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# Fast pyrolysis of biomass for bio-oils

S.Keles[1,a], K.Kaygusuz[1]

[1] Karadeniz Technical University, Chemistry, Trabzon, Turkey.

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**Abstract**
This paper gives a proper overview on various possibilities for power generation from biomass in small-scale. One should note that the concept power generation from biomass in the article refers straight to combined heat and power (CHP) production based on biomass. Fast pyrolysis of hazelnut cupula was also investigated experimentally in a fixed-bed reactor under various conditions. The fixed-bed fast pyrolysis experiments have been conducted on a sample of hazelnut cupula in a fixed-bed reactor to determine particularly the effects of pyrolysis temperature, and ZnO catalyst on the pyrolysis product yields and the quality of liquid products. The reactor was heated at a heating rate of 200 $^{o}$C per minute to a pyrolysis temperature of 400, 500, 600 and 700 $^{o}$C. Experiments show that the maximum oil yields of 52.5% and 57.6% were obtained without and with catalyst at 600 $^{o}$C, respectively. An increased of 5.0 percent was achieved when compared without catalyst.

*Keywords:* Woody biomass; pyrolysis; electric power; hazelnut cupula; sustainable future

## 1. Introduction

Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis [1]. Pyrolysis processes have been improved and are now widely used with coke and charcoal production [2]. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly [3].

In contrast to fossil fuels, the use of biomass for energy provides significant environmental advantages [4]. Plant growth needed to generate biomass feedstocks removes atmospheric carbon dioxide, which offsets the increase in atmospheric carbon dioxide that results from biomass fuel combustion [5]. There is currently no commercially viable way to offset the carbon dioxide added to the atmosphere that results from fossil fuel combustion. The climate change effects of carbon dioxide from fossil fuels are now generally recognized as a potential serious environmental problem [6]. To meet the goals of the Kyoto agreement, Turkey must reduce greenhouse gas (GHG) emissions to a level 7% below the 1990 emissions in 2010 [7]. Carbon dioxide is the predominant contributor to the increased concentration of GHGs. The combustion of fossil fuels accounts for two-thirds of global anthropogenic CO2 emissions, with the balance attributed to land use changes [8-18].

Biomass is plant matter such as trees, grasses, agricultural crops or other biological material that can be used as a solid fuel, or converted into liquid or gaseous forms, for the production of electric power, heat, chemicals, or fuels. Figure 1 clarifies the bio-energy chain from biomass origin to energy usage [3, 17]. Biomass energy, one type of renewable energy, is important from two perspectives: firstly, from the perspective of climate change and energy; and secondly, from the viewpoint of a recycling society. Biomass energy is superior to other forms of renewable energy sources in its ease of storage and transportation [11]. Promoting the use of biomass energy has the potential to mitigate climate change, offer a sustainable energy supply, and achieve a sustainable and recycling social system for the future. In spite of the advantages of biomass energy, various barriers such initial high costs, insufficient biomass energy resources and insufficient market development must be solved for the use of biomass energy to progress [9-14].

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[a] Corresponding author;
Phone: +90-462-377-4275, Email: sedat725@hotmail.com

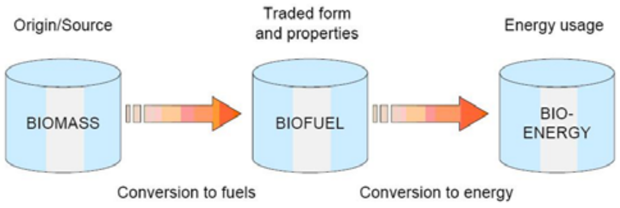


Figure 1. Bioenergy chain.

## 2. Biomass conversion technologies for energy

Biomass conversion is about converting solid biofuels into such form that are usable for energy generation. Biomass conversion technologies can be divided into biological, chemical and thermo-chemical conversion methods [1-3]. The thermo-chemical methods involve heat treatment of the biomass material, the biological conversion uses microbiological action to convert the biomass material into usable fuel, while chemical conversion makes use of the technologies of extraction and transesterification [4, 10, 11].

