

Processing Natural Waste Oils over ZSM-5 Catalyst as an Initial Stage of Bioparaffin Production

Łukasz Jęczmionek*

Oil and Gas Institute, Fuel Department, Lubicz 25A St.
31-503 Kraków, Poland

Received: 26 April 2013

Accepted: 3 November 2013

Abstract

This publication presents the results of research concerning an improvement of low-temperature properties of HVO paraffinic biocomponents by utilizing zeoformed waste natural oils. The process was performed using a special zeolite catalyst based on the hydrogen form of the ZSM-5 zeolites. This method is generally recognized as a new approach for obtaining low-temperature performance improvements of the HVO biocomponents.

Keywords: vegetable oil, biocomponents, low-temperature properties

Introduction

Low-temperature properties of paraffins obtained from natural oils and fats with linear carbon chains generally do not meet diesel fuel standards [1]. Therefore, their properties should be improved. Detailed information concerning practically applied, different solutions can be found in the literature [2-8]. Some of those solutions consist of isomerization of n-paraffins obtained by hydroconversion in the second reactor (the second stage of the process). The most widely known are: NExBTL (developed by Neste Oil) [7] and Ecofining (developed by Honeywell UOP) [8]. Other processes belonging to the same group are: Vegan, Bio Verno, or Biosynfining. The dewaxing process used for improving the low temperature properties of paraffinic fractions obtained from natural triglycerides is mentioned in [9] and in other works [5]. The dewaxing process also was considered for use in co-processing, that is, for hydroconversion of mixtures of fatty oils and hydrocarbon fractions; e.g. straight-run fuel

oil fraction [5, 10]. However, a part of n-paraffins obtained by hydroconversion is lost during the process, an initial boiling point of the product is lowered, and the lighter parts of the conversion (kerosene, gasoline fraction, and gases) must be separated, therefore reducing the efficiency of this solution [10]. Besides, it should also be remembered that the application of dewaxing or hydrosomerization of the biocomponents obtained by co-processing causes conversion of the whole mixture, not only of the bio-derived paraffins.

In my previous articles [11, 12], a method of improving the low-temperature properties of the paraffinic biocomponents (called: HVO – hydrotreated vegetable oil) obtained from the zeoformed fresh rapeseed oil was presented.

In this publication the results concerning an improvement of the low-temperature properties of the HVO paraffinic biocomponents utilizing zeoformed waste natural oils are presented. The processing was performed over a special zeolite catalyst, based on the hydrogen form of zeolite from the ZSM-5 family [13-17].

*e-mail: jeczmiunek@inig.pl

Experimental Procedure

Numerous research results [5, 11-16] indicate that the fatty acid chains in contact with the ZSM-5 catalyst (similar to n-paraffins) undergo dehydrogenation, then isomerization or even cyclization. Other processes based upon decomposition of waste natural oils also are commonly known [17].

It has been found that the decomposition of triglycerides over the ZSM-5 catalyst to partially isomerized ones, free acids or hydrocarbons, can occur [5, 11, 12]. Natural fatty oils modified by mild processing may then be processed to fuel HVO biocomponents by hydroconversion (and also by co-processing) [5, 11, 12].

Being distinct from our previous works [5, 11, 12], this experiment is focused on determining the effect waste oil modified by mild processing has on the properties of the biocomponent (obtained by its following hydroconversion).

Research and Measurement Methods

The methods used in this research for determination of physical and chemical properties of feedstock and its conversion products (hydroraffinates) are listed in Table 1.

Feedstock and Catalysts Used

The research was performed using waste (used in gastronomy for frying) natural oils. The properties of the petroleum fraction (kerosene) obtained from atmospheric tower were the following: boiling range 433-518 K (160-245°C), cloud point below 233 K (-40°C), sulphur content 0.18%, n-paraffins total content about 20%, shown in Table 2. That fraction did not contain paraffins higher than C₁₅ (Table 2).

