UDC 665.64 : 665.11

DOI: 10.15372/CSD20170404

Joint Transformations of Vegetable Oils with Vacuum Gas Oils under Catalytic Cracking Conditions

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(Received May 15, 2016; revised July 14, 2017)

Abstract

The paper studied joint transformations of vacuum gas oils characterised by the group composition with various vegetable oils under catalytic cracking conditions. It was determined that the distribution of target cracking products depended not only on the carbon component of mixed raw materials but also on the fatty acid composition of vegetable oils. The greater was the number of C=C double bonds in the composition of triglycerides of vegetable oil, the more pronounced promoting effect it had for vacuum cracking of gas oil, as established. This was related to the progression of hydrogen transfer reactions. Olefins that act as hydrogen acceptors were formed during cracking of initial glycerides, and paraffins and naphthenes in vacuum gas oils were donors. Herewith, an increase in the contents of mono- and polyaromatic hydrocarbons was noted in the composition of liquid products. Additionally, it was found that the higher was the content of unsaturated fatty acids in the composition of glycerides of vegetable oils, the higher was the yield of target cracking products (light olefins, gasoline). It was demonstrated that a high content of aromatic hydrocarbons in the composition of vacuum gas oil during the transformation of mixed raw materials resulted in a decrease in the yield of target cracking products with a simultaneous increase in the yield of liquid products and coke. This is related to the fact that aromatic hydrocarbons were poorly subjected to transformations and concentrated in highly-boiling fractions, with the result that an increase in the yields of light and heavy gas oils was observed. Additionally, heavy aromatic hydrocarbons actively took part in condensation reactions with the formation of polyaromatic compounds and coke, as evidenced by the increased formation of coke deposits on catalysts.

Key words: catalytic cracking, vacuum gas oil, vegetable oil, gasoline, triglyceride, C_3–C_4 olefins, aromatic hydrocarbons

INTRODUCTION

Currently, oil and gas are the most important world energy resources. Preparation of motor fuels, and also the production of various petrochemical products are the major areas of the use of oil stock. One of the possible methods of using renewable raw materials is their involvement in oil refining processes. This will allow decreasing emissions of carbon, sulphur, and nitrogen oxides to which great importance is given. In this regard, the use of vegetable oils that do not comprise nitrogen and sulphur compounds is of great value. Significant progress has been made in such techniques as transesterification of oils with alcohols in the presence of catalysts [1, 2], and also on non-catalytic reduction technology under supercritical conditions [3], obtaining biofuel by pyrolysis of vegetable oils *etc.* [4–6].

Catalytic cracking is one of the most important oil refining processes and mainly used for the production of high-octane gasoline and C_3–C_4

olefins. Vacuum gas oil (VGO) is traditional raw materials for catalytic cracking. The use of pure vegetable oils as raw materials is not economically feasible since costs for their preparation are higher than the cost of crude oil. Special attention should be paid to the fact that the primary products of thermal decomposition of initial triglycerides in vegetable oils have high reactivities [7], which may affect both the quality and amounts of target cracking products. In this regard, the method of joint transformation of gas and vegetable oils under catalytic cracking conditions appears relevant.

A great deal of work devoted to catalytic cracking of vegetable oils has been published in the literature [7–18]. The authors of paper [7] found that an increase in the conversion of raw materials containing 3.0–10.0 mass % of sunflower oil, and also the yield of the gasoline fraction were observed. A further increase of oil content in a cracked stock leads to catalyst coking and its deactivation. The authors determined that small amounts of oil in mixed raw materials contributed to the activation of paraffinic and naphthenic hydrocarbons contained in oil stock under cracking conditions.

Papers [15, 16] carried out the study of cracking of vacuum gas oil with the addition of 20 mass % of various vegetable oils (rapeseed, soy, and palm). By the results of catalytic trials, it was found that the distribution of target products varied insignificantly. The content of vegetable oils in mixed raw materials almost does not affect the yield of the gasoline fraction that has high octane characteristics. However, the presence of oil leads to a decrease in the yield of hydrocarbon gases, though they contain high amounts of light olefins.

