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# Fixed Bed Pyrolysis of *Euphorbia Tirucalli* Biomass for Bio-oil Production

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# Abstract

Pyrolysis is a thermochemical method for biomass conversion resulting from char, bio-oil and gas. Bio-oil can be used as a valuable renewable fuel or as a chemical in various industries. Char can also be used as a solid fuel, a cheap adsorbent, and raw materials for the production of bio-char derivatives and for agricultural applications. In the present study, the biomass pyrolysis of *Euphorbia tirucalli* was performed in a fixed bed reactor. Pyrolysis experiments for this study were to investigate the effect of temperature (450-530 °C) on the yield of pyrolysis products. Characteristics of pyrolysis products (bio-oil and bio-char) using instrumental chemistry methods such as field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), thermal gravimetric analysis (TGA) and Gas chromatography–mass spectrometry (GC/MS) was investigated. The results showed that with increasing temperature, the yield of bio-oil and gas increases and the amount of bio-char decreases. The maximum yield of bio-oil (38%) was obtained at a temperature of 530 °C. Also, the maximum yield of various gases was about 39%. The highest thoracic effusion was observed at temperatures between 250-350 °C. The resulting acidic liquid is dark in color with a combination of chemical compounds including acids, alcohols, aldehydes, furfural, furan, phenols and some aromatic substances.

Keywords: Biofuel, Biomass, Euphorbia tirucalli, Petroleum, Pyrolysis

# پیرولیز بستر ثابت گیاه ایفوربیا تیروکالی برای تولید نفت زیستی

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# چکیدہ

پیرولیز یا آتشکافت یک روش ترموشیمیایی برای تبدیل زیست توده بوده و آن را به ذغال، نفت زیستی و گاز تبدیل می کند. روغن زیستی می تواند به عنوان یک سوخت تجدیدپذیر یا به عنوان ماده شیمیایی با ارزش در صنایع مختلف استفاده شود. همچنین می توان از ذغال به عنوان سوخت جامد، جاذب ارزان قیمت و تولید مواد اولیه برای مصارف کشاورزی استفاده کرد. در مطالعه حاضر، پیرولیز زیست توده حاصل از گیاه ایفوربیا تیروکالی (Euphorbia tirucalli) در یک راکتور بستر ثابت انجام شد. آزمایشهای پیرولیز برای این مطالعه، به منظور بررسی اثر دما (۴۵۰ تا ۵۳۰ درجه سلسیوس) بر عملکرد محصولات تولیدی واکنش انجام شد. ویژگیهای محصولات پیرولیز (نفت و کربن زیستی) با استفاده از روشهای مانند میکروسکوپ الکترونی روبشی انتشار میدانی (FE-SEM) ، طیف سنجی اسعه ایکس پراکندگی انرژی (EDX)، تجزیه و تحلیل وزن گرما (TGA) و کروماتوگرافی گازی طیف سنجی جرم (GC/MS) بررسی شد. نتایج نشان داد که با افزایش دما، عملکرد نفت زیستی و گاز افزایش می یابد و میزان کربن زیستی کاهش می یابد. بیشترین عملکرد نفت زیستی ( ۲۵۰ تا ۲۵۰ درجه سلسیوس بدست آمد. همچنین حداکثر عملکرد گازهای می ایک و کرما (TGA) و کروماتوگرافی گازی طیف سنجی جرم (GC/MS) بررسی شد. نتایج نشان داد که با افزایش در معملکرد نفت زیستی و گاز افزایش می یابد و میزان کربن زیستی کاهش می یابد. بیشترین عملکرد نفت زیستی (۲۵۰ ترصد) در ماه دار یا درجه سلسیوس بدست آمد. همچنین حداکثر عملکرد گازهای مختلف حدود ۳۹ درصد بود. بالاترین کاهش وزنی در دمای بین ۲۵۰ تا درجه سلسیوس مشاهده شد. مایع اسیدی حاصل، متشکل از ترکیبات شیمیایی از جمله اسیدها، الکلها، آلدئیدها، فورفورال، فوران، فنلها و برخی مواد معطر دارای رنگ تیره است.