The purpose of conversion methods is to convert solid biomass feedstock into a form usable for energy production, as solid biomass can be utilized in direct combustion methods only. Figure 2 presents the main potential pathways for bio-fuel based power generation, starting from grouping of conversion technologies and resulting in technological alternatives for power generation [1, 3, 10]. Biomass conversion technologies illustrated in the Figure 2 are currently the main "starting points" to electricity generation from biomass. Other known biomass conversion methods that are not shown in the Figure 2 are liquefaction and hydro thermal upgrading [17].

Possible biomass based fuels for engines are bioethanol, biogas, biodiesel, bio-oil and fuel gas from biomass gasification (Figure 2). Currently, the most effective way to generate electricity out of biomass is the gasification and the use of the gas in gas engine: the conversion of the organic carbon with the gasification of biomass in higher than 95% [3]. Biomass gasification represents a rather new generation of biomass energy conversion processes and thus, electricity production based on a fixed-bed gasifier system coupled to a gas engine has been the focus of many R&D projects in Europe during the last few years. It should be noted, though, that this kind of technology is still in the stage of development and has not yet reached commercialization [17].

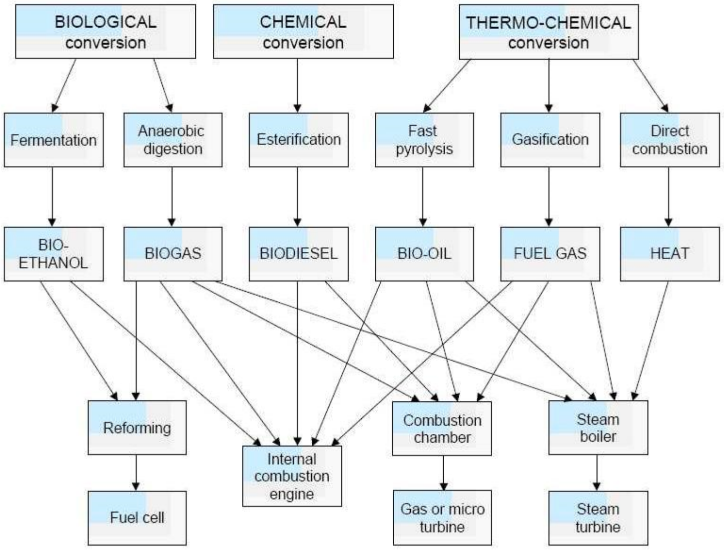


Figure 2. Overview of the major technological routes for biomass based power generation.

## 3. Applications of biomass energy

Technological development and governmental subsidies directed towards environmentally sustainable electricity generation have increased the share of distributed generation in many countries during recent years. Combined production of heat and power is suitable for small-scale applications, and micro and small-scale biomass-fired CHP units are one of the alternatives for distributed generation [3]. This relatively new technology has reached the commercialization stage and could replace conventional boilers in dwellings and provide both electricity and heating to dwellings concerned [1-3].

More specifically out sorted, the smallest biomass based CHP systems with power output under 10 kWe, (Stirling engines and fuel cells) could replace the conventional boiler in a dwelling and provide both electricity and heating to that dwelling, possibly with surplus electricity exported to the local grid. Systems with power output ranging from 10 kWe to 100 kWe, in turn, are applicable to blocks or groups of dwellings, as well as nondomestic buildings [1, 3, 17]. The aptitude of small scale biomass CHP technologies for different applications is the most extensive in size class between 100 kWe - 1 MWe, as all presented technologies are included in this size category (Table 1) [17]. Possible applications for systems having power output between 100 kWe and 1 MWe are hospitals, green houses, small sized industry, swimming halls, and also bigger schools and hotels. On the other hand, possible applications for biomass CHP systems with power output rate from 1 MWe to 10 MWe are small regional electricity and heating systems, university campus areas, i.e. the ones in USA, and medium sized industry. Technologies included in this size category are internal combustion engines.

