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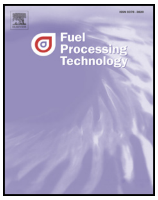

Conversion of rapeseed oil via catalytic cracking: Effect of the ZSM-5 catalyst on the deoxygenation process

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ABSTRACT

In the present paper rapeseed oil was considered as a potential biomass-based source of motor fuels and petrochemicals. The conversion of pure rapeseed oil and its mixture with hydrogenated vacuum gas oil (HVGO) under simulated fluid catalytic cracking conditions via MAT-test was investigated. Besides inorganic gases (CO, CO_2) and water there were also organic oxygenated compounds (alkylphenolics, carboxylic acids etc.) found in the organic phase of the liquid product. For their removal we proposed to improve the catalytic system consisting predominantly of pure standard FCC equilibrium catalyst by the ZSM-5-based FCC catalyst additive. The extent of liquid product deoxygenation and the yield of gasoline were the main monitored parameters. The use of the catalyst mixture containing 10 wt.% of ZSM-5 catalyst additive and 90 wt.% of the standard FCC-catalyst in the case of pure rapeseed oil resulted in a practically complete removal of the organic oxygenates from the liquid product. In the case of the feed mixture rapeseed oi–-vacuum gas oil (1:9) there was found virtually no organic oxygenates in the liquid product with the gasoline yield close to the one of the pure HVGO cracking.

1. Introduction

In recent years many negatives and positives have been credited to the production of biofuels. Considering the fact that the exploration of crude oil has shifted to higher effectivity regarding conventional crude oil reservoirs (e.g., horizontal drilling) or unconventional crude oil resources (shale oil), the role of biofuels is more significant in the field of lowering the fuel emissions than lowering the dependence on crude oil. It is well known that in the combustion process of fossil fuels extensive amounts of CO_2, photochemical oxidants, particulate matter etc., are being released into the atmosphere [1,2]. Replacing the CO_2 from fossil fuel combustion by the one from the biofuel combustion could lead to a significant decrease in the CO_2 novel-production as biomass-based fuels are practically CO_2 neutral [3].

There are basically two types of biofuels (first generation) worldwide known and produced i.e., biodiesel and bioethanol. Biodiesel as a product of the transesterification of vegetable oils can be produced by several routes [4–6]. Bioethanol is produced mainly through the fermentation process of simple or complex sugars [7–10]. Though, these biofuels possess several drawbacks in comparison with their fossil analogs. In the case of bioethanol it is mainly its low heating value and high miscibility with water and in the case of biodiesel it is a low production cost effectivity, low engine compatibility to be used solely [11,12], inconvenient cold fuel properties (CFPP) and higher acidity.

A promising alternative would be the production of more "fossil-like" biofuels that would be similar to the fossil ones in terms of chemical composition and fuel properties [1]. For this purpose implementing processes based on thermochemical cleavage with more severe conditions can be convenient [13,14]. Considering the economical site of the complex process it would be advantageous to make use of already existing and technologically assimilated processes i.e., fluid catalytic cracking (FCC), hydrocracking, etc. depending on the desired output (diesel or gasoline) [15–17]. Although the fuel demand in Europe prefers diesel production, taking into account that the fulcrum of the world economics is slowly being shifted to the east, high demand for gasoline in the eastern region and also in the U.S. [18] can be of a great interest. Based on the latter the process of fluid catalytic cracking can be regarded as very attractive, with simultaneous advantage of no additional hydrogen consumption during the process.

As a potential feed to the catalytic cracking process nonedible and used vegetable oils can be used. There are several papers dealing with the catalytic cracking of vegetable oils (fresh and used) using different catalytic systems, mostly based on solid acid catalysts — zeolites [19–28]. The product stream of the vegetable oil cracking is very similar to the one of the crude oil based feed (HVGO), consisting of a so called dry gas (C_1–C_2), LPG, gasoline, middle distillate (light cycle oil, LCO), heavy fraction (heavy cycle oil, HCO) and coke. The difference is in the presence of CO and CO_2 in the gaseous product and in the two-phase

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system formed in the liquid product (water and organic phase). As many research papers state the oxygen contained in the triglyceride-based feed is converted mainly to inorganic gases and water, though only a few of them deal with the fact that there is also a small amount of organic oxygenates, i.e., alkylphenolics, carboxylic acids, etc., present in the organic liquid phase. There is an imminent negative effect of these types of chemical compounds on the storage and fuel properties i.e., corrosion value, freezing point, CFPP, lower heating value, etc. [29]. Doronin et al. [30] presented the amount of the feed oxygen transformed into liquid organic oxygenates of ca. 6 wt.%. The fact is that this only represents the oxygen transformation but considering the actual yield of above mentioned organic oxygenates containing oxygen, related to the amount of the whole feed the yield of oxygenated organics can reach up to 3–4 wt.%. This could seem negligible but speaking in terms of industrial scale where the liquid product stream amount counts for about 60 tones/h, 4 wt.% stand for nearly 2.5 tones/h which is a number that has to be dealt with. In order to lower the amount or eventually to remove the organic oxygenates from the liquid product, modifying the catalytic system can be one of the options. Inspiration can be taken from the commercially very well established methanol-to-gasoline (MTG) technology, where an oxygenated organic compound (methanol) is converted into gasoline-range hydrocarbons. The conversion is provided by the specially designed zeolite ZSM-5 as a catalyst whose use ensures 85–90 wt.% yield of gasoline [31]. Similar system can be derived in the case of vegetable oil cracking where the use of ZSM-5 zeolite can be convenient, preferably in a hydrothermally stabilized form so the catalyst is persistent against the high temperature and the steam deactivating effect. To meet the optimal relation of gasoline yield vs. the organic oxygenate removal a catalytic system consisting of conventional FCC catalyst (based on zeolite Y) and of the ZSM-5 additive can be used.