**واژههای کلیدی:** ایفوربیا تیروکالی، بیومس، پیرولیز، سوخت زیستی، نفت

## Introduction

In recent years, global energy needs have increased due to declining fossil fuel reserves. Problems with environmental pollution and fuel transportation, petroleum-derived chemicals, global warming and greenhouse gas emissions such as carbon dioxide, methane and nitrogen monoxide have spread (Baquero et al., 2011; Taghizadeh-Alisaraei *et al.* 2019, 2017). Because of these problems, special studies are being conducted focusing on replacing biofuels with fossil fuels (Buijs *et al.* 2013).

Bio-refinery is a comprehensive system for converting biomass into fuels, energy and chemicals (Hassan et al., 2019; Ingle et al. 2020). In recent years, lignocellulose materials have been recognized as one of the most important sources of biomass in the world, with great potential and high availability for the production of biofuels and chemicals through advanced technologies, conversion and separation (Bajpai, 2013; Qureshi et al. 2014). The raw materials for bio-refinery are agricultural wastes such as wheat straw, rye, cereals, corn, sugarcane bagasse and corn; other plants also have good potential for bio-refinery. Primary fractionation of biomass to the main groups of raw materials is essential for ease of use in the bio-refinery system. These materials must then be converted into industrial intermediaries and final products (Luque and Clark, 2010).

Bio-refinery derivatives include a wide range of high value-added products such as biofuels, xylitol, furfural, bio- plastics, and more (Bajpai, 2013). The most important products of this technology are the types of fuels that are obtained from biomass resources. These fuels include liquid ethanol, methanol, biodiesel, and gaseous diesel fuels such as hydrogen and methane. The primary sources of these fuels are wood waste, agricultural waste, sugarcane, cereals, plant extracts and vegetables (Kapdan and Kargi, 2006; Zoia et al. 2017). Nowadays, most countries in the energy sector are pushing their needs and demands towards the use of such fuels. Problems such as high environmental pollution, fossil fuels that in turn disrupt ecological conditions. The limited fossil fuel reserves have led to more attention being paid to this type of energy.

Among the thermochemical technologies available to produce biofuels, pyrolysis is a promising way to convert lignocellulose biomass into biofuels and chemicals. Pyrolysis is usually performed in the absence of oxygen at 400-600 °C. High conversion efficiency and environmental compatibility are the most important advantages of using fast pyrolysis, which solid biomass can be converted directly into liquid fuels (Basu, 2010; Zhan et al., 2017). Fast pyrolysis mainly produces liquid fuel, known as biofuel. Slow decomposition produces some gas and solid char. Pyrolysis promises to convert biomass waste into complete fuels and unlike combustion, it is not heat-generating. The primary products of pyrolysis are condensable gases and solid char. Condensable gases may be decomposed into noncondensable gases (carbon monoxide, carbon dioxide,

hydrogen and methane), liquid and char (Basu, 2010; Rosendahl, 2013).

*Euphorbia tirucalli*, known as aveloz or pencil tree, is a cactus but thorny but usually reaches a height of three to five meters. It is very easy to propagate by cuttings, the most widespread in Brazil (Avelar *et al.* 2011; Mwine *et al.* 2013; Zhang *et al.* 2008). This plant has been used to repel pests, insects and fences to prevent animals from entering agricultural farms, which has played a significant role (Mwine *et al.* 2013).