Initial processing of triglycerides was performed over a catalyst containing the hydrogen form of the ZSM-5 with the silicon module (SiO₂/Al₂O₃ molar ratio) 90-94 and bulk density 690 kg/m³ [5, 11].

A NiMo type catalyst on the Al₂O₃ carrier was used for the hydroconversion of the petroleum fraction and waste natural oil (initially zeoformed or not zeoformed). The catalyst was developed for deep hydrotreating of middle petroleum distillates, especially for deep hydrodesulphurization [5, 11, 12, 14].

Experiment

The waste natural oil processing was realized in a laboratory reactor set OL-150, consisting of two reactors (each of 100 ml capacity) placed in series. The apparatus was equipped with a feedstock pump, a separator, and a receiver with a cooling system for collection of liquid fraction (product). The feedstock delivery rate and the amount of exhaust gases were determined using an appropriate measuring system.

The process was performed within the range of 523-573 K (250-300°C). After each temperature stabilization period (usually 14,400 s) it ran for 72,000 s (20 hours). Samples of

Table 1. Research methods.

Determined parameter	Research method
Density	PN-EN ISO 12185
Fractional composition	PN-EN ISO 3405
Sulphur content	PN-EN ISO 20884
Cloud point	PN-EN ISO 3015
N-paraffins content by chromatography	PN EN 14105
Bromine number	PN-85/C-04520/03
Acid number	PN-EN 14104
Rapeseed oil content (triglycerides)	PN-EN 14105
Fatty acids in rapeseed oil triglycerides (determined by esterification)	PN-EN ISO 5509 PN-EN ISO 5508

Table 2. N-paraffin content in petroleum fraction (kerosene).

N-paraffins	N-paraffins content in hydrocarbon fraction, wt. %
C ₇	0.17
C ₈	0.43
C ₉	1.02
C ₁₀	4.26
C ₁₁	5.15
C ₁₂	4.34
C ₁₃	3.10
C ₁₄	1.33
C ₁₅	0.04
Total	19.84

the liquid product had been taken continuously during the 72,000 s time period.

The exhaust gases were analyzed using chromatography. The processed waste natural oil (zeoformed) under different circumstances was analyzed to determine changes to the fatty acid structures in triglycerides. To find the composition of fatty acids (according to PN-EN ISO 5508) some chosen samples were subjected to esterification (a method described in PN-EN ISO 5509 standard).

To investigate the expected triglyceride structures decomposition during processing, a sample of modified (at 573 K) waste natural oil was analyzed (after esterification). The analytical column used for gas chromatography contained a non-polar stationary phase (methyl silicone type).

In the next stage of the experiment, modified (zeoformed by processing at two different temperatures: 523 and 573 K) waste natural oil products were mixed with straight-run petroleum fraction and subjected to hydroconversion. The mixtures contained 20 vol. % of the modified (zeoformed) waste natural oils and were used as a feedstock.

Parameters of the process were the following: LHSV = 1.0 h⁻¹, the hydrogen feed rate related to the feedstock (H₂/feedstock) 300 Nm³/m³, 3.0 MPa pressure, and the temperature of the hydroconversion 593 K.

The petroleum fraction containing 20 vol. % of non-zeoformed waste natural oil, with the same content of biologically derived component like in other varieties of feedstock, was used as a reference feedstock.

The obtained hydorraffinates were treated with hydrogen for 1 hour to remove dissolved gases. The complete conversion of triglycerides into hydorraffinates was confirmed by chromatography.

To confirm possible reactions connected with cracking of fatty acid chains occurring during processing, distillation curves were determined. The bromine numbers of the obtained hydorraffinates were determined to confirm full hydrogenation of the feedstock.

Discussion of Results

The waste natural oil products obtained by zeoforming were clear, transparent, and homogeneous liquids with a viscosity index similar to the feedstock. Only their color was different. Processing of natural oil changed their color, which became darker with the higher zeoforming temperature (from yellow – starting temperature oil, to dark yellow – oil modified at 523 K, and to dark yellow – brownish for oil modified at 573 K).

