pine cone are utilized as raw materials in rapid pyrolysis studies. All biomass samples utilized are first cut into 1–2 cm spalls, and each biomass sample is ground in a mill. Afterward,

the samples are passed through appropriate sieves to separate the ground samples into the predetermined particle size. When agricultural products are placed in a particular environment, they exchange moisture with their environment. If the vapor pressure of the water in the product is greater than the partial vapor pressure of the water vapor in the ambient air, water vapor is released from the product into the environment. Conversely, water vapor transfers from the ambient air to the product. These moisture transitions continue until the vapor pressures of both environments equalize. When the equilibrium condition occurs, changes in the moisture value of the product cease. For this purpose, biomass sample mixtures were mixed in equal proportions and spread in a thin layer on a flat, clean surface for ten days to equilibrate with the humidity in the laboratory environment. The pyrolysis studies were carried out in a 70 cm³ fixed-bed tubular reactor built of stainless-steel pipe and put in an insulated ceramic pipe. While Figure 4 shows the raw materials and mixtures used in fast pyrolysis experiments, Figure 5 depicts the fast pyrolysis reactor [15, 16].



Figure 4. The biomass samples; 1. mixed biomass samples, 2. walnut shell, 3. tea bush, 4. pine cone.

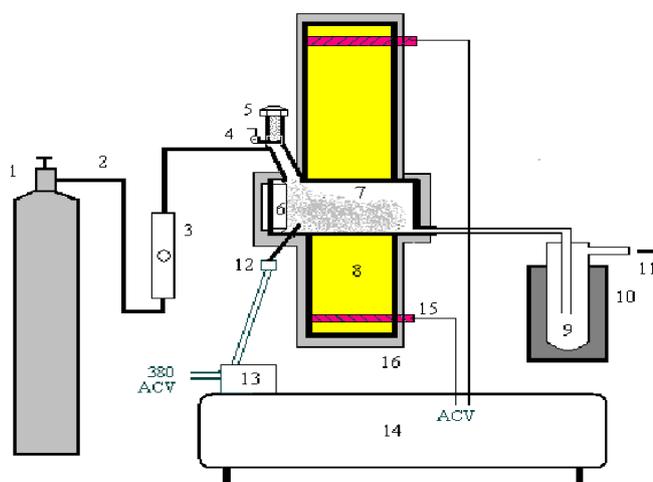


Figure 5. Fixed-bed reactor for experimental purposes; 1. N₂ gas tube, 3. Flow-meter, 5. Valve, 7. Pyrolysis unit, 8. Inductive reactor, 9. Liquid collecting container, 10. Cooling unit, 11. Gas to atmosphere, 14. Power supply.

3.2. Effect of Temperature on Pyrolysis Product Yields

The temperature parameter used in the pyrolysis experiments of biomass significantly affects the yield and amount of the product formed as a result of pyrolysis. The bio-oil yields typically reach their highest concentrations between 400 and 550 °C and then start to fall as the heating process continues. The dominating secondary cracking reactions cause the bio-oil and char products to turn into gas at temperatures greater than 600 °C [16]. The bio-oil polar, aliphatic, and aromatic fractions are enhanced by raising the temperature from 300 to 500 °C to 600 to 800 °C [15]. The decarboxylation and dehydration

processes at temperatures above 700 °C often increase the carbon content of bio-oils in the form of polycyclic aromatic hydrocarbons like pyrene and phenanthrene. While the liquid product efficiency increases at medium temperatures (400–500 °C), it declines as the temperature rises due to secondary processes that favor vapor breakdown [16]. The figures show the influence of pyrolysis temperature on product efficiency at dissimilar heating rates of the biomass combination employed at 300, 400, 500, 600, and 750 °C, as well as at 50 cm³.min⁻¹, where the maximum liquid production is obtained. Figure 6 and 7 show the maximum liquid yield is obtained at 500 °C, with a value of 69.77 wt% [15].

