Two-step pyrolysis of safflower oil cake

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ABSTRACT

The thermal and catalytic pyrolysis of safflower oil cake was studied in a dual reactor system over catalyst; the first reactor containing no catalyst whereas the second reactor containing catalyst to upgrade the thermally cracked products. For comparison, pyrolysis experiments were also carried out in a single reactor system. The aim was to study the effect of catalyst and temperature on the product yields and composition of the bio-oil. The used catalysts are fluid catalytic cracking catalyst, red mud and activated red mud. The pyrolysis experiments were carried out at varying temperatures between 300 and 600 °C in thermal reactor and 300–500 °C in catalytic reactor. Although, the catalysts had no considerable effect on the yield of the pyrolysis product, they affected the bio-oil composition. It was very important observation that the amount of pyrolytic lignin compounds (11.8–27.5 wt%) was significantly lower and extractives (50.0–65.1 wt%) were higher in case of catalytic experiments. The H/C_{eff} ratio of bio-oils indicated that used catalysts had effective on deoxygenation. The gas chromatography–mass spectrometry analysis showed that the phenols were the dominant species in all bio-oils and their relative amounts, ranging from 26 to 35 wt%, did not significantly changed with the pyrolysis conditions. The spent fluid catalytic cracking catalyst was successfully regenerated to achieve their original activity.

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1. Introduction

It is common knowledge that the earth's fossil fuel supplies are limited and that carbon dioxide a by-product of fossil fuel combustion contributes to the global climate change [1]. It is being recognized that sustainable, clean-energy sources must be produced and used more extensively than ever before. One of those sources is bio-energy, which is produced when chemical energy stored in biomass is utilized. While bio-diesel is produced mainly from vegetable oils and animal fats, commercial bio-ethanol is produced from starch and sugar biomass. The main issue associated with the first generation bio-fuels is the global increase in food prices as food crops being the most used feedstocks for production of first generation bio-fuels. Therefore, there is a growing attention on "second generation" bio-fuels (bio-ethanol and syngas based on lignocelluloses, bio-oil, biogas and bio-hydrogen) as they do not compete with food and feed resources [2]. Biomass can be converted to bio-oil via pyrolysis, which refers to the heating of biomass in the absence of oxygen. This process breaks down the structure of the biomass and yields three products: condensable gases (bio-oil), solid char, and non-condensable gases. The char is burned to provide the process heating and it can be also used as a fertilizer. The non-condensable gases are used to generate combined heat and power (CHP).

Bio-oil can be substituted for heavy fuel oil (HFO), light fuel oil (LFO) or natural gas in a number of applications, including boilers, gas turbines and other heating and power generation applications. However, bio-oil is a dark-brown, acidic (pH 2–3), and thermally unstable and contains high proportion of water and oxygenated compounds [3]. Possibilities in upgrading of bio-oil have been reviewed many years ago by Elliott et al. [4] and also recently by Choudhary and Phillips [5]. Several methods have been testing for upgrading and improving bio-oil quality, such as hydrodeoxygenation [6–11], catalytic cracking of pyrolysis vapors [12,13], extracting chemicals [14], and esterification [15,16].

Hydrodeoxygenation refers to the process in which bio-oil is hydro-treated under hydrogen pressure. A major disadvantage of hydrodeoxygenation is the significant hydrogen requirement. On the other hand, catalytic cracking of pyrolysis vapors (in situ catalytic upgrading) is a process in which bio-oil is thermally treated in a gas-solid phase at an atmospheric pressure without hydrogen. Although in situ catalytic upgrading led to formation a coke (on catalyst bed) and additional water, the quality of the bio-oil is enhanced.

Zeolites have been widely used as catalyst for in situ catalytic upgrading. It is known that zeolites are potentially promising catalyst for removing oxygen from organic compounds and converting them to hydrocarbons in upgrading of bio-oil [11,17]. But main

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problems for zeolites are the fast deactivation of the catalysts by coke deposition, the low yields of organic liquids and the formation of polycyclic aromatic hydrocarbons (PAHs) [18]. Besides conventional zeolites, the modified zeolite catalysts were also tested for the upgrading of pyrolysis vapors. Aho et al. [19] studied the catalytic upgrading of woody biomass derived pyrolysis vapors over iron modified zeolites in a dual-fluidized bed reactor. They reported that the iron modified zeolites led to an increase in the amounts of methyl substituted phenols while a decrease in methoxy substituted phenols. Pattiya et al. [20] studied the fast pyrolysis of cassava rhizome in the presence of ZSM-5, two aluminosilicate mesoporous materials Al-MCM-41 and Al-MSU-F. Results showed that all the catalysts produced aromatic hydrocarbons and reduced oxygenated lignin derivatives, and among the catalysts, ZSM-5 exhibited the highest catalytic activity.

Iliopoulou et al. [21] tested two mesoporous aluminosilicate Al-MCM-41 materials as catalysts for the in situ upgrading of biomass pyrolysis vapors. The mesoporous aluminosilicate Al-MCM-41 materials were found to be promising, with respect to improving the quality of bio-oil as source of useful chemicals via increasing the concentration of phenols and decreasing of corrosive acids. Higher Si/Al ratios (i.e. lower Al content and lower number of acid sites) of the Al-MCM-41 samples increased the yield of the organic phase of the bio-oil, while lower Si/Al ratios favored the conversion of the hydrocarbons of the organic phase toward gases and coke. Lu et al. [22] found that the use of the Pd/SBA-15 completely eliminated the anhydrosugar products and cracked the lignin-derived oligomers to monomeric phenolic compounds. The ZnO was also tested in bio-oil upgrading [12]. Although it had no effect on the product yields, it decomposed the water-soluble anhydrosugars and polysaccharides in bio-oil. Fast pyrolysis of poplar wood followed with catalytic cracking of the pyrolysis vapors was performed by Lu et al. [23]. The catalysts applied in their study were nano MgO, CaO, TiO_2, Fe_2O_3, NiO and ZnO all of which, except for NiO, reduced the amount of anhydrosugars. Moreover, the catalysis by Fe_2O_3 resulted in the formation of various hydrocarbons. However, none of these catalysts except CaO were able to greatly reduce the acids. On the other hand, The ZrO_2 and TiO_2 based catalysts were found to be the most effective to change the pyrolytic products. They significantly reduced the phenols, acids and sugars, and meanwhile, increased the hydrocarbons, linear ketones and cyclopentanones [17]. It should be noted that most of those studies were performed using analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