The acid numbers were determined to be in the range 5–10 mg KOH/g. These relatively high acid values of the zeoformed also indicate that such decomposition of triglycerides into free fatty acids indeed occurs.

Significant differences between the amount of yielded liquid fraction and the amount of utilized feedstock were not observed (mass measurement revealed loss below 1%).

Table 3. Gaseous hydrocarbon content in exhaust gases from zeoforming reactor at 573 K, LHSV 1 h⁻¹.

Hydrocarbon	Content, wt. %
Ethane	3.2
Propane	4.7
Isobutane	10.1
N-butane	57.3
Isopentane	10.4
N-pentane	14.3

When the process was performed at 573 K the amount of emitted light gases reached 1.4 cm³/s.

The chromatographic analysis of these gases revealed the presence of carbon oxide, light hydrocarbons (mainly n-butane, isobutane and pentanes – Table 3) and water vapor. The chemical compounds containing oxygen may indicate triglyceride structure decomposition (decarboxylation, decarbonylation), whereas the light hydrocarbon presence confirms the cracking processes.

The zeoformed waste natural oil products and also unprocessed waste oils were used as feedstock hydroconversion into the HVO biocomponents. After passing through the second stage all the hydorraffinates (obtained from the feedstock containing 20% wt. of modified or not modified waste natural oil) were clear, homogenous, colorless liquids. The bromine numbers determined for all hydorraffinates were below 0.10 gBr₂/100g, confirming complete hydrogenation of fatty acids. The chromatographic analysis of the liquid phase showed that the hydorraffinates obtained from modified waste natural oil differ from the hydorraffinates obtained from the reference feed – they

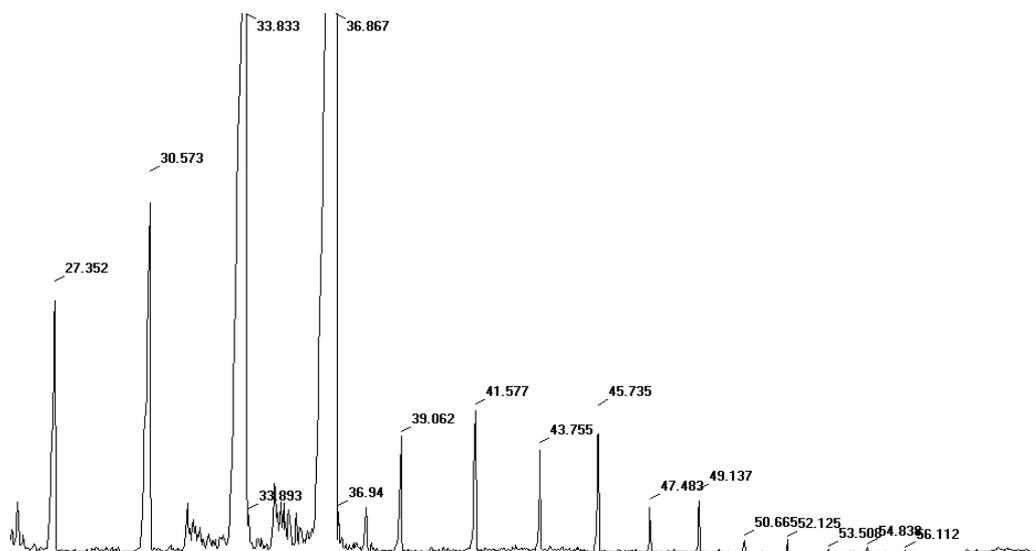


Fig. 1. The chromatogram of a hydorraffinate obtained from the feedstock containing waste natural oils modified by zeoforming. Process parameters: temperature 573 K, LHSV 1 h⁻¹. The highest peaks, C₁₇ and C₁₈, are characteristic for n-heksadecane (C₁₇) and n-octadecane (C₁₈).