In the present work we are dealing with the issue of biofuel production via catalytic cracking of rapeseed oil. The main monitored parameters are the yield of gasoline, propylene, C_4 unsaturated hydrocarbons and the yield of undesired products, as well as the end product quality by means of the content of organic oxygenated compounds in the organic phase of the liquid product. Based on the latter, three catalytic systems have been studied: pure FCC equilibrium catalyst, pure FCC-ZSM-5 for obtaining an inside view on its influence on deoxygenation and a mixture of standard FCC catalyst containing 10 wt.% of FCC-ZSM-5.

2. Materials and methods

2.1. Catalytic system

Basically two types of commercially available catalytic cracking catalysts were tested. The one representing the standard fluid catalytic cracking equilibrium catalyst (ECAT), which is based on ultra-stable zeolite Y and the other representing the FCC-ZSM-5 additive, which is based on zeolite ZSM-5. The average particle size distribution of the FCC-ECAT is 80–120 μm and for the FCC-ZSM-5 it is 75 μm. Also a mixture of the two catalysts was prepared containing 10 wt.% of FCC-ZSM-5. Textural properties were measured by physical adsorption of nitrogen at the temperature of liquid N_2 (-196 °C) using ASAP-2400 (Micromeritics). Catalyst samples were evacuated overnight at 350 °C prior to the adsorption analysis. Specific surface area S_{BET} was calculated using the conventional BET isotherm (relative pressure range $p/p_0 = 0.05–0.3$). The external surface area comprising also the surface of mesopores S_t and the volume of micropores V_{micro} were calculated from the t-plot using Harkins–Jura master isotherm. The value of the total pore volume V_p was calculated from adsorption data at relative pressure $p/p_0 = 0.99$. Catalyst acidity was examined using temperature programmed desorption of ammonia (TPD) in the temperature range of 220–650 °C with a heating rate of 12 °C/min. Obtained textural properties and acidity values of the two pure catalysts are listed in Table 1.

Table 1
Textural characteristics of used catalyst samples.

Catalyst	S_{BET} (m^2/g)	S_t (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	Acidity (mmol H^+/g)
FCC ECAT	161	56.8	0.243	0.054	0.15
FCC ZSM-5	56.3	13.1	0.112	0.023	0.29

2.2. Catalytic cracking experiments

Commercial rapeseed oil (RO) was used as a biomass-based feed in the cracking experiments. For the potential use in industrial scale there will be rather a mixture of RO with the conventional FCC feed used in the process than the rapeseed oil solely. Therefore a feed mixture of RO and hydrotreated vacuum gas oil (HVGO) was prepared. For the preparation of the feed mixture hydrotreated vacuum gas oil was obtained from a commercial refinery. The feed mixture contained 90 vol.% of HVGO and 10 vol.% of rapeseed oil. Elemental analysis of both types of feed was performed using vario Macro cube from Elementar. Helium (4.6 purity) was used as inert gas in the procedure, whereas for sample oxidation (combustion) oxygen (4.5 purity) was used. Sulfanilamide (N—16.25%, C—41.81%, S—18.62%, H—4.65%) was used as standard. The analysis method for vegetable samples "Plant" was used with the sample weight of 20 mg. Elemental analysis of rapeseed oil feed and the distillation characteristics of HVGO feed are listed in Table 2.

Catalytic cracking experiments were carried out via microactivity test (MAT) a standard method for testing FCC catalyst activity. The experimental setup was set according to ASTM D3907 [32]. The catalyst of 4.00 ± 0.05 g weight was deposited on the fixed bed of the tubular reactor. Nitrogen at the constant flow of 30 cm^3/min was used as a purge gas in order to maintain the inert atmosphere. The feed was fed into the reactor via linear injection with varying catalyst/oil ratio of 2, 4, 6 and 12, with the C/O = 12 being closest to industrial conditions. The reaction of catalytic cracking was carried out at 525 ± 1 °C. Condensable cracking products were liquefied in a series of coolers right at the reactor output resulting in the formation of the liquid product. Gaseous products were collected in a water gas reservoir. The solid product of the cracking reaction, represented by the coke, was deposited on the deactivated catalyst whose amount was determined from the weight balance after the catalyst regeneration via coke burn-off.

2.3. Analysis of the cracking products

Gaseous products were analyzed offline using gas chromatograph HP 6890+ with a two parallel branch GC system. The first consists of

Table 2
Key characteristics of the used feedstock.

VGO		Rapeseed oil	
[a]Kinematic viscosity (mm^2/s)	40	[c]Kinematic viscosity (mm^2/s)	35.16
[b]Density (g/cm^3)	0.900		
Sulfur (wt.%)	0.031	[d]Density (g/cm^3)	0.899
Nitrogen (ppm)	949		
Amount distilled (vol. %)	Temperature (°C)	Elemental analysis	(wt.%)
Start	316	N	0.01
10	371	C	77.24
30	415	H	13.64
50	457	S	0.15
70	497	O	8.97
90	538		
End	565		

[a] Measured at 50 °C.
[c] Measured at 40 °C.
[b] Measured at 20 °C.
[d] Measured at 23 °C.

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