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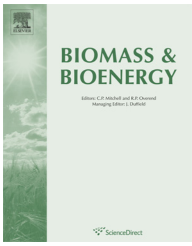

Slow catalytic pyrolysis of rapeseed cake: Product yield and characterization of the pyrolysis liquid

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ABSTRACT

The performance of three catalysts during slow catalytic pyrolysis of rapeseed cake from 150 to 550 °C over a time period of 20 min followed by an isothermal period of 30 min at 550 °C was investigated. Na_2CO_3 was premixed with the rapeseed cake, while γ-Al_2O_3 and HZSM-5 were tested without direct biomass contact. Catalytic experiments resulted in lower liquid and higher gas yields. The total amount of organic compounds in the pyrolysis liquid was considerably reduced by the use of a catalyst and decreased in the following order: non-catalytic test (34.06 wt%) > Na_2CO_3 (27.10 wt%) > HZSM-5 (26.43 wt%) > γ-Al_2O_3 (21.64 wt%). In contrast, the total amount of water was found to increase for the catalytic experiments, indicating that dehydration reactions became more pronounced in presence of a catalyst. All pyrolysis liquids spontaneously separated into two fractions: an oil fraction and aqueous fraction. Catalysts strongly affected the composition and physical properties of the oil fraction of the pyrolysis liquid, making it promising as renewable fuel or fuel additive. Fatty acids, produced by thermal decomposition of the biomass triglycerides, were converted into compounds of several chemical classes (such as nitriles, aromatics and aliphatic hydrocarbons), depending on the type of catalyst. The oil fraction of the pyrolysis liquid with the highest calorific value (36.8 MJ/kg) was obtained for Na_2CO_3, while the highest degree of deoxygenation (14.0 wt%) was found for HZSM-5. The aqueous fraction of the pyrolysis liquid had opportunities as source of added-value chemicals.

1. Introduction

The majority of world's energy is still supplied by fossil fuels, although their use has led to serious environmental problems such as global warming, atmospheric pollution and acid rain. Moreover, fossil fuels also serve as raw materials for a wide range of industrial organic chemicals. Growing environmental concern, rising oil prices, supply oscillations and predictions of scarcity further stimulate the search for environmentally friendly and renewable sources of energy and chemicals [1,2].

Renewable energy includes technologies such as solar, water and wind power as well as biomass. The latter has even been described as renewable energy source with the highest potential to contribute to the energy needs of modern society [3]. However, conversion of biomass into more manageable forms is necessary. Pyrolysis is a thermochemical technique

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that converts biomass into solid (char), liquid and gaseous fractions at moderate temperature and in absence of oxygen. Product yield is strongly dependent on pyrolysis conditions such as pyrolysis temperature, heating rate and vapor residence time [4]. Concerning the production of renewable fuels, pyrolysis is of particular interest since it converts solid biomass (mainly) into an easy transportable and storable liquid form [3]. However, since pyrolysis liquid is a complex mixture of compounds derived from cellulose, hemicellulose and lignin, upgrading is inevitable to meet the quality standards of conventional petroleum-derived fuels. Particularly, high viscosity, corrosiveness, instability and low calorific values due to high oxygen and water contents are reported as major barriers to use pyrolysis liquids directly as renewable fuels [5,6].

Upgrading of pyrolysis liquids essentially corresponds to performing a deoxygenation step. Catalytic hydrotreating (high pressure, consumption of hydrogen) and catalytic upgrading (atmospheric pressure) are two commonly used methods [6,7]. The latter can be performed as post-treatment or as *in situ* catalytic pyrolysis. Post-treatment upgrading is carried out after production of the pyrolysis liquid, making costly condensation and re-evaporation steps necessary. During *in situ* catalytic pyrolysis, both production and upgrading of the pyrolysis liquid simultaneously occur in a special designed reactor. The catalyst is mixed with the biomass (in-bed mode) or placed separately from the biomass (ex-bed mode) [8]. Catalytic deoxygenation enhances the physical properties of the pyrolysis liquid (higher calorific value, lower oxygen and water content, and higher stability). However, the use of a catalyst frequently reduces the liquid yield due to coke formation and more severe cracking of pyrolysis vapors into non-condensable gases [9].