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

| Mode | Conditions | Liquid (%) | Char (%) | Gas (%) |
|---|---|---|---|---|
| Fast pyrolysis | Moderate temperature, short residence time | 75 | 12 | 13 |
| Carbonisation | Low temperature, very long residence time | 30 | 35 | 35 |
| Gasification | High temperature, long residence time | 5 | 10 | 85 |

## 4. Biomass pyrolysis

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. It is important to differentiate pyrolysis from gasification. Gasification decomposes biomass to syngas by carefully controlling the amount of oxygen present. Pyrolysis is difficult to precisely define, especially when applied to biomass. The older literature generally equates pyrolysis to carbonization, in which the principal product is a solid char. Today, the term pyrolysis often describes processes in which oils are preferred products. The time frame for pyrolysis is much faster for the latter process [1, 3, 11].

Conventional slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow wood pyrolysis, biomass is heated to ~500 oC. The vapor residence time varies from 5 min to 30 min. Vapors do not escape as rapidly as they do in fast pyrolysis. Thus, components in the vapor phase continue to react with each other, as the solid char and any liquid are being formed. The heating rate in conventional pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock can be held at constant temperature or slowly heated. Vapors can be continuously removed as they are formed. Vacuum pyrolysis at slow or fast heating rates is another variant. The definition of a “slow” heating rate versus a “fast” heating rate is arbitrary in many respects [1, 2, 10, 11].

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen. Biomass decomposes to generate vapors, aerosols, and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. Fast pyrolysis produce 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases, depending on the feedstock used. No waste is generated, because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process.

Heating rates of 1000 oC/s, or even 10000 oC/s, at temperatures below ~650 oC have been claimed [11]. Rapid heating and quenching produced the intermediate pyrolysis liquid products 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. The main pyrolysis variants are given in Table 2 [3].

Cellulose is the major constituent of wood, and its pyrolysis occurs over almost the entire range of pyrolysis temperatures. Pure cellulose pyrolysis has been investigated to help understand its decomposition mechanism during wood pyrolysis [18]. An excellent review by Mohan et al [3] has described the classes of mechanisms that had been previously proposed for wood pyrolysis and that of other cellulosic materials [2, 11, 15]. Design variables required for fast pyrolysis include the following: feed drying, particle size, pretreatment, reactor configuration, heat supply, heat transfer, heating rates, reaction temperature, vapor residence time, secondary cracking, char separation, ash separation, and liquid collection [16].

Table 2. Pyrolysis methods and their variants

| **Pyrolysis technology** | **Residence time** | **Heating rate** | **Temperature ($^o$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 |
| Methano-pyrolysis | < 10 s | High | > 700 | chemicals |

## 5. Experimental Set-up

A schematic diagram of the pyrolysis system used in this study is shown in Fig. 3 [15]. This set-up mainly consisted of flowmeter, the fixed- bed reactor, liquid collecting system and power supply. The fixed-bed reactor had a volume of 90 cm3 (20 mm i.d.). During the experiments, heating rate and pyrolysis temperature of the hazelnut cupula were controlled by a PT100 temperature controller. As can be seen, temperature measurements were taken in the bed, with the thermocouple in the middle of the fixed-bed reactor, in order to control the reactor temperature. Temperature measurements were taken from a meter in the controlling panel. Table 3 shows the main characteristics of hazelnut cupula [15].

The pyrolysis experiments were performed sweep gas atmosphere in a fixed bed reactor. In this experiments, 2 g of the air-dried sample, sieved the average particle size of 0.250< Dp <0.150 mm was used. After all connections were made, a nitrogen gas flow rate of 200 cm3. min-1 was maintained and measured with a flowmeter. Experiments were carried out in two series. The first was to determine the effect of the pyrolysis temperature on pyrolysis yields under a nitrogen atmosphere without catalsyt. The second groups of experiments were performed in the fixed bed reactor in order to establish the effect of ZnO catalyst on the pyrolysis yields under a nitrogen atmosphere. At the first group experiments, the reactor was heated at a heating rate of 200 °C. min-1 to a pyrolysis temperature of 400, 500, 600, 700 °C and finally 2 g of the air-dried sample ejected in the reactor.