The objective of this study was to investigate the pyrolysis of safflower oil cake by one-step and two-step pyrolysis, comparably. Oil seed crops have always been an important sector of agriculture in Turkey. Although major oil seeds are sunflower and cotton seeds, safflower seed is gaining importance. Safflower seed production for the year 2009 is about 20,076 metric tons in Turkey (FAOSTAT, 2009). Safflower seed oil is useful edible oil for cooking, salad oil and margarine. It may also be taken as a nutritional supplement. Due to its high oleic acid content, safflower oil can potentially compete with canola oil as bio-diesel feedstock. In addition, safflower crop is drought resistant which offers the potential to provide significant oil feedstocks for biodiesel. Production of bio-diesel based on safflower is widely promoted in Turkey. It looks safflower oil will be the dominant bio-diesel feedstock in our country. Safflower seed contains 35–50% oil, 15–20% protein and 35–45% hull fraction [24] and after oil extraction cake are used for animal feeding. In this study, pyrolysis of safflower oil cake was performed in a semi-batch reactor at different temperatures, and the pyrolysis vapour was led through a catalyst bed, which was present in the second reactor. Red mud and commercial fluid catalytic cracking (FCC) catalyst were used as catalyst. The catalyst performance on the upgrading of vapor has been evaluated compared to non-catalytic experiments.

For comparison, some experiments were also performed by conventional one-stage pyrolysis process.

2. Materials and methods

2.1. Materials

Safflower oil cake (a by-product of safflower oil production) was provided by an oil company (Sivas, Turkey). It was grinded to particle size less than 2 mm and then dried overnight at 105 °C.

Catalysts used in this study were fluid catalytic cracking (FCC) and red mud (activated and non-activated forms). The commercial equilibrium FCC catalyst was supplied by Izmir refinery, Turkey (ReUS-Y) faujasite; Si/Al = 1.35; total surface area: 255 $m^2 g^{-1}$; pore volume: 0. 25 cc g^{-1}. The red mud (RM), as sludge, was supplied by Seydisehir Aluminium Company, Turkey. It contains mainly Fe_2O_3 (37.72%), Al_2O_3 (17.27%), SiO_2 (17.10%), TiO_2 (4.81%), Na_2O (7.13%), and CaO (4.54%). RM receiving from plant was filtered and dried at 105 °C. The dried RM was calcined at 550 °C for 2 h and used as non-activated red mud (NRM). The RM was activated by literature [25]. Activation consisted of boiling the RM in aqueous HCl for 2 h and adding aqueous ammonia to pH ∼ 8. The resulting precipitate was filtered, washed with distilled water, dried at 105 °C and calcined at 500 °C for 2 h. Activated RM was denoted as ARM. ARM contains mainly Fe_2O_3 (41.10%), Al_2O_3 (21.32%), SiO_2 (17.02%), TiO_2 (5.47%), Na_2O (1.25%), and CaO (2.47%). RM and ARM have surface areas of 16 $m^2 g^{-1}$ and 158 $m^2 g^{-1}$, respectively.

In the case of two-step pyrolysis, the catalysts were pelletized into 25 mm diameter and 0.51 mm height cylinder pellets. The pellets were crushed and sieved in order to obtain granular particles (0.5–1.0 mm); which is suitable for catalyst bed loading. The bulk densities of FCC and red muds are 0.78 g cm^{-3} and 0.75 g cm^{-3}, respectively.

2.2. Experimental setup

Thermal and catalytic pyrolysis experiments were conducted in one-step and two-step reactor at different temperatures.

2.2.1. One-step pyrolysis

Biomass samples were pyrolyzed in a semi-batch design using a stainless steel reactor (L, 210 mm; ∅, 60 mm) which was placed in an electrical heating furnace. In a typical pyrolysis experiment, a quantity of 100 g of biomass and 5 g catalyst (in catalytic experiments) as filled into the reactor. And then the reactor temperature was increased by a heating rate of 7 °C min^{-1} up to pyrolysis temperature and held for 1 h at the desired temperature. The reactor was continuously purged with nitrogen at a flow rate 25 ml min^{-1}. The nitrogen gas swept the volatile products from the reactor into the ice-cooled traps. The condensable volatiles were collected as total liquid products in the traps. The non-condensable volatiles (gases) were collected in Tedlar bag.

After pyrolysis, reactor was cooled down under nitrogen gas stream. All traps were weighted before and after each run. Total liquid amount was determined by difference. The yields of liquid products and char were determined gravimetrically. In catalytic experiments, the char amount was calculated by subtraction of catalyst weight from solid residue in reactor. The amount of gas was determined by difference. The liquid product consisted of two phases; aqueous phase and oil phase. The aqueous phase was separated from oil phase by separatory funnel and weighed. All the yields were calculated on biomass as received and experiments were performed in duplicate. The repeatability of the experimental data was within ±3.5%.