In different countries, this plant is used for the production of adhesives, antibacterial latex and rubber (Avelar et al. 2011) as well as for the treatment of diseases and tumors (Valadares et al. 2006). Numerous studies have been conducted on the use of opioids in the production of biodiesel (Khaleghian et al. 2011) and biogas (Rajasekaran et al. 1989). But according to studies, there have been no direct reports of the use of Euphorbia tirucalli plants to produce biofuels using pyrolysis. The following are research reports that can be related to the present study. Various researchers have reported the use of Euphorbia tirucalli for bio-refinery purposes. Research by (Rajasekaran et al. 1989) examines the potential of Euphorbia tirucalli for gas production. Their findings show that the use of 375 grams of Euphorbia tirucalli (one centimeter in size) in combination with 375 grams of cow manure and 750 grams of water in one reactor resulted in the production of 19.2 liters of biogas compared to pure cow manure (16.5 liters) in 9 weeks. The values of cellulolytic, methanogenic and proteolytic organisms in the treatment containing Euphorbia tirucalli were higher than in the treatment containing pure cow manure. Khaleghian et al. (2011) studied the production of biodiesel from Euphorbia tirucalli and obtained two compounds, phorbol and ingenol. It was also found that the resulting biodiesel had a density of 0.88 g/cm<sup>3</sup> and a flash point of 130 °C, which was much higher than the flash point of diesel oil (64 °C) and gasoline (-45 °C). They noted that the latex Euphorbia tirucalli milk plant, which has latex, could also be used to make gasoline. Also, many researchers have used bioreactor pyrolysis reactors to produce biogas, char and gas from various lignocellulose materials. For example, (Gonçalves et al. 2017) studied the effect of operating conditions (temperature, particle size, heating rate and nitrogen gas flow rate) on sugarcane bagasse pyrolysis in a fixed bed reactor. Their results showed that the effect of operating conditions (except for nitrogen gas flow velocity) on biofuel efficiency was not significant, but had a significant effect on other pyrolysis products (char and gas). The maximum bio-oil (54%) was obtained at a temperature of 600 °C, a heating rate of 15 °C/min., a flow rate of 200 ml/min and a particle size of 0.5-1 mm. Gautam and Chaurasia (2020) used some agricultural waste (bamboo, rice husk, sugarcane bagasse, and neem bark) in a fixed bed reactor to investigate the impact of operating conditions such as temperature, residence time and reactor length. The maximum yield of bio-oil (46.93%) and bio-char (26.2%) was obtained for bamboo at 450 °C. The highest levels of pure gas (carbon monoxide and hydrogen) were obtained for the bark of the neem tree (52.61%). According to Gogoi et al. (2020), pyrolysis of sesame stalk was performed at different temperatures (350-650 °C) in a fixed bed reactor. They found that with increasing pyrolysis temperature, the amount of char decreased and the amount of gas increased significantly. The maximum yield of bio-oil (24.85%) and its higher heating value (HHV) was 26.89 MJ/kg. Vieira et al (2020) in a study of optimizing the rice husk pyrolysis process in a fixed bed reactor found that temperature is the most important parameter of slow pyrolysis. The maximum bio-oil yield (39.84%) was obtained at 400 °C and 10 °C/min heating rate.

One of the strategic factors in discussing sustainable energy in biological refineries is the use of non-edible lignocellulose sources (for livestock and humans) to produce biofuels. According to the reviewed studies, the production of biofuels from the *Euphorbia tirucalli* plant has not been studied. Accordingly, the objective of the present study is to produce bio-oil from the *Euphorbia tirucalli* plant as a highly desirable potential in pyrolysis for the production of biogas, char and gas. Laboratory analysis of the materials obtained will also be performed.

#### 2. Materials and Methods

#### 2.1. Raw materials

In this study, dry biomass of *Euphorbia tirucalli* was used (Fig. 1). First, the raw (wet) biomass was cut into small pieces and after drying at room temperature for 7 days, it was screened by a vibrating sieve machine to a size of 1-2 mm. The composition of the *Euphorbia tirucalli* was determined by proximate analysis (moisture, volatile matter, fixed carbon and ash) and ultimate analysis (carbon, hydrogen, nitrogen, sulfur and oxygen).



Fig 1. Euphorbia tirucalli biomass

# 2.2. Different techniques used for characterization of biomass and pyrolysis products

Proximate analysis results (dry base) based on ASTM methods (D3173 for moisture, D3174 for ash and D3175 for volatile materials). The amount of fixed carbon was calculated by difference. The ultimate analysis was calculated by analyzing the EDX elements. Determination of lignin was determined based on TAPPI T 222 method, cellulose was determined based on TAPPI T202 method and Holocellulose was determined based on Zoia et al (2017) method.

#### 2. 3. Pyrolysis process

In this study, a fixed bed pyrolysis system was designed and built as shown in Fig. 2. The device includes a fuel system, a char collection tank and a bio-oil collection system. The laboratory fixed bed reactor is made of stainless steel and consists of a cylindrical tube with dimensions (length 20 cm and inner diameter 10 cm) which is heated directly by the gas heater. In each experiment, 20 g of raw material was placed inside the reactor and then the fixed bed reactor was kept in the average temperature range of 450-530°C. Bio-fuel collection equipment was cooled using water. Pyrolysis biomass was transferred to the GC/MS device by gasmass chromatography, and the mass balance was measured by weighing all inputs and outputs into the pyrolysis system. All components of the test system, such as the char tank reactor and electric sediment, were weighed separately before and after each test to determine the amount of char and biofuel. The yield of gas, bio-oil and char was calculated by the ratio between the collected materials and the biomass consumed in the pyrolysis process.