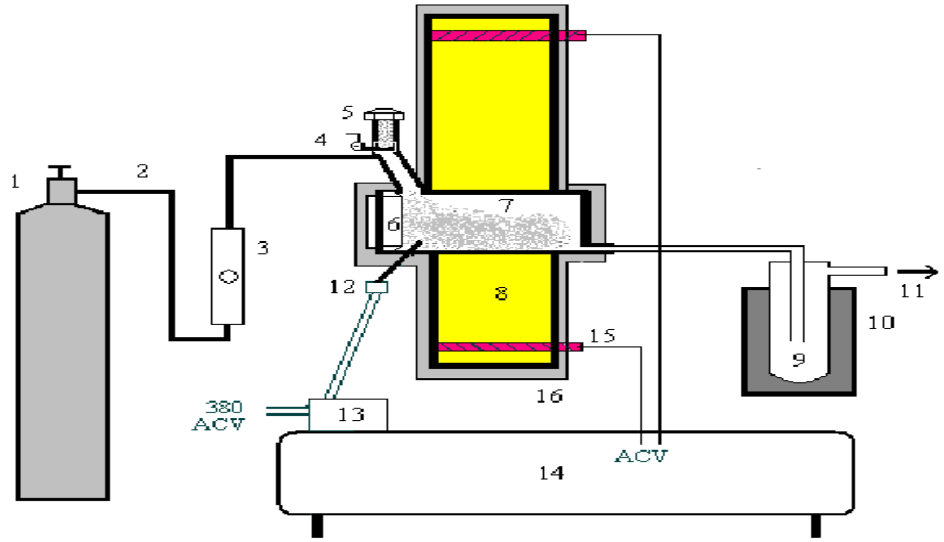
At the second groups of experiments, 2 g of the air-dried sample was mixed ZnO (6 wt% of feed) and then put into the reactor. After placing the sample put into the reactor, each mixture was heated up to a final temperature (400, 500, 600, 700 °C) at a constant heating rate of 200 min-1 and held there for a minimum of 30 min or until no further significant release of gas was observed. The liquid phase was collected in a cold trap maintained liquid nitrogen. After pyrolysis, the solid char was removed and weighed. The gas yield was calculated by difference. The liquid phase consisted aqueous and oil phases, which were separated and weighed. The solvent part of pyrolysis liquid phase dissolved dichloromethane was extracted in a rotary evaporator, and thus, the quantity of the bio-oil was established.

Table 3. Main characteristics of hazelnut cupula

| **Characteristics** | **Values** |
|---|---|
| Moisture content[a] (%) | 9.86 |
| Holocellulose content[a] (%) | 64.30 |
| Cellulose content[a] (%) | 30.69 |
| Hemicellulose content[a] (%) | 33.61 |
| Lignin content[a] (%) | 16.14 |
| Organic extractive[a] (%) | 3.68 |
| | |
| *Proximate analysis (%)* | |
| Volatiles | 70.16 |
| Fixed carbon | 13.96 |
| Ash | 6.02 |
| | |
| *Ultimate analysis[a] (%)* | |
| Carbon | 51.15 |
| Hydrogen | 5.89 |
| Nitrogen | 2.12 |
| Oxygen[b] | 40.84 |
| H/C molar ratio | 1.38 |
| O/C molar ratio | 0.60 |
| Empirical formula | $CH_{1.38}O_{0.60}N_{0.03}$ |
| **Higher calorific value ($MJ/m^3$)** | **20.55** |

[a] as received

[b] by difference



1. $N_2$ gas tube
2. $N_2$ flow line
3. Flowmeter
4. Sample transfer valve to reactor
5. Sample filling valve
6. Cover for draining char
7. Pyrolysis unit
8. Inductive reactor
9. Liquid collecting container
10. Cooling unit
11. Gas to atmosphere
12. PT100 temperature controller
13. Reactor temperature electronic control unit
14. Power supply
15. Reactor electric input and output linking apparatus
16. Isolation

Figure 3. Process flow diagram of the fixed-bed reactor.

