Fuel xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Fuel

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

Catalytic cracking of vegetable oils and vacuum gas oil

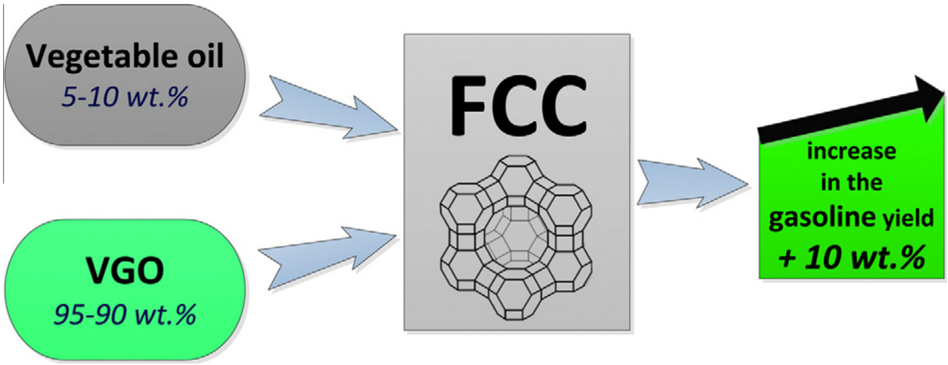
V.P. Doronin, O.V. Potapenko *, P.V. Lipin, T.P. Sorokina

Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences, Neftezavodskaya 54, 644040 Omsk, Russia

HIGHLIGHTS

- ▶ Co-conversion of vegetable oil and VGO allows to increase the gasoline yield by 10%.
- ▶ High gasoline yield explained by facilitating of hydrogen transfer reactions.
- ▶ Maximum promoting effect is provided by the addition of 5–10 wt.% vegetable oil.
- ▶ To provide a maximum effect, high unsaturated vegetable oil should be added.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form 2 November 2012
Accepted 5 November 2012
Available online 20 December 2012

Keywords:
Catalytic cracking
Mixed feed
Vegetable oil
VGO
Gasoline

ABSTRACT

The effect of vegetable oil unsaturation on the distribution and composition of the products of oil conversion over an equilibrium cracking catalyst was studied. Co-conversion of vacuum gas oil and vegetable oils under catalytic cracking conditions make it possible to increase the yield of gasoline fraction by 10 wt.%. A maximum promoting effect is attained by the addition of 5–10 wt.% vegetable oil. Investigation of joint transformations of *n*-undecane, tetralin and sunflower oil upon cracking revealed that an increase in the yield of gasoline fraction can be related to the occurrence of hydrogen transfer reactions and manifestation of the competitive sorption effect.

1. Introduction

In the recent decade, numerous studies were devoted to the production of motor fuels and feedstock for petrochemistry from renewable natural materials, in particular, vegetable oils. The chemical composition of vegetable oils is a mixture of triglycerides that comprise residues of saturated and unsaturated fatty acids bound to a glycerol base. Various processes of vegetable oil conversion into motor fuels are known. Biodiesel is produced by transesterification of oils with alcohols in the presence of catalysts [1,2] or by non-catalytic technology under supercritical conditions [3]. Bio-oil is obtained by pyrolysis of vegetable oils [4–8]. The resulting liquid products have a high content of the oxygen-containing compounds: acids, alcohols, aldehydes, ketones, and phenolic components. In our opinion, catalytic cracking is the most promising way for vegetable oil processing. This process is a basis for the production of high-octane gasoline and light olefins; it has some advantages over other methods of vegetable feedstock processing [9].

Various aspects of vegetable oil cracking are widely discussed in the literature [10–18]. Special attention is paid to their transformations over zeolite-containing catalysts, because the choice of a zeolite strongly determines the distribution of target products. Cracking of palm oil over zeolites H-ZSM-5, Beta, USY and their mixtures were examined in [11,18]. The authors demonstrated

---

* Corresponding author.
E-mail address: potap@ihcp.ru (O.V. Potapenko).

0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.11.027

Nomenclature

X	conversion (wt.%)
S	selectivity (%)
y_i	yield of *i*th product (wt.%)
x_i	molar fraction of the *i*th fatty acid in the oil (mol.%)
$N_{d.b.,i}$	number of double bonds in the *i*th acid
$N_{C,i}$	number of carbon atoms in the *i*th acid
m	mass of *i*th product (g)
E_a	activation energy (kJ mol^{-1})
R	gas constant (J mol^{-1} K^{-1})
k	rate constant (s^{-1})
k_0	pre-exponential factor (s^{-1})
T	temperature (K)
τ	contact time (s)
ϖ_i	mass concentration of *i*th product
ϖ_0	mass concentration of *i*th product
WHSV	weight hour space velocity (h^{-1})

Subscripts

C:O	catalyst-to-oil mass ratio
VGO	vacuum gasoil fraction ($t_{b.r.}$ = 288–561 °C)
gasoline	gasoline fraction ($t_{b.r.}$ = i.b.p.–200 °C)
LGO	light gas oil fraction ($t_{b.r.}$ = 200–350 °C)
HGO	heavy gas oil fraction ($t_{b.r.}$ = 350–f.b.p. °C)
P, I, O, N, A	*n*-paraffins, iso-paraffins, olefins, napthenes, arenes respectively

that activity and selectivity of zeolite-containing catalysts during vegetable oil cracking are determined by the zeolite acidity, size and shape of its channels. Upon cracking, H-ZSM-5 zeolite showed the highest values of palm oil conversion, yield of gasoline and gaseous products as well as the highest selectivity for aromatic hydrocarbons at a low yield of coke. It was found that upon cracking of the vegetable oil over a mixture of H-ZSM-5 and USY zeolites, the transformations of long-chain hydrocarbons proceed over USY, whereas secondary cracking of the generated molecules takes place on H-ZSM-5. The indicated regularities agree with the results obtained for rapeseed oil cracking [10].

