



Effects of catalysts on pyrolysis of castor meal



Guan-Bang Chen ^{a,*}, Yueh-Heng Li ^{a,b,**}, Guan-Lin Chen ^c, Wen-Teng Wu ^c

^a Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan, ROC

^b Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC

^c Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

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ABSTRACT

In this study, γ -alumina and zeolite ZSM-5 were used as catalysts to examine their effects on the pyrolysis of castor meal. The operation conditions for the pyrolysis were a pyrolytic temperature of 400 °C, residence time of 120 min, heating rate of 20 °C/min, and nitrogen flow rate of 200 mL/min. With the addition of catalysts, significant variations in pyrolytic products was observed, and the presence of γ -alumina and zeolite ZSM-5 slightly reduced the pyrolytic oil yield. However, the thermal analysis results demonstrate that the catalysts changed the pyrolysis mode and enhanced the hydrogenation/deoxygenation reaction and removed oxygen as CO, CO₂, and H₂O. Gas chromatography-mass spectrometry, elemental analysis, and viscosity analysis were also performed. With the addition of catalysts, the pyrolytic oil consisted of lighter compounds. The viscosity of the pyrolytic oil decreased significantly, and its viscosity index and calorific value increased. Therefore, catalytic pyrolysis can improve the quality of pyrolytic oil, and adding γ -alumina decreases the pyrolysis temperature from 339 °C to 284 °C. In addition, for the deoxygenating ability, the effect of γ -alumina will be greater than that of zeolite ZSM-5.

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1. Introduction

According to the International Energy Agency (2015), global energy consumption stratified by power source was 31.1% oil, 28.9% coal/peat, 21.4% natural gas, 10.2% biofuel/waste, 4.8% nuclear, 2.4% hydro, and 1.2% other renewable energy sources such as solar, geothermal, and wind. Currently, global energy supply is largely fossil fuel-based, which has led to the rapid depletion of fossils fuel and a substantial increase in greenhouse gas (GHG) emissions. To mitigate the increase in GHG emissions, improving the efficiency of fossil fuel utilization [1–3] and partially replacing fossil fuels with alternative fuels [4,5] are regarded as feasible and timely measures. Biomass is recognized as a promising ecofriendly alternative source of renewable energy, and it has high availability worldwide. Compared with conventional fossil fuels, biomass generally contains small amounts of sulfur, nitrogen, and ash. Biofuel combustion emits lower amounts of harmful gases such as nitrogen oxides (NO_x) and sulfur dioxide (SO₂), and soot [6]. In addition, the use of

biomass fuels provides substantial environmental benefits. Biomass absorbs carbon dioxide during growth and emits it during combustion. Therefore, biomass facilitates atmospheric carbon dioxide recycling and does not contribute to the greenhouse effect.

In terms of converting biomass into biofuel, there are two quintessential methods: biochemical conversion (BCC) and thermochemical conversion (TCC). BCC involves using fermentation and other biological conversion processes to produce biofuels. For example, waste cooking oil is used to produce biodiesel through transesterification, and starchy crops are used to produce bioethanol through fermentation. Biofuels have advantages in storage and transport, as well as versatility in such applications as combustion engines, boilers, turbines, and fuel cells. TCC can be further categorized into direct combustion, gasification, pyrolysis, and liquefaction, and the resulting materials can be used directly as fuels, specialty chemicals, or electricity precursors.

Compared with other biomass-to-energy conversion processes, thermal pyrolysis has attracted more interest from the viewpoint of obtaining liquid fuel product from various biomass species such as woody biomass [7], bagasse [8], straw [9], miscanthus [10], oil palm fiber [11], and municipal solid waste [12,13]. Depending on the operating conditions, pyrolysis can be classified into three main categories: slow, fast, and flash. In addition, the products of pyrolysis processes depend strongly on the heating rate, heating

* Corresponding author.

** Corresponding author. Dept. of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC.

E-mail addresses: gbchen26@gmail.com (G.-B. Chen), yueheng@mail.ncku.edu.tw (Y.-H. Li).

temperature, vapor residence time, biomass particle size, and biomass water content. In fast pyrolysis, biomass is generally heated rapidly to a high temperature in the absence of oxygen and yields 60%–75% oily products, 15%–25% solid products, and 10%–20% gaseous products by weight. However, the product yield of biomass pyrolysis can be approximately maximized for charcoal by employing a low-temperature, low-heating-rate process; for liquid products by employing a moderate-temperature, high-heating-rate, short gas-residence-time process; and for fuel gas by employing a high-temperature, low-heating-rate, long gas-residence-time process [14–16].