The composition and yield of target cracking products will mainly depend on characteristics of initial raw materials, particularly, on the group chemical composition during the transformation of vegetable oils, as with refining of oil fractions. Therefore, the purpose of this work is the study of regularities of joint transformations of vegetable oils with various fatty acid compositions and vacuum gas oils that differ by group composition under catalytic cracking conditions.

EXPERIMENTAL

Three types of vacuum gas oils in different group compositions were used in the work as raw materials of oil origin (Table 1). The following vegetable oils were used as raw materials of plant origin: sunflower, rapeseed, and palm. The fatty acid composition was determined by hydrolysis of initial triglycerides and analysis of the resulting acids (Table 2). The ratio of the oil and vegetable components in model mixtures was 90/10 mass %, respectively.

To characterize unsaturated fatty acids, one proposes to use the unsaturation index that is calculated by the formula:

$$\mathrm{UI} = \sum_{i=1}^{N} x_i \frac{N_{d.b,i}}{N_{\mathrm{C},i}}$$

where, x_i is the mole fraction of the i-th fatty acid in oil; $N_{d.b.,i}$ is the number of double bonds in the i-th acid; $N_{C,i}$ is the number of carbon atoms in the i-th acid.

Transformation studies of model mixtures were performed over cracking catalysts that comprised zeolite Y in the cation-decationized form and a matrix, the composition of which consisted of amorphous aluminosilicate, alumina, and bentonitic clay [19]. Selected microcrystalline zeo-

TABLE 1

Main characteristics of vacuum gas oils

Indicators	Vacuum gas oils		
	VGO No. 1	VGO No. 2	VGO No. 3
Density at 15 °C, g/cm^3	0.858	0.903	0.9137
Group composition, mass %			
paraffin-naphthene hydrocarbons	93.7	68.1	65.0
light aromatic hydrocarbons	6.3	15.4	10.9
medium-sized aromatic hydrocarbons		3.3	5.8
heavy aromatic hydrocarbons		9.7	16.1
resins		3.5	2.2
Sulphur content, ppm	13.7	558	8600
Cokability, mass %	0.01	0.07	0.20

TABLE 2

Main characteristics of vegetable oils

Indicators	Vegetable oils		
	Palm	Canola	Sunflower
Density at 20 °C, g/cm^3	0.912	0.911	0.894
Oxygen content, mass %	11.2	10.9	10.8
Fatty-acid composition, mass %			
palmitic (C16:0)	19.3	18.9	6.9
stearic (C18:0)	13.2	3.4	1.9
oleic (C18:1)	13.5	65.8	19.7
linoleic (C18:2)	6.0	9.2	71.3
linolenic (C18:3)	–	0.2	–
Unsaturation index	1.2	4.7	9.0

lite Y due to its characteristics (the average size of the zeolite crystals is 0.5 μm, and the content of oxides of rare earth elements (REE) is 5.1 mass %, sodium oxide content is 0.33 mass %, zeolite lattice module defined by the X-ray phase analysis method is 19.84) can be used as the active component of cracking catalysts for transformation of raw materials of vegetable origin.

Cracking of mixed raw materials was carried out in a fixed-bed catalyst laboratory flow setup in the amount of 5 g at 450 °C and the weight feed rate of raw materials of 30 h^{-1}. Raw materials were dosed out for 30 s. The reactor system was nitrogen purged with a consumption of 30 mL/min. The error in the determination of conversion is 0.7 %, those of the gasoline fraction are 0.4 %, light olefins – 0.2 %.

The composition of gaseous cracking products (CO, CO_2 и C_1–C_{5+}), and also purge gas content (Na_2) were defined chromatographically using Crystal 5000 1 device equipped with a GS-Alumina capillary column (50 м × 0.53 mm), steel packed column (3 м × 3 mm, adsorbent NaX of 45/60 mesh fraction), flame-ionisation and thermal conductivity detectors.

Qualitative analysis of liquid cracking products was carried out in accordance with ASTM method D 2887 (simulated distillation methods) using Rtx-2887 capillary Shimadzu GC-2010 chromatograph (10 m × 0.53 mm × 2.65 μm) and flame-ionisation detector. All liquid hydrocarbons with boiling points less than 200 °C were related to the gasoline fraction. Analysis of the chemical composition of cracking products was carried out using Agilent Technologies 6890/5973N gas chromatograph-mass spectrometer with HP-5ms chromatography column (30 m × 0.25 mm × 0.25 μm).