## 6. Results and discussions

The fast pyrolysis oils (bio-oils) are acidic, viscous, reactive and thermally unstable. Due to these properties many problems arise in their handling and utilization. Therefore, some upgrading, e.g. catalytic conversion is required. Pyrolysis experiments are carried out at 600 °C, with and without ZnO catalyst. The product yields obtained with and without catalyst are compared in Figure 4, 5 and 6 for pyrolysis conversion, liquid, gas and char, respectively.

As shown in Fig. 4, the conversion efficiency increased when the final pyrolysis temperature was raised from 400 to 700 °C for with and without ZnO catalyst. Conversion efficiency increased from 66.94% to 76.00% without catalyst, and from 68.90% to 78.90% with ZnO catalyst. The conversion efficiency, which was 76.00% without catalyst, reached the value of 78.90% by using ZnO catalyst at 700 °C. This increased in conversion was reflected in the increase in the gas yield and bio-oil yields.

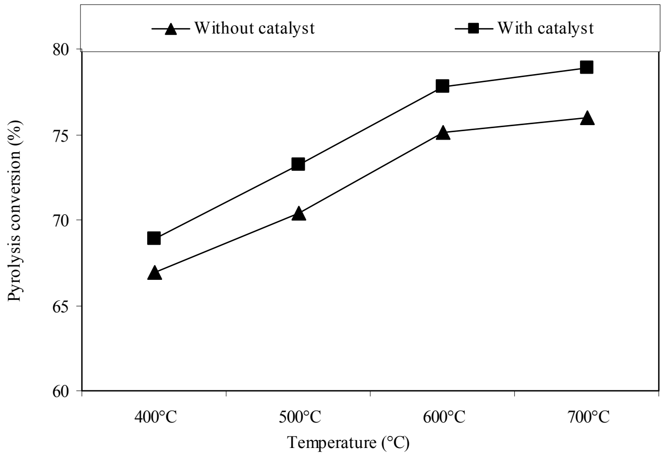


Figure 4. Comparison of pyrolysis conversion with and without ZnO (6 wt% of feed) catalyst (the heating rate of 200 °C min$^{-1}$, the sweeping gas velocity of 200 cm$^3$ min$^{-1}$, the average particle size of 0.250< $D_p$ <0.150 mm).

As shown in Figure 6, the gas yield increased from 23.34% to 31.30% for without catalyst and increased from 23.34% to 31.30% for with ZnO catalyst as the final pyrolysis temperature was raised from 400 °C to 700 °C. When the pyrolysis temperature came up to 600 °C the gas yield tends to become constant however, further increase the temperature up to 700 °C gas product yield severe increased. When the pyrolysis temperature increases, the gas yield will increase. The increase in gaseous product is thought to be predominantly due to secondary cracking of the pyrolysis vapors at higher temperatures.

The oil yield increased as the pyrolysis temperature was raised from 400 to 600 °C, although at the much higher pyrolysis temperature of 700 °C a decrease in the oil yield was observed for with and without ZnO catalyst (Fig. 5). The maximum oil yields of 52.52% and 57.60% were obtained without and with catalyst at 600 °C, respectively. Then at the final pyrolysis temperature of 700 °C, the oil yields decreased to 44.90% and 46.30% for without and with catalyst. An increased of 5.08% was achieved when compared without catalyst. The most important effect of the catalyst is the increase in the yields of oil.

