Microporous and Mesoporous Materials 128 (2010) 126–135

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Conversion of rapeseed cake into bio-fuel in a batch reactor: Effect of catalytic vapor upgrading

Kanellina Giannakopoulou [a], Michael Lukas [b], Aleksey Vasiliev [c], Christoph Brunner [b], Hans Schnitzer [a,b,*]

[a] Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 21a, A-8010 Graz, Austria
[b] Institute of Sustainable Techniques and Systems, Joanneum Research, Elisabethstrasse 16, A-8010 Graz, Austria
[c] East Tennessee State University, P.O. Box 70695, Johnson City, TN 37614, USA

ARTICLE INFO

Article history:
Received 5 May 2009
Received in revised form 21 July 2009
Accepted 11 August 2009
Available online 23 August 2009

Keywords:
Zeolite catalysts
Low pressure conversion
Rapeseed cake
Vapor upgrading
Bio-fuel

ABSTRACT

The objective of this work is the development of a method for the catalytic conversion of biomass into liquid products, which could be further treated for the production of bio-fuels. Rapeseed cake was used as a source of biomass, while H-ZSM-5 and H-Beta zeolites were used as catalysts. The process was carried out at 400 °C, in a batch reactor with two configurations. In the first configuration, produced vapors were condensed and collected. In the second configuration, a fixed bed catalytic vapor upgrading section was added into the reactor. The conversion of the rapeseed cake resulted in the formation of two liquid phases (an organic and an aqueous phase), gases and a solid residue. The highest organic liquid phase yield was attained on H-ZSM-5 zeolite at the use of the vapor upgrading section. The aqueous phases contained a mixture of water-soluble substances, mainly N-heterocyclic compounds. The catalyst regeneration studies showed that H-ZSM-5 zeolite in both the reactor and the vapor upgrading section was more stable than H-Beta.

1. Introduction

Pyrolysis and liquefaction are the two thermochemical processes that directly convert biomass into liquid bio-fuels (bio-oils). Therefore, they require less energy than indirect processes, i.e. gasification/Fischer–Tropsch, where biomass is intensively decomposed into gases and then re-composed into liquid bio-fuels.

One of the most important sources of biomass is rapeseed. Rapeseed is widely used not only for the edible-oil manufacture but also for the biodiesel technology. A large rapeseed cake amount is obtained as a by-product of rapeseed oil production by the press and extraction method. The properties of the cake can change with the type of rapeseed plant, for instance canola can be used as a cattle-feed [1]. For the other rapeseed cake types, this is not possible. The increased production of the rapeseed cake as a by-product reduces its demand. Therefore, other fields of applications of rapeseed cake have to be found. One possible solution to this problem is its conversion to high added value products that can help the economics of biodiesel production plants.

Bio-oils are mixtures of compounds of different types and molecular weights, derived from cellulose, hemicellulose and lignin depolymerization and fragmentation. Therefore, the elemental composition of bio-oils and petroleum-derived fuels is different [2]. Bio-oils, produced from pyrolysis or liquefaction processes, cannot be used directly as fuels in the transportation sector. Their property improvement to meet the fuel standards requires the application of upgrading techniques [2,3].

The recent bio-oil upgrading techniques to produce liquid bio-products with improved characteristics are: (a) (partial) hydrodeoxygenation with typical hydrotreating catalysts (sulfided CoMo or NiMo) and (b) catalytic upgrading [2–4]. Increased interest has been focused in the catalytic upgrading, since hydrotreating requires high-pressure systems and the use of H_2 which has to be additionally produced [4].

The catalytic upgrading of bio-oils can be performed *in situ* in specially designed reactor systems, by mixing the biogenic feedstocks with the catalysts [5–12]. Alternatively, it can be performed in series with the thermochemical process [13–15], by evaporating the produced bio-oil and bringing it in contact with the upgrading catalyst, including a costly vapor condensation/re-evaporation step.

Catalysts are not only used in the upgrading the produced bio-oil, but they can also be used during the primary thermochemical biomass conversion process. Many catalytic applications in biomass conversion and upgrading processes involve zeolite catalysts. Synthetic zeolite catalysts, such as Y, ZSM-5 [3,5,7,12–14,16,17], Al-MCM-41 [10,11], Beta [7,17], mordenite [7,17] and MSU-S mesoporous aluminosilicates synthesized from zeolite seeds [16] have been tested. In most of the cases, the produced bio-oils

---

* Corresponding author. Address: Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 21a, A-8010 Graz, Austria. Tel.: +43 316 873 7467; fax: +43 316 873 7963.
E-mail address: Hans.Schnitzer@tugraz.at (H. Schnitzer).

1387-1811/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2009.08.022

exhibited an increased thermal stability in comparison with that of the non-catalytically produced bio-oils. Enhanced production of valuable compounds such as hydrocarbons and aromatics was proved, which increased the bio-oil heating value. On the other hand, the catalytic runs usually revealed a reduction in the organic liquid yield due an increase in the coke production in the presence of catalysts [5,7,10,14,16]. During upgrading processes, the oxygen in oxygenated compounds of biomass is mainly converted to CO, CO_2 and H_2O [18].