The amount of obtainable water was determined from ^{1}H NMR spectra by the ratio of the peaks of acetone and water. Acetone was introduced into a mixture in the known amount to homogenize liquid products. Proton NMR spectra were recorded using Bruker Avance-400 spectrometer with a PARBO BB broadband multicore sensor in standard vials (∅ 5 mm), during the one-pulse experiment with the following parameters: the Larmor frequency is 400 MHz for ^{1}H nuclei. Tetramethoxysilane was used as reference.

The content of coke deposits over catalysts was determined by sample mass loss after calcination at 550 °C.

RESULTS AND DISCUSSION

By the chemical composition, vegetable oils are a mixture of triglycerides (95–97 %) consisting of three residues of fatty acids coupled with glycerine base [20]. An opportunity to involve vegetable oils into the catalytic cracking process as a component of raw materials is based on the fact that heavy-oxygen-containing compounds (mainly monobasic fatty acids) are formed resulting from thermal decomposition of initial triglycerides [21, 22]. Further, the resulting compounds undergo deoxygenation with the formation of inorganic (CO, CO_2 and H_2O) and (C_{15}–C_{17} hydrocarbons) products that are involved in cracking processes. The composition of organic products will largely depend on the fact, which fatty acids prevail in the composition of triglycerides of vegetable oils. The more is the number of C=C double bonds in hydrocarbon fragments of triglycerides, the higher is the content of high-molecular-weight olefins in oil cracking products. On the one hand, olefins have high reactivities under cracking conditions [23]. They readily form carbocations involving active acid sites of catalysts, which has promoting effects on the progression of the process. On the other hand, olefins with 2 and 3 C=C double bonds are actively involved in aromatization reactions, which may compete with cracking reactions. Thus, the type of the selected oil is of particular importance in transformations of vegetable oils, as this significantly affects the composition and quality of final products.

Analysis of the fatty acid composition of vegetable oils (palm, rapeseed, and sunflower) used in the work demonstrated (see Table 1) the substantial difference in the number of double C=C bonds in the hydrocarbon fragment of initial triglycerides. Therefore, in order to characterize unsaturation of fatty acids, it was proposed to use the unsaturation index. The chemical meaning of this parameter consists in the fact that it reflects the percentage of double C=C bonds attributable to the carbon atom in fatty acid molecules considering their percentage content in vegetable oil. Sunflower oil containing great amounts of unsaturated fatty acids with one and two double bonds in the composition of triglycerides has the maximum unsaturation index of 9.0 %. This value for palm oil containing the maximum number of unsaturated fatty acids is minimal – 1.2 %.

By the results of catalytic trials (Table 3), it was determined that the conversion level of model mixtures was significantly dependent on the type of vacuum gas oil used. Thus, a decrease in conversion, compared to cracking of pure vacuum gas oil is observed during joint transformations of vacuum gas oil No. 1. With increasing the content of aromatic hydrocarbons in oil gas oils, the presence of vegetable oils contributes to an increase in conversion. This is particularly shown for the heaviest type of vacuum gas oil – VGO No. 3. The observed promoting effect is probably related to the progression of hydrogen transfer reactions [24]. It is known that the addition of olefins in low concentrations to traditional raw materials of cracking contributes to an increase in conversion [25–27]. Thus, olefins formed resulting from thermal decomposition of vegetable oils act as hydrogen donors, and paraffins and naphthenes of vacuum gas oils – as donors. Consequently, carbocations that are easily and quickly adsorbed over catalytic acid sites are formed. Therefore, there is a competition in the adsorption in the active catalyst surface with aromatic hydrocarbons of initial oil raw materials that are characterised by stability to transformations under cracking conditions.