Fig 2. Schematic of the device and the pyrolysis process.

## 2. 3. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX)

The field emission electron microscope (FE-SEM) of the MIRA3 TESCAN-XMU model was used to study the char morphological features. For this purpose, the samples were first dried for 24 hours at 60 °C. The

samples were then coated for 15 minutes with a metalizer with argon gas (as a carrier) and gold (for conduction). Gold-coated samples were observed at a voltage of 15 kV.

#### 2. 4. Thermal gravimetric analysis (TGA)

This analysis is a method that measures the change in mass of a sample as a function of temperature in the superstructure mode or a function of time in the cooperative state. Heat changes are measured in relation to sample mass changes such as decomposition, sublimation, reduction, and adsorption and evaporation with TGA. This method can be used to be aware of weight loss as well as thermal stability during the thermal period. For this analysis, the TGA model (STA 503) was used under conditions of 15 mg of the sample under oxygen atmosphere at a rate of 50 ml/ min gas flow and 10 °C/min at a temperature range of 0-600 °C.

# 2. 5. Gas chromatography-mass spectrometry (GC/MS)

Gas chromatography–mass spectrometry (GC/MS) of bio-oil from pyrolysis operations was performed with an Agilent / HP 6890N GC equipped with 5973N MSD and auto-sampler with split injection system. The temperature of the GC oven was programmed to be kept at 50 °C for 4 minutes, then the temperature program was increased from 70-120 °C with an increase of 5 °C/min, an increase from 120-140 °C with an increase 8 °C/min and hold there for 10 min at 240 °C. The temperature of the injector and detector was 250 °C and 280 °C, respectively. The non-dilute bio-oil sample was injected into the GC/MS device at a rate of 2 microliters with a 1 to 20 split ratio. Chromatogram analysis was performed by National Institute of Standards and Technology (NIST) library of mass spectra data base.

## 3. Results and discussion

#### 3. 1. Characteristics of biomass

The results of proximate analysis (moisture, ash) and final (carbon, hydrogen, nitrogen, sulfur and oxygen) are presented in Table 1. The values of cellulose, hemicellulose and lignin are 32.5, 26.1 and 15.4%, respectively. These values are similar to some lignocellulose materials such as wheat straw (Maache-Rezzoug et al., 2011), bagasse (Mkhize et al., 2016) and rice straw (Singh et al., 2014). Quantitative biomass analysis of Euphorbia tirucalli reported values of 22-26% of cellulose, 12-32% of hemicellulose and 4-38% of lignin (Abay et al., 2017; Augustus et al., 2003; Rajeswari et al., 2013; Sake et al., 2013). The total volatile solids of Euphorbia tirucalli used in this study were 74.6%. The low amount of lignin in lignocellulose materials eliminates the sequences of chemical pretreatment to remove lignin and is considered a superior advantage for substrates suitable for anaerobic digestion and biogas production (Abay et al., 2017).

 Table 1. Main characteristics of the Euphorbia

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tirucalli		
Characteristics	Value	
Cellulose	32.5	
Hemicellulose	26.1	
Lignin	15.35	
Proximate		
1 1011111110		
analysis/%		
Moisture	10	
Ash	2.9	
Fixed carbon*	12.5	
Volatile matter	74.6	
Ultimate analysis/%		
Carbon (C)	48.7	
Hydrogen (H)	4.3	
Nitrogen (N)	0.11	
Sulfur (S)	0.02	
Oxygen** (O)	46.87	

\*\*Measure by difference (Fixed carbon% =100- (%Moisture+ %Volatile matters+ %Ash)

\*\* By difference

#### 3. 2. Pyrolysis products yield

Fig. 3 shows the yield of pyrolysis products in a fixed bed reactor. *Euphorbia tirucalli* contains more carbon and less oxygen than other lignocellulose materials. Not only does this increase its calorific value compared to other lignocellulose materials, but it also reduces the cost of producing biofuels. The mass balance of products from pyrolysis *Euphorbia tirucalli* shows that the maximum bio-oil yield is about 38% at 530 °C. The pyrolysis products yield of *Euphorbia tirucalli* is relatively similar to that of related studies (Table 2).

