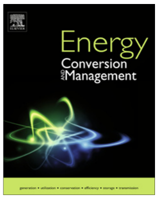
Energy Conversion and Management 129 (2016) 81–88

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman



Production of aromatic hydrocarbons via catalytic co-pyrolysis of torrefied cellulose and polypropylene

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ARTICLE INFO

Article history:

Keywords:
Torrefaction
Catalytic co-pyrolysis
Cellulose
Polypropylene

ABSTRACT

The effects of the torrefaction of cellulose on catalytic co-pyrolysis with polypropylene (PP) over HZSM-5 and HBeta catalysts were examined in a pyrolyzer-GC/MS/TCD/FID system. Torrefied cellulose produced larger quantities of aromatic hydrocarbons during catalytic pyrolysis over both BETA and HZSM-5 catalysts than raw cellulose due to the change in crystallinity and structure of cellulose. Among the catalysts tested, HZSM-5(30) showed the highest performance for the production of aromatic hydrocarbons from the catalytic pyrolysis of torrefied cellulose. The synergy effect for the production of aromatic hydrocarbons was also observed on the catalytic co-pyrolysis of torrefied cellulose and PP over HZSM-5, even when a low catalyst to sample ratio was applied. The maximum BTEXs yield (33.4 wt.%) was achieved from the catalytic co-pyrolysis of torrefied cellulose and PP at a catalyst to sample ratio of 3/1 and a torrefied cellulose to PP ratio of 1/3.

1. Introduction

Severe environmental problems and climate change caused by the intensive use of fossil fuels has intensified the focus on renewable energy. Among the various kinds of renewable energy resources, biomass is considered a valuable energy source because it is an abundant carbon source with CO_2 neutrality and can produce valuable byproducts via thermochemical techniques, such as gasification and pyrolysis [1–3]. Among the various kinds of thermochemical technologies, pyrolysis is regarded as an effective process for liquid biofuel production from various types of biomass, such as wood, agricultural waste, and fruit peel.

Although it is possible to produce a liquid fuel, called a bio-oil or a pyrolysis oil, from the pyrolysis of biomass, it is difficult to use bio-oil as a fuel directly because of its low quality [1]. To upgrade the quality of bio-oil, torrefaction and the catalytic pyrolysis of biomass or catalytic co-pyrolysis with plastics have been suggested [4–16].

Torrefaction is a mild pyrolysis carried out between 200 and 300 °C under an inert atmosphere and can be used for the thermal pretreatment of lignocellulosic biomass to increase the amounts of high quality oils obtained from its thermal or catalytic pyrolysis. Torrefaction can increase the carbon density by lowering the O/C ratio of biomass because hemicellulose can be eliminated from biomass by torrefaction [4]. The torrefaction of biomass can also provide the convenience for the storage and transportation of biomass due to the increased density of biomass by torrefaction. Owing to the advantages of torrefied biomass, torrefaction is used widely as the pretreatment method of biomass prior to the incineration or gasification. Recently, many researchers have considered the use of torrefaction as a pretreatment step prior to the pyrolysis of biomass [4,5].

Many studies have reported the pyrolysis and catalytic pyrolysis of torrefied biomass, such as corncobs [6], pine wood [7], rice husk [8], sewage sludge [9], and lignocellulosic components of biomass [10–12]. Zheng et al. [6] obtained high-quality bio-oil with higher heating values and higher pH from the pyrolysis of corncobs torrefied between 250 and 300 °C. On the other hand, the yields of bio-oil obtained from torrefied corncobs were lower than those from raw ones because devolatilization, crosslinking, and charring

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http://dx.doi.org/10.1016/j.enconman.2016.10.001
0196-8904/

of corncobs occurred during torrefaction. Neupane et al. [7] reported the effects of the torrefaction conditions, such as temperature (225, 250, and 275 °C) and reaction time (15, 30, 45 min), on the production of aromatic hydrocarbons during the catalytic pyrolysis of pine wood. They suggested that the deacetylation and decomposition of hemicellulose, partial decomposition of cellulose, and the aryl ether linkage cleavage of lignin took place during the torrefaction of pine wood, which led to higher yields of aromatic hydrocarbons during the catalytic pyrolysis of torrefied pine wood. Srinivasan et al. [10] also obtained increased yields of aromatic hydrocarbons from the catalytic pyrolysis of torrefied cellulose and reported that the formation of an open chain cellulose structure due to torrefaction could be responsible for the increased formation of aromatic hydrocarbons. Aromatic hydrocarbons are the important chemicals which can be used not only as the fuel additive to boost the octane number of gasoline but also as the chemical feedstock in the manufacturing process of plastics or synthetic fibers [13].

The catalytic co-pyrolysis of biomass and plastics is also considered a candidate method to produce large amounts of aromatic hydrocarbons in the final oil products. The synergy effect for the formation of aromatic hydrocarbons by the co-pyrolysis with plastics in the biomass pyrolysis system have been reported. Many types of plastics, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), were co-fed into the catalytic pyrolysis system of biomass and biomass components. The plastic co-feeding with biomass in pyrolysis provide additional advantages because the pyrolysis oil properties of plastics are similar to the chemical feedstock for the petrochemical industry. This means that the oils produced by the catalytic co-pyrolysis of biomass and plastics can be used as the feeding materials for petrochemical processes, such as FCC refinery process [14].