As to the pyrolysis system, so far, various types of pyrolyzer have been proposed and tested. According to the gas-solid contacting mode, the major designs of pyrolyzer include fixed bed, fluidized bed, entrained bed, rotating cone reactor, ablative reactor, vacuum reactor and so on. Different pyrolyzers have different design configuration and operating characteristics. A brief introduction about these pyrolyzers can be found in the literary work of Basu [17]. In a commercial pyrolyzer, first, a heat-transfer medium is heated up in the reactor. Then it transfers the heat to the feedstock. The heat transfer medium can be the reactor wall (for vacuum reactor), carrier gas (for entrained-bed or entrained-flow reactor) or heat-carrier solids (for fluidized bed) [17].

1.1. Biomass feedstock

Among the various raw materials that can be converted to biomass energy, castor has received considerable attention because of its vitality, ability to grow in barren lands, and excellent soil and water conservation abilities. Castor matures in 6 months, and can be harvested two or three times a year. The oil content of castor seeds is more than 50%, and the annual output of castor oil can reach 10–15 tons per hectare. Fig. 1 shows the castor seeds, which are provided by the Asian Green Energy company, and the castor meals is used in the study. Castor is currently one of the world's top ten oil crops, and its main distribution areas include Africa, South America, Asia, and Europe, with castor seed production in India, China, and Brazil accounting for 81.2% of the global total. Castor seeds are oval-shaped (Fig. 1) and divided into two parts: the kernel and the shell. The kernel accounts for approximately 70%–75% of the total weight of a seed. Castor seeds are rich in oil and have thus been referred to as “green renewable petroleum.” Castor oil can be extracted under pressure, with or without heating, or by using



Fig. 1. Photograph of castor seeds.

solvents [18]. Castor oil is a critical industrial raw material, with the international market concentrated mainly in North America, Europe, and China. The residue left after the oil has been pressed out of the castor seeds is called castor meal, and it is an abundant biomass feedstock.

Castor oil is generally obtained by squeezing castor seeds, a process that can be accomplished via either cold or hot pressing. With cold pressing, castor oil is obtained without steam heating. With this approach, the resulting castor oil is not exposed to high temperatures, and thus its medicinal properties are preserved. By contrast, with hot pressing, castor oil is obtained through steam heating. A slow heat treatment process can reduce the viscosity of the residual castor oil, thus rendering it possible to extract oil that could not be obtained through cold pressing alone [19]. However, conventional squeezing methods have some limitations, and we demonstrated in a previous study [20] that castor meal retains a certain amount of oil.

1.2. Catalysts in pyrolysis

In addition to increasing the reaction rate and yield, catalysts are employed in biomass pyrolysis to improve product quality. Catalysts are used to enhance pyrolysis reaction kinetics through the cracking of higher molecular weight compounds into lighter hydrocarbon products [21]. In addition, introducing an appropriate catalyst to a biomass pyrolysis process can boost the biomass conversion efficiency, reduce tar formation, and increase the target product yield. Pyrolytic oil obtained from biomass cannot be applied directly as fuel because it is corrosive, has high viscosity, and low heating value. Deoxygenation and moisture content reduction are often performed to improve the quality of pyrolytic oil [22,23]. Two methods have been applied to reduce the oxygen content of pyrolytic oil: hydrogenation with high-pressure hydrogen and carbon monoxide, and using catalysts (zeolite, Si–Al, molecular sieves) to promote pyrolysis at atmospheric pressure. The second method is used extensively in industry because of the following advantages: (1) no hydrogen is used; (2) the process takes place at atmospheric pressure, which means decreased costs; and (3) the operating temperature is analogous to the desired temperature for bio-oil production.

Babich et al. studied the pyrolytic conversion of chlorella algae to a liquid fuel precursor in the presence of a catalyst (Na_2CO_3) [24]. Thermogravimetric analysis (TGA) showed that adding Na_2CO_3 influenced the primary conversion of chlorella by decreasing the decomposition temperature. In the presence of Na_2CO_3 , the pyrolytic gas yield increased and the pyrolytic liquid yield decreased at a given pyrolysis temperature. However, the higher heating value, higher aromatic content, and lower acidity of the obtained pyrolytic oil show promise for the production of high-quality bio-oil from algae through catalytic pyrolysis.

Pütün studied the pyrolysis of cotton seeds in a tubular fixed-bed reactor under various sweeping gas (N_2) flow rates and various pyrolysis temperatures [25]. Without a catalyst, the maximum available bio-oil yield was approximately 48.3 wt% at 550 °C and a nitrogen flow rate of 200 mL/min. Under the optimum conditions, biomass samples were catalytically pyrolyzed with various amounts of MgO catalyst (5 wt%, 10 wt%, 15 wt%, and 20 wt% of raw material). Experimental results indicated that the presence of the catalyst decreased the bio-oil yield but improved its quality in terms of heating value, hydrocarbon distribution, and the removal of oxygenated groups. Moreover, adding greater amounts of catalyst lowered the bio-oil yield but raised the yield of gas and char.

Wang et al. investigated the pyrolysis of herb residue in a fixed-bed reactor to determine the effects of pyrolysis temperature and

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