The maximum yield of various gases from *Euphorbia tirucalli* pyrolysis was about 39%. High gas yield in the pyrolysis process is attributed to factors such as aromatic rings and methoxyl functional groups in the lignin sample, because the  $H_2$  produced by organic gases is mainly due to cracking and deformation of the carbon-carbon double bond. CH<sub>4</sub> is mainly generated by crackling of methoxyl groups. The higher yield of CO gas in cellulose is higher due to the amount of carbonyl. Hemicelluloses have the highest CO<sub>2</sub> yield due to their higher carboxylic content (Yang *et al.* 2007).



Fig 3. Product yield from *Euphorbia tirucalli* pyrolysis

 
 Table 2. Compare the efficiency of the present research products with other biomass resources

Temperature         530         550         400-6           (°C)         (°C)	Reactor type         Fixed bed         Reactor-         Fixed           furnace         system	Biomass Euphorbia Sesame Sugarcane tirucalli stalk bagasse
400-600 550		Fixed bed Reactor- furnace system
	600	FI
30-40	350-650	350-650 Semi batch reactor

In general, temperature, type of lignocellulose material, reactor type, catalytic improvers, pyrolysis time, pyrolysis atmosphere, bio-oil collection system type, etc. determine the yield of pyrolysis (Basu, 2010; Ghorbannezhad *et al.* 2018b, 2018a). The reason for the difference in the amount of yield obtained in this study with the results of these researchers can be considered the

different structure and composition of the lignocellulose materials used by them. However, in various studies, the type of bio-oil collection systems reported for different pyrolysis operations has been reported. In some pyrolysis reactors, tubular condensers and cooling traps are used to capture the lower and upper compounds of the dew point. Ice and water are used in these units to cool pyrolysis vapors. Floating glass traps in a mixture of ethanol and liquid nitrogen at -40 °C are also used to remove pyrolysis vapors, which include water and light volatile compounds such as aldehyde form and some ketones with low boiling points to cool pyrolysis gases. The use of these systems can increase and improve the efficiency of bio-oil production operations by 5-15%. The relative yield of products obtained from pyrolysis varies depending on the temperature used. At a temperature of 400-500 °C, more char is produced, while at temperatures above 700 °C, the product moves more towards the production of liquid and gaseous compounds (Winsley, 2007).

The composition of bio-oil depends on the type of biomass used and the method of processing (Ghorbannezhad et al., 2018b, 2018a; Suriapparao and Vinu, 2018). The basis of pyrolysis is the separation of the main biomass compounds (cellulose, hemicelluloses and lignin) to produce a liquid product. This liquid product contains a wide range of high value-added materials that are very valuable for its separation and purification (Basu, 2010). Biomass pyrolysis generally produces a low quality bio-oil due to its high oxygen content, high acidity and low biomass thermal value. Pyrolysis with various catalysts (HZSM-5, MCM-41, TiO<sub>2</sub>, ZrO<sub>2</sub>, Mg (Al) O) has been proven to be the most effective process for deoxygenating bio-oil to produce high quality biofuels and chemicals (Ghorbannezhad et al., 2018b, 2018a; Zhan et al., 2017).