Dorado et al. [15] used various types of biomass (such as xylan, cellulose, lignin, and switchgrass) and plastics (PE, PP, polyethylene terephthalate (PET), and PS) for catalytic co-pyrolysis. They revealed a synergistic effect for the production of aromatic hydrocarbons via the catalytic pyrolysis of biomass and plastics over HZSM-5. Li et al. [16] obtained high selectivity toward aromatic hydrocarbons from the catalytic pyrolysis of cellulose and LDPE over HZSM-5. They obtained a higher experimental aromatic yield than that calculated theoretically from the yields obtained separately from the catalytic pyrolysis of cellulose and LDPE. They also reported that a smaller amount of coke was formed by co-pyrolysis with biomass and plastics. The production of high-quality oil by the catalytic co-pyrolysis will be very helpful for the actual commercialization of biomass thermal conversion process due to its increased efficiency. Large amount of waste plastics can also be treated via the catalytic co-pyrolysis, and this process will be more helpful for the treatment of municipal and agricultural solid wastes because both of them contain not only biomass but also waste plastics [13,15].

Based on these reports, a combination of biomass torrefaction and co-feeding of plastics can be an effective method to produce large amounts of aromatic hydrocarbons via catalytic pyrolysis. On the other hand, only a few studies reported the use of torrefied biomass for the catalytic co-pyrolysis of biomass and plastics [17]. Therefore, this study examined the catalytic co-pyrolysis of torrefied biomass and plastics. Cellulose and PP were selected as the biomass and plastic materials, respectively, because cellulose comprises the largest fraction (~50%) in lignocellulosic biomass and large amounts of waste PP are generated. HZSM-5 and HBeta, having different pore structures and acidities with various SiO_2/Al_2O_3 ratios, were used as the catalyst. The influences of the mixing ratio of the feedstock samples (torrefied or raw cellulose and PP) and total catalyst to sample ratio on aromatic production were also examined to identify the appropriate feedstock mixing ratio and catalyst dose. To clarify the effects of torrefaction, catalytic co-pyrolysis of raw cellulose and PP were also performed.

2. Materials and methods

2.1. Torrefied cellulose and PP

A commercially available cellulose (Cell, Sigma Aldrich) was torrefied at 250 °C for 1 h under 50 mL/min of a nitrogen atmosphere using a fixed bed reactor. The torrefaction of cellulose was performed using a fixed bed reactor system with a U-type quartz reaction tube. The system consisted of a furnace, nitrogen gas controller, temperature controller, liquid product condenser, and gas sampling parts. The products emitted from the reactor during torrefaction were transferred to the liquid product condenser at −20 °C. Non-condensable gas was collected by a Teflon gas bag connected to the outlet of the liquid collection flask. The yields of the liquid and solid products were determined by actual weight measurements after the reaction. The gas yield was calculated by subtracting the summed yield of the liquid and solid products from 100%. After torrefaction, 97.4 wt.% of solid was recovered as the torrefied cellulose (TCell); 1.4 wt.% of liquid (mainly water) and 1.2 wt.% of gas (mainly CO_2) were produced during cellulose torrefaction. The powder forms of random PP was purchased from a local chemical company.

2.2. Catalysts

Two types of catalyst, HZSM-5 ($SiO_2/Al_2O_3 = 30, 50, 80$) and HBeta ($SiO_2/Al_2O_3 = 25$), were purchased from Zeolyst. All catalysts were calcined at 550 °C for 3 h in air atmosphere prior to the experiment.

2.3. Catalytic co-pyrolysis

The pyrolyzer (Py-2020iD, Frontier laboratories, Ltd., Japan)-gas chromatography (7890A, Agilent Technology)/mass spectrometry (5975 inert)/thermal conductivity detector/flame ionization detector (Py-GC/MS/TCD/FID) system was used for the catalytic pyrolysis of TCell and PP over the HZSM-5 catalyst. For this, a mixture of TCell, PP, and catalyst was injected into the preheated furnace (550 °C) by free falling and the products emitted from the sample cup were analyzed by gas chromatography/mass spectrometry/thermal conductivity detector/flame ionization detector (GC/MS/TCD/FID). In this study, different kinds of analytical techniques such as GC/MS, GC/TCD, and GC/FID (Supplementary Information, Table S1) were applied depending on their purpose (i.e., identification of product by GC/MS (#1), quantification of aromatics (#2) by GC/FID, quantification of CO and CO_2 by GC/TCD (#3), and quantification of C_1-C_4 hydrocarbons by GC/FID (#4)). For the quantitative analysis, the certified chemical standard mixture samples, a mixture of aromatic hydrocarbons and a gas mixture containing CO, CO_2, and C_1-C_4 hydrocarbons, were purchased and calibration curves was made by the external standard calibration method. All the calibration curves had R-squared values higher than 0.995. To check the replicability of the experiments, all experiments were conducted more than three times and their RSD values were less than 3%.

3. Results and discussion

3.1. Change of cellulose by torrefaction

Table 1 lists the physico-chemical properties of raw and torrefied cellulose. Elemental and proximate analysis showed that