The effect of the unsaturation index of vegetable oils on the conversion of model mixed raw materials can be characterised by the following regularity. An increase in conversion values is observed for all types of vacuum gas oils during their joint transformations with vegetable oils with an increasing unsaturation index value. This is driven by the fact that the higher the unsaturation index is, the higher the content of olefins in organic products of thermal decomposition of oil triglycerides is. Therefore, the stronger promoting effect on the conversion of vacuum gas oil, vegetable oil exerts.

It can also be seen from the data of Table 3 that there is an increase in the yield of light olefins and gasoline fraction that are target products of catalytic cracking for all types of mixed model raw materials with increasing the unsaturation index of vegetable oils. This is particularly typical for relatively heavy vacuum gas oils No. 2 and 3.

TABLE 3

Values of conversion and yields of cracking products of model mixtures

Model mixed raw materials VGO + vegetable oil	Conversion and yields of target cracking products, mass %		
	Conversion	C_3–C_4 olefins	Gasoline
VGO No. 1	78.8	8.2	57.7
Same + palm oil	75.5	6.8	57.3
Same + rapeseed oil	76.5	7.2	57.5
Same + sunflower oil	77.5	7.5	57.8
VGO No. 2	64.7	6.7	45.3
Same + palm oil	64.3	5.0	46.5
Same + rapeseed oil	64.6	5.2	47.1
Same + sunflower oil	65.4	5.6	47.2
VGO No. 3	60.7	7.0	40.3
Same + palm oil	61.2	5.0	43.2
Same + rapeseed oil	61.4	5.1	43.8
Same + sunflower oil	62.4	5.4	44.2

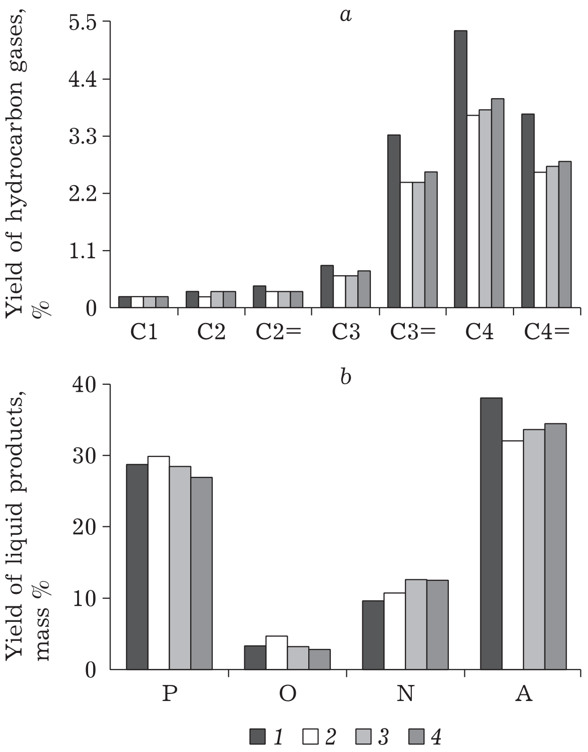

Fig. 1. Composition of hydrocarbon gases (*a*) and the hydrocarbon fraction of liquid products (*b*) in cracking of model compounds: VG No. 3 (*1*); VGO No. 3+ palm oil (*2*); VGO No. 3 + rapeseed oil (*3*); VGO No. 3 + sunflower oil (*4*). P – paraffins; O – olefins; N – naphthenes; A – arenes.

The study of cracking on an example of model mixtures containing vacuum gas oil No 3 demonstrates (Fig. 1, *a*) that with increasing the unsaturation index of vegetable oil, an increase in the yield of the propane-propylene (PPF) and butane-butylene (BBF) fractions with a simultaneous increase in the content of olefins therein. Herewith, an increase in PPF happens mainly due to a rise in the unsaturation index. The yields of C_1–C_2 hydrocarbons almost do not change upon an increase in the unsaturation index. Composition analysis of the hydrocarbon fraction of liquid products (see Fig. 1, *b*) demonstrates that there is a rise in the contents of mono- and especially polyaromatic hydrocarbons with increasing the unsaturation index. This is due to the fact that oils with high contents of unsaturated fatty acids in the composition of initial triglycerides mainly crack with the formation of highly reactive olefins. These hydrocarbons are readily subjected to cyclisation followed by dehydrogenation, with the result that various aromatic hydrocarbons [9, 28] are formed with a simultaneous decrease in the yields of paraffins and olefins. Thus, there is an increase in the yield of C_3–C_4 hydrocarbons, and also a rise in the content of various aromatic hydrocarbons in liquid products during transformation of oils that mainly consist of 2 or 3 double C=C.