Upgrading catalysts are usually categorized into four main classes: activated alumina, molecular sieve catalysts, sodium carbonate and transition metal catalysts [1]. Both acidity and shape selectivity are important catalyst characteristics that strongly affect yield and composition of the pyrolysis products [10,11]. For instance, the HZSM-5 zeolite is a crystalline and shape selective catalyst that shows mild secondary cracking activity, whereas the amorphous γ-Al_2O_3 catalyst is not shape selective and enhances secondary cracking reactions. Typically, highly oxygenated compounds are converted by these catalysts into hydrocarbons and/or aromatics while releasing oxygen as H_2O, CO and CO_2 [12,13]. The influence of zeolites during catalytic pyrolysis of several lignocellulosic biomass samples was studied by Mihalcik et al. [14]. The HZSM-5 zeolite was found to be most effective in producing aromatics from oxygen-rich vapors. The effects of zeolites on the conversion of rapeseed cake were investigated by Giannakopoulou et al. [15]. These authors concluded that the quality of the pyrolysis liquid was improved the most by HZSM-5. Dupain et al. reported that triglyceride degradation occurs in two successive steps under fluid catalytic cracking (FCC) conditions [16]. First, triglycerides decompose into fatty acids by a fast thermal radical cracking process. Then, secondary catalytic reactions (such as dehydration, decarboxylation and aromatization reactions) further convert the fatty acids into smaller, less oxygenated compounds. Saturated fatty acids are preferably converted into aliphatic hydrocarbons, while highly unsaturated fatty acids enhance the formation of aromatics. Babich et al. studied slow catalytic pyrolysis of microalgae in presence of Na_2CO_3 [17]. Higher calorific values, increased aromatic contents and lower acidities were found by these authors for the catalytically produced pyrolysis oils.

In this study, slow catalytic pyrolysis of rapeseed cake was investigated. Rapeseed cake is a biomass waste that is formed during cold pressing of rapeseed to produce rapeseed oil. This rapeseed oil can be used as edible oil or be converted into biodiesel by transesterification. Frequently, cake derived from (00)-kind rapeseed (with a low content of erucic acid and glucosinolates) is valorized as animal feedstock because of high protein and triglyceride contents [18,19]. However, since not all types of rapeseed cake can be used as animal feedstock due to high contents of erucic acid and glucosinolates, other valorization pathways for rapeseed cake are also desirable. Therefore, the opportunities of slow catalytic pyrolysis to convert rapeseed cake into added-value products were investigated. Experiments were carried out in a horizontal tubular quartz reactor up to 550 °C. Three types of catalysts were tested in an *in situ* reactor setup. Ex-bed mode (no direct contact between biomass and catalyst) was used for the acidic catalysts (γ-Al_2O_3 and HZSM-5), while the alkaline Na_2CO_3 catalyst was tested in in-bed mode. The influence of each catalyst on the product yield was determined and compared with the yield of a non-catalytic test. All pyrolysis liquids spontaneously separated into an oil and aqueous fraction. Both fractions were characterized by complementary analytical techniques and major chemical classes of compounds were determined in order to study the influence of each catalyst on the chemical composition. Several physical properties (see Material and methods) were measured to evaluate the potential of the oil fraction of the pyrolysis liquid to be valorized as renewable fuel or fuel additive.

2. Material and methods

2.1. *Rapeseed cake*

The rapeseed cake was obtained by cold pressing of (00)-kind winter rapeseed (Brassica *napus* L.) with a small screw press at ACRO (Diepenbeek, Belgium). The temperature during pressing was kept below 60 °C to ensure good oil quality. Prior to all analyses and pyrolysis experiments, the rapeseed cake was first ground to achieve a particle size smaller than 2 mm and then dried to constant weight at 105 °C.

2.2. *Catalysts*

Three types of catalysts were tested during slow catalytic pyrolysis of rapeseed cake (Table 1). Activated alumina (γ-Al_2O_3) and sodium carbonate (Na_2CO_3) were used as purchased. The HZSM-5 zeolite was prepared from ZSM-5 zeolite by ion-exchange [20]. First, the ZSM-5 zeolite (20 g) was heated at 550 °C for 2 h in nitrogen atmosphere to remove moisture. Then, it was converted into the NH_4-form by ion-exchange in three consecutive steps. Therefore, the ZSM-5 zeolite was added three times to a 1 M ammonium nitrate solution (750 mL) and heated at 90 °C for 3 h. The excess of nitrate ions