In [17], transformations of unsaturated mono-, di- and triglycerides were considered to demonstrate the preferential formation of aliphatic hydrocarbons C_6—C_7 and alkyl-substituted mono- and bicyclic arenes upon cracking over faujasite. Propylene and monocyclic arenes (benzene and toluene) were found to be the main products when cracking of the indicated glycerides was performed over H-ZSM-5 zeolite.

It was shown that the structure of the hydrocarbon residue of fatty acids constituting triglycerides strongly affects the composition of final products upon cracking of the acids [10,19]. The transformations of stearic acid (a saturated fatty acid) provided a higher yield of gasoline fraction and gaseous products as compared to cracking of rapeseed oil and oleic acid (fatty acid with a double bond) [10]. The content of aromatic hydrocarbons in gasoline fraction obtained by cracking of stearic acid is much lower than in the case of rapeseed oil and oleic acid. Independent of the structure of fatty acid composition, the oxygen of triglycerides predominantly passes into inorganic products – water and carbon mono- or dioxide. As shown in [19], upon cracking of soybean oil, which has a high content of unsaturated fatty acids in triglycerides, the fraction of aromatic hydrocarbons in the liquid products is higher as compared to cracking of palm oil and animal fats, which have a high content of saturated fatty acids.

In terms of practical implementation, a combined cracking of petroleum and bio-feedstocks is the most promising technology [19–25]. The literature provides only scarce data on the transformation pathways of such feedstock and on the factors determining the composition of its catalytic cracking products. In [19], the regularities of vacuum gas oil transformations in a mixture with vegetable (soybean and palm) oils, nonedible animal fats and waste vegetable oils upon cracking on equilibrium catalyst were examined. The introduction of 30 wt.% vegetable oil into the feed was found to decrease the yield of liquid products and increase the yield of gaseous products and coke. In [20], cracking of a feedstock comprising vacuum gas oil and rapeseed oil in the amount of 0.0–100.0 wt.% was examined. An increase in the content of vegetable oil in the feed exerted virtually no effect on the gasoline yield, whereas the yield of hydrocarbon gases decreased and the content of olefins in the gases increased. Upon cracking of vegetable oil, the gasoline fraction had a high content of aromatic hydrocarbons and cycloolefins, while the content of cycloparaffins, *n*-olefins and isoparaffins was low. The produced gasoline was free from the oxygen-containing compounds; this indicates a complete transition of oxygen from triglycerides to inorganic products: CO, CO_2 and H_2O. The authors of [21] investigated cracking of petroleum feedstock in a mixture with various vegetable oils and concluded that the oil composition had virtually no effect on the yields of gasoline and coke. However, a great number of unsaturated bonds in the fatty acids constituting triglycerides of soybean and rapeseed oils increased the content of aromatic hydrocarbons in the liquid cracking products and decreased the yield of hydrocarbon gases. It should be noted that in these works an elevated yield of gasoline was obtained at a relatively low (20 wt.%) content of vegetable oils in the blend feed. However, the authors did not provide any interpretation of this fact.

The present work was aimed at studying the transformation of a blend feed consisting of hydrotreated vacuum gas oil and various vegetable oils under catalytic cracking.

2. Experimental

2.1. Feedstock and catalyst

Hydrotreated vacuum gas oil (VGO) and model hydrocarbons: *n*-undecane (Aldrich, ⩾99 wt.%) and tetralin (Sigma–Aldrich, 99 wt.%), were used as a petroleum-derived feedstock. Biofeedstock was represented by sunflower, rapeseed, mustard and palm vegetable oils. Fatty acid composition of the oils was found

Table 1
Main characteristics of the feedstock.

Properties	VGO	Vegetable oil			
		Palm	Rapeseed	Mustard	Sunflower
Density (20 °C) (g/cm^3)	0.899	0.912	0.911	0.915	0.894
Oxygen (wt.%)	–	11.2	10.9	11.0	10.8
Paraffins (wt.%)	46.0	–	–	–	–
Naphthenes (wt.%)		–	–	–	–
Arenes (wt.%)	54.0	–	–	–	–
Acids (wt.%)					
Palmitic (C16:0)[a]	–	19.3	18.9	22.0	6.9
Stearic (C18:0)	–	13.2	3.4	9.4	1.9
Oleic (C18:1)	–	13.5	65.8	34.5	19.7
Linoleic (C18:2)	–	6.0	9.2	6.3	71.3
Linolenic (C18:3)	–	–	0.2	22.5	–
Unsaturation index	–	1.2	4.7	6.4	9.0

[a] The number of carbon atoms and the number of double bonds in the fatty acid.

Please cite this article in press as: Doronin VP et al. Catalytic cracking of vegetable oils and vacuum gas oil. Fuel (2013), http://dx.doi.org/10.1016/j.fuel.2012.11.027