By the results of catalytic trials, it was found that oxygen of triglycerides of vegetable oils mainly turns into water and carbon oxides. Herewith, the yields of these inorganic products do not depend on the fatty acid composition of oils.

The quality of hydrocarbon raw materials, particularly, their group composition is one of the major factors that have effects on both the quality and yields of target cracking products. Paraffins with the normal and isomeric structures are the ground of vacuum gas oils. These hydrocarbons are converted into lower molecular mass paraffins and olefins in accordance with the ideas of carbonium ion theory of cracking [29] upon breaking of C–C bonds of the chain under catalytic cracking conditions. Naphthene hydrocarbons contained in cracking raw materials may turn into two main areas [30, 31]. The first area is naphthene ring opening followed by cracking of hydrocarbon chains with the formation of paraffins and olefins. The second one is the formation of hydrocarbon chains due to the progression of the dehydrogenation reaction. The third component of vacuum gas oils is aromatic hydrocarbons. Aromatic rings are stable under catalytic cracking conditions [9, 23], however, they may participate in condensation reactions with the formation of aromatic compounds and coke. Herewith, such chains comprising of more than three carbon atoms of alkyl substituted aromatic compounds may undergo transformations in various directions. The resulting monoaromatic compounds (benzene, toluene, and xylenes) are contained in the gasoline fraction, and di- and triaromatic compounds in light and heavy gas oils are not available for further cracking [15].

Cokability may be a possible criterion of the group composition of vacuum gas oils. This indicator is a qualitative characteristic of oil fractions. It demonstrates fraction ability to form a residue as coke under conditions without air access, *i.e.* constitute a proxy indicator of the content of aromatic fractions from the viewpoint of cracking of aromatic fractions.

On an example of cracking of model mixtures containing various kinds of vacuum gas oils and one type of vegetable oil (sunflower), it was found (Table 4) that a significant decrease in conversion is observed with increasing cokability value. Herewith, a decrease in the yield of gaseous products is noted mainly due to hydrocarbons of propane-propylene and particularly butane-butylene fractions. On the contrary, the yield of liquid products increases, however, substantial re-

TABLE 4

Composition of cracking products of model mixtures

Product yield, mass %	Model raw materials: VGO + sunflower oil		
	VGO No. 1	VGO No. 2	VGO No. 3
Conversion	77.5	65.4	62.4
Gaseous products	15.7	12.0	11.7
$CO + CO_2$	0.6	0.6	0.8
$C_1 - C_2$	0.6	0.8	0.8
PPF,	4.1	3.4	3.2
including propylene	3.4	2.7	2.6
BBF,	10.4	7.2	6.9
including butylenes	4.1	2.9	2.8
Liquid products	81.1	82.7	82.6
Water	0.8	0.9	0.8
Gasoline	57.8	47.2	44.2
Light gas oil	20.7	28.3	29.8
Heavy gas oil	1.8	6.3	7.8
Coke	3.2	5.3	5.7

distribution of the yield of hydrocarbon fractions is observed. Thus, the yield of gasoline is drastically reduced from 57.8 mass % (the mixture of WGO No. 1) to 44.2 mass % (the mixture of WGO No. 3), and the yields of light and heavy gas oils increase by 9.1 and 6.0 mass %, respectively. Additionally, an increase in the yield of coke is noted with increasing cokability of vacuum gas oils. A change in the composition of cracking products of model mixtures is driven by an increase in cokability values. Thus, the higher this indicator is, the higher the contents of middle-sized and heavy aromatic hydrocarbons in vacuum gas oil are (see Table 1). As noted above, light hydrocarbons are stable to transformations and concentrated in high-boiling fractions under cracking conditions. Additionally, heavy aromatic hydrocarbons may participate in condensation reactions with the formation of polyaromatic compounds and coke. This is proven by an increase in the content of coke deposits over catalysts.