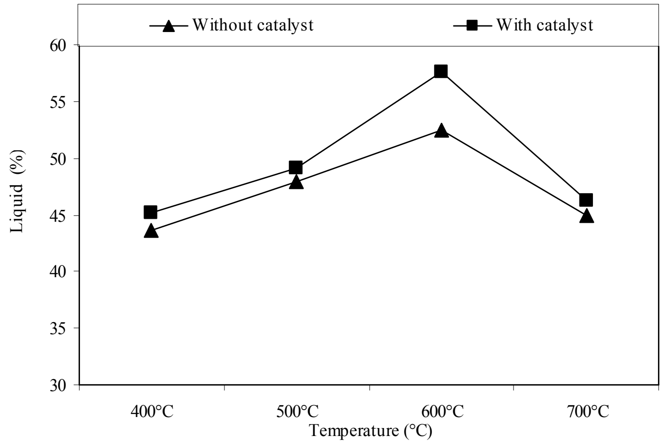


Figure 5. Comparison of liquid yields with and without ZnO (6 wt% of feed) catalyst (the heating rate of 200 °C $min^{-1}$, the sweeping gas velocity of 200 $cm^3$ $min^{-1}$, the average particle size of $0.250< D_p <0.150$ mm).

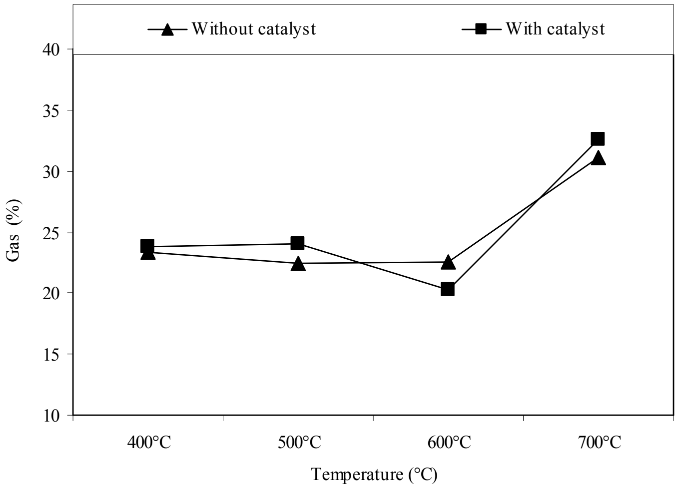


Figure 6. Comparison of gas yields with and without ZnO (6 wt% of feed) catalyst (the heating rate of 200 °C $min^{-1}$, the sweeping gas velocity of 200 $cm^3$ $min^{-1}$, the average particle size of $0.250< D_p <0.150$ mm).

## 7. Conclusions

The use of biomass, including biogas, for electricity generation represents an insufficiently used potential. At the same time, biomass provides additional perspectives for the domestic agriculture and forestry. The compensation rates have been increased substantially above the rates laid down in the 1991 law in order to enable operators of biomass installations to operate their installations cost-effectively, thereby initiating a dynamic development. Compensation rates differ in accordance with the electrical capacity of installations in order to give due account to the fact that power production costs of smaller decentralized installations are higher. Renewable energy has an important role in reducing CO2 emissions for increasing sustainability and fulfilling Kyoto commitments as a major Community policy objective.

In this study, fast pyrolysis of hazelnut cupula with and without catalyst was conducted in a fixed-bed to determine to effect of pyrolysis temperatures and ZnO catalyst on the product yields and the quality of liquid products. Hazelnut cupula, an agricultural by-product, was selected as raw material for pyrolysis experiments. The liquid yield first increased and then decreased with the increase of pyrolysis temperature from 400 °C to 800 °C for catalytic and non-catalytic pyrolysis experiments. The maximum oil yields of 52.52% and 57.60% were obtained without and with catalyst at 600 °C, respectively. An increased of 5.08% was achieved when compared without catalyst. On the other hand, the char yield decreased from 33.06% to 24.00% for without catalyst and decreased from 31.10% to 21.10% for with ZnO catalyst as the final pyrolysis temperature was raised from 400 °C to 700 °C. When the pyrolysis temperature came up to 600 °C the gas yield tends to become constant however, further increase the temperature up to 700 °C gas product yield severe increased.

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