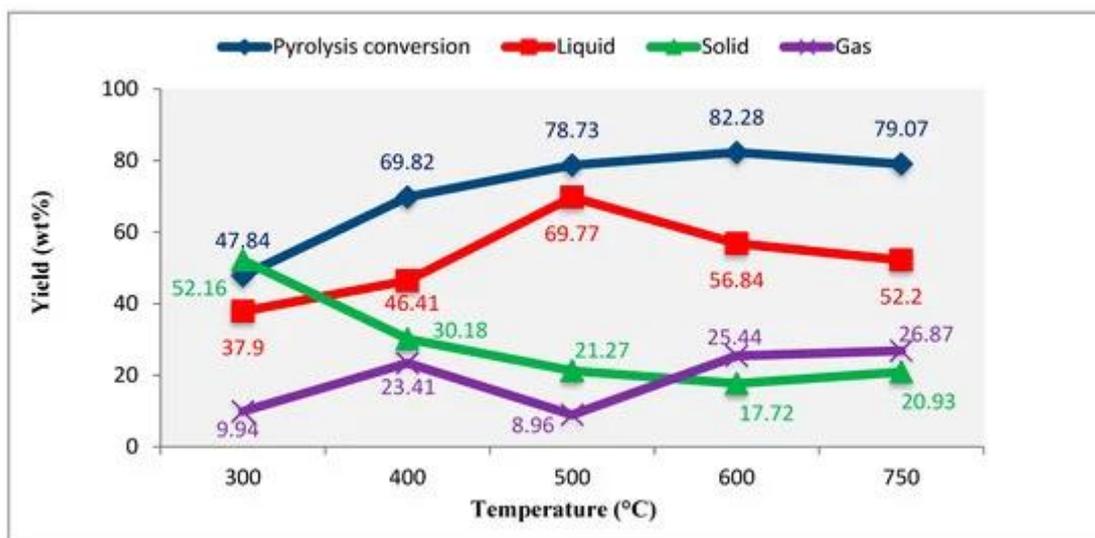


Figure 6. The effect of pyrolysis temperature on the product yield of 50 cm³.min⁻¹ nitrogen flow rate and 100 °C.min⁻¹ heating rate on biomass mixture pyrolysis.

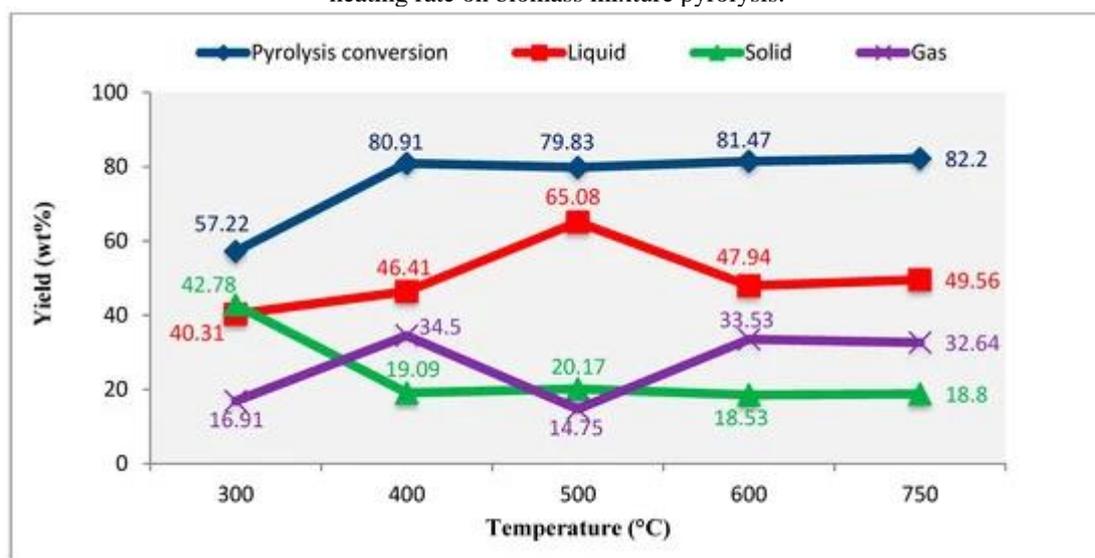


Figure 7. The effect of pyrolysis temperature on the product yield of 50 cm³.min⁻¹ nitrogen flow rate and 250 °C.min⁻¹ heating rate on biomass mixture pyrolysis.

5. Conclusions

Biomass is a source of gaseous, liquid, charcoal fuels, and chemical raw materials. The biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing. For maximization of the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For a high char production, a low temperature, low heating rate process would be chosen. For maximization of the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred.

After the proximate analysis procedures and the calorific value of the combination are determined, the heating value of the bio-oil acquired from the fast pyrolysis experiments under the most efficient circumstances ($50 \text{ cm}^3 \cdot \text{min}^{-1}$, $500 \text{ }^\circ\text{C}$, $100 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$) is 5900 cal/gr . When the heating value of the raw material mixture is compared with the heating value of the bio-oil obtained as a result of fast pyrolysis, it is seen that the heating value of the raw bio-oil is practically 39.91% higher than the raw material mixture. This increment in energy content is suitable for converting biomass directly used as fuel into liquid products with a higher energy content by fast pyrolysis. The solid product yield is typically high in this study's experiments conducted between 300 and $400 \text{ }^\circ\text{C}$; the liquid product yield generally rises at 500 and $600 \text{ }^\circ\text{C}$, which are considered medium temperatures for fast pyrolysis, and at high temperatures (600 – $750 \text{ }^\circ\text{C}$). The influence of the solid and gas product yields reduces the liquid product yield.

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