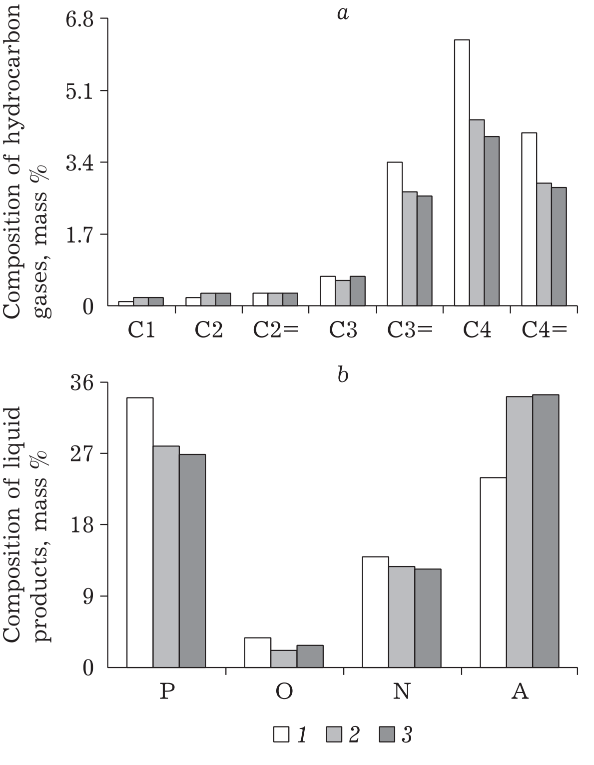

Fig. 2. Composition of hydrocarbon gases (*a*) and the hydrocarbon fraction of liquid products (*b*) in cracking of model mixtures with sunflower oil: VGO No. 1 (*1*); VGO No. 2 (*2*); VGO No. 3 (*3*). P – paraffins; O - olefins; N – naphthenes; A – arenes.

During analysis of the composition of hydrocarbon gases and the hydrocarbon fraction of liquid products (Fig. 2), the high formation of propane-propylene and butane-butylene fractions with high contents of olefins therefrom upon the use of vacuum gas oil No. 1 was determined. This is related to high contents of the paraffin-naphthene fraction in this type of vacuum gas oil. Herewith, it was found the composition of a part of liquid products during transformations of model mixtures with gas oils No. 2 and 3 was characterised by high contents of polyaromatic hydrocarbons, and also an increase in the yield of coke was observed. As noted earlier, these regularities are driven by the group composition of vacuum gas oils. Thus, high contents of heavy aromatic hydrocarbons in cracking raw materials lead to an increase of heavy gas oil content in liquid products. Additionally, an increase in the yield of coke is driven by the fact that polyaromatic hydrocarbons and resinous substances are quickly adsorbed on the catalytic surface, which results in its deactivation.

CONCLUSION

By the results of catalytic studies of joint transformations of vegetable oils and vacuum gas oils that are different in the group composition, it was found that an increase in conversion values of model mixtures was observed with increasing unsaturation index values. This is driven by the fact that olefins are formed resulting from the thermal transformation of vegetable oils. Afterwards, they readily form carbocations that interact with paraffins and naphthenes of oil raw materials. Thus, the greater the number of C=C double bonds in hydrocarbon fragments of glycerides is, the higher the promoting effect of vegetable oil is. However simultaneously with this, the resulting olefins with two and more double bonds actively take part in aromatization reactions, with the result that an increase in the contents of mono- and polyaromatic hydrocarbons is noted in liquid products.

In joint transformations of various vacuum gas oils with one type of vegetable oil, it was determined that the group composition of mixed raw materials had a substantial effect on the composition and yields of cracking products. High contents of aromatic fractions in vacuum gas oil led to a decrease in the yield of the gasoline fraction and C_2–C_4 olefins with simultaneous increasing the yields of light and heavy gas oils and raising the formation of coke deposits over catalysts. This is related to the fact that medium-sized and heavy aromatic hydrocarbons have low activities in cracking reactions but actively take part in condensation reactions with the formation of polyaromatic compounds and coke.

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