### 3. 3. Thermal gravimetric analysis (TGA)

Euphorbia tirucalli thermal gravimetric analysis (TGA) is presented in Fig. 4. The initial weight loss began with the evaporation of water absorbed at a temperature of about 100 °C in the sample, which is about 4.5% of the initial weight loss. The highest thoracic effusion was observed at temperatures between 250-350 °C, which is related to the thermal decomposition of their main compounds (cellulose, hemicelluloses and lignin). The curvature of the Differential thermal analysis (DTA) in the diagram, which occurs at a temperature of about 320 °C, is related to hemicelluloses degradation. The remaining amount of material from the heat weight analysis is about 20% of the dry weight of the raw material, which mainly includes char and inorganic compounds in the ash. There are large differences between the three components of pyrolysis behavior. Hemicellulose is composed of various saccharides (xvlose. mannose. glucose, galactose. etc.). Hemicelluloses begin to decompose easily at 315-220 °C. Cellulose pyrolysis is concentrated in a higher temperature range (315-400 °C). When temperatures rise above 400 °C, almost all cellulose decomposes. Among the above three natural polymers, lignin has the most difficult thermal decomposition. Lignin decomposition occurs slowly in the entire range of 0-600 °C. Differences in the intrinsic structures and chemical nature of these three components probably account for the different behaviors observed. This result is compatible with the literature (Varma and Mondal, 2017; Vieira *et al.* 2020; Yang *et al.* 2007).



Fig 4. TGA/DTA measurement curves on *Euphorbia tirucalli* 

#### 3. 4. Chemical characteristics of bio-oil

Thermal degradation of lignocellulose biomass consists mainly of a complex mixture of organic compounds. Depending on their functional groups, these compounds can be divided into aromatic, aliphatic, nitrogencontaining, oxygen-containing, and polycyclic compounds (Ghorbannezhad *et al.* 2018a).

Fig. 5 shows the GC/MS distribution products derived from *Euphorbia tirucalli*. According to this major form, products derived from pyrolysis of *Euphorbia tirucalli* at 530 °C include Acetic acid, 2-propenoic acid, furanone, phenol, methyl cyclo pentane dione, methyl vinylcarbinol, homocatechol, syringol, resorcinol, 4-ethyl, guaiacylacetone, homovanillic acid, and 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo [1,2-a;1',2'-d] pyrazine.



9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00

Fig. 5. GC/MS of Euphorbia tirucalli at 530 °C.

#### **3.4.** Characteristics of bio-char

The apparent morphology of biofuel produced by of *Euphorbia* tirucalli with field emission electron microscope (FE-SEM) with a magnification of 500 times was investigated. Energy-dispersive X-ray spectroscopy (EDX) was also used to analyze elemental composition. According to Fig. 6, due to the release of volatile substances in pyrolysis, the surface of the bio-char is roughened and the number of pores increases. Initially, the morphology of the pores shows irregular properties and tends to be uniform (Wang *et al.* 2020). The presence of pores plays an important role in increasing the level and capacity of biofuels. Very porous biological char has a greater number of absorption sites that provide space for water and nutrient / pollutant storage (Varma and Mondal, 2017).

The results of bio-char EDX analysis also confirm the presence of substances such as nitrogen and silica. These materials are very suitable for soil fertility. The quality of biofuels can be improved by using improver chemicals for use in the adsorption process. In addition, it can be converted to bio-char with better properties after shaving processes (Varma and Mondal, 2017). The biochar obtained from the pyrolysis of lignocellulose materials have many uses. It is capable of increasing soil fertility and increasing agricultural yield, so that the soils of areas containing bio-char are among the most fertile soils (Harel et al. 2012). It is also considered a protective agent against some soil and plant diseases (Elad et al. 2011; Frenkel et al. 2017). There are also many reports of the use of bio-char from pyrolysis of lignocellulose materials to absorb heavy metals (chromium, cadmium, mercury, lead, copper, aluminum, cobalt, nickel, zinc, magnesium and iron) and phenol (Han et al. 2013; Komkiene and Baltrenaite, 2016; Xu et al. 2016).



#### Conclusions

The aim of this study was to investigate the aphrodisiac pyrolysis at a temperature of 450-530 °C. Particle size 1-2 mm and without a catalyst in a fixed- bed reactor. The results of this study showed that the final pyrolysis temperature has a major effect on the yield and products of pyrolysis. Bio-oil yields increase with increasing pyrolysis temperature. The maximum bio-oil was 38% at 530°C. The maximum yield of bio-oil (38%) was obtained at a temperature of 530 °C. Also, the maximum yield of various gases was about 39%. The highest thoracic effusion was observed at temperatures between 250-350 °C. Fast pyrolysis of agricultural lignocellulose wastes, in addition to being able to generate energy from renewable sources, has the potential to produce chemicals used in industries that are often made from fossil oil resources. The GC/MS results also showed that biofuels mainly contain phenolic compounds.

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