Zeolite ZSM-5 catalysts have a strong acidity, high activities and shape selectivities, which can convert the oxygenated bio-oil to light hydrocarbons C1–C10 by dehydration and deoxygenation reactions [18]. In previous studies about the upgrading of a fast pyrolysis bio-oil with different catalysts in a fixed bed micro-reactor, it has been found that acidic zeolite catalysts, especially H-ZSM-5, were more effective in converting the bio-oil to hydrocarbons than the less acidic silica–alumina and non-acidic silicalite [5]. Zeolite Beta catalysts have a medium acidity and larger pore size than zeolite ZSM-5, which makes easier the access to active sites, located inside its pores, for large molecules of biomass origin.

The presence of a significant water amount in the liquid products can affect the structure and acidic properties of the zeolite catalysts [19–24]. It may significantly change the catalytic properties of zeolites due to migration of framework Al to extraframework positions resulting in formation of new Lewis acid sites and reduction of pore sizes.

The aim of this research was to study the effect of the catalyst in the low pressure catalytic conversion of rapeseed cake performed in a batch reactor with two configurations: (a) *in situ* catalytic biomass conversion and (b) *in situ* catalytic biomass conversion in combination with a section for the catalytic upgrading of the produced vapors. A non-catalytic test was also performed as a reference for comparison. The low pressure conversion can give the possibility to better regulate the residence time of produced vapors into the reactor system, enabling the increase of the liquid product yield without the use of high-investment reactors, e.g. fluidized bed. The catalyst addition into the reactor system is expected to produce a bio-fuel with improved chemical composition, by the production of fuel-valuable compounds. The presence of an additional catalytic vapor upgrading section can increase the contact surface between the catalyst and the produced vapors.

2. Experimental

2.1. Materials

2.1.1. Rapeseed cake

The rapeseed cake was obtained via the mechanical cold press extraction method at Biodiesel Kaernten, in the area of Carinthia, Austria. Its main characteristics are presented in Table 1. For the experiments, the rapeseed cake was milled and sieved and a fraction of 0.5–1.0 mm particle diameter was used. Prior to the tests, it was dried to ensure a water content <10 wt.%.

Table 1
Properties of the used rapeseed cake.

Water content (wt.%)	10.4
Ash content (wt.% dry)	11.52
Ultimate analysis (%)	
Carbon	44.67
Hydrogen	6.76
Oxygen (by difference)	35.35
Nitrogen	1.00
Sulfur	0.70
Empirical formula	$C_{17}H_{30}O_{10}N_{0.3}S_{0.1}$

2.1.2. Catalysts

Zeolite catalysts of two different types were used for the experiments: H-ZSM-5 and H-Beta. The zeolites were synthesized at SüdChemie AG. Prior to the tests, the catalysts were thermally activated at 500 °C for 1 h. During the activation, the water absorbed inside the pores of the catalytic material was removed.

2.2. Experimental unit and procedure

All experiments took place in the Technical Laboratory of the Institute of Sustainable Techniques and Systems of Joanneum Research, situated in Graz, Austria. The unit configuration is presented in Fig. 1.

The unit consisted of a batch, stirred, stainless steel reactor (12 L), a vapor cooling section (reflux cooler), a vacuum pump as well as systems for collecting the liquid and gas samples and temperature/pressure/energy consumption controllers and recorders. In order to prevent gases from contaminating the vacuum pump, a cold trap containing liquid nitrogen was added after the vapor cooling section and before the vacuum pump.

In the second reactor configuration, a fixed bed catalytic vapor upgrading section was added into the reactor, so that produced vapors could pass through it before they exit the reactor system.

Non-catalytic and catalytic tests with two different types of catalysts were performed. Rapeseed cake (500 g), an inert solid material (1500 g) and the catalyst (15 g) were mixed and fed into the reactor. In the case when the vapor upgrading section was used, catalyst (50 g) was also added in the section. The reactant system was sealed and the oxygen was removed from the system. The temperature was set and controlled through a temperature control system. During the experiments, the pressure was controlled and set at slight vacuum (0.9 bar). The final reaction temperature used for the presented experiments was 400 °C and a heating rate of 6 °C/min was used. The parameters of the process were selected to achieve the highest conversion of biomass to liquid products at relatively mild conditions that could increase the energy efficiency of the process. The mixture was vigorously stirred during the test. The produced vapors exited the reactor, due to the slight vacuum applied into the system. They were condensed at the vapor cooling section and collected in the liquid products' flask. The non-condensable gases exited the vapor cooling section and were trapped in the cold trap. Gases that were non-condensable in the cold trap exited the system via the vacuum pump and were guided into a gas collection system. The experimental apparatus was held at the final temperature until no further significant release of vapors was observed (~120 min). After the end of the test, the cold trap was isolated from the system, the liquid nitrogen was removed and the gases were guided into a gas collection system.

2.3. Analysis of products

After the end of the experiment, the liquid products and the residues were weighed, while the gas products were measured volumetrically.

The liquid and gas products were analyzed with the help of an Agilent 6890N Gas Chromatographer equipped with a 5973 Mass Selective Detector. The compounds were identified using the Wiley 275 library. For the liquid samples (organic and aqueous phases), the separation was performed on a HP5-MS column (Agilent Technologies) with (5% phenyl)methyl-polysiloxane layer (30 m × 0.25 mm i.d. × 0.25 μm film thickness) with the aid of helium as a carrier gas (0.3 mL/min). The inlet temperature was set at 240 °C (split ration 20:1) while the oven temperature started at 40 °C with a gradient of 5 °C/min to 300 °C where the temperature was held for 2 min. The injection volume was 1 μL. For the gas