Table 4. N-paraffin content in hydorraffinates (total*). Hydroconversion parameters: temperature 593 K, pressure 3.0 MPa, $H_2/\text{feedstock} = 300 \text{ Nm}^3/\text{m}^3$, LHSV = 1.0 h^{-1} .

	Hydorraffinate of the feedstock containing 20 vol. % of :		
	Unmodified waste natural oil (reference feedstock)	Waste natural oil modified by zeoforming at 573 K	
		LHSV 1 h^{-1}	LHSV 3 h^{-1}
C ₇	0.14	0.13	0.14
C ₈	0.37	0.36	0.34
C ₉	0.91	0.97	0.92
C ₁₀	3.22	3.20	2.95
C ₁₁	4.50	4.29	3.80
C ₁₂	3.74	3.48	3.31
C ₁₃	2.73	2.40	2.30
C ₁₄	1.09	1.05	1.04
C ₁₅	0.70	0.63	0.68
C ₁₆	1.02	1.14	1.18
C ₁₇	7.98	4.03	4.85
C ₁₈	7.53	7.47	8.44
C ₁₉	0.29	0.14	0.17
C ₂₀	0.11	0.19	0.20
C ₂₁	0.24	0.11	0.12
C ₂₂	0.07	0.16	0.17
C ₂₃	0.03	0.04	0.05
C ₂₄	0.02	0.05	0.05
C ₂₅	0.01	0.01	0.02
C ₂₆	0.01	0.01	0.01
Total* n-paraffins	34.71	29.86	30.74
C ₁₇ -C ₁₈	15.51	11.50	13.29

*total – sum of paraffins from kerosene (unchanged) and the new ones

contained not only n-paraffins but also non-linear hydrocarbons (most probably iso-paraffins).

Fig. 1 depicts a chromatogram of the hydorraffinate sample obtained from the feed containing waste natural oil modified by processing (zeoforming) at 573 K. There are visible numerous relatively small peaks located between very high peaks characteristic for n-paraffins: hexadecane and octadecane (between corresponding peaks characteristic for n-C₁₆ and n-C₁₇, and also n-C₁₈ and n-C₁₉). Most probably they were derived from branched paraffins formed as a result of the two-stage process. The first stage: processing (zeoforming) of triglycerides, and the second stage: hydrogenation and hydroconversion of processed

triglycerides (possibly partly decomposed triglycerides) in a mixture with petroleum fraction. It should be emphasized that these peaks are not present in the chromatogram of the hydorraffinate obtained from the feedstock containing non-modified waste natural oil. The peaks characteristic for paraffins (n- and -iso) introduced with the petroleum fraction (Fig. 1 and Table 4) were observed within retention times below 25 minutes.

The total content of n-paraffins in the range of C₈-C₁₅ is similar for both raffinates (with zeoformed and non-zeoformed waste natural oil) (Table 5). An increase of the n-paraffins C₈-C₁₅ content is not noted. Such an increase could confirm crucial cracking reactions of long fatty acid chains. In the hydorraffinate obtained from the feedstock containing rapeseed oil modified by zeoforming, the content of C₁₇ and C₁₈ n-paraffins was lower (by about 5%) than in the hydorraffinate obtained from non-modified waste natural oil (Table 4).

The acid numbers of the products obtained by processing waste natural oil over the ZSM-5 catalyst are relatively high (above 10 mg KOH/g) and indicate that during the initial processing triglycerides are subjected to partial decomposition into fatty acids.

Table 5 shows cloud points of hydorraffinates obtained from the feedstock containing modified and non-modified waste natural oil (reference hydorraffinate).

The cloud points of the hydorraffinates obtained from the feedstock containing modified waste natural oil are lower than for non-modified ones. Best improvement of low temperature properties of the hydorraffinate was observed for the feedstock containing the waste natural oil modified at the highest processing temperature (573 K). It may be stated that the improvement of the hydorraffinate low temperature properties is connected with the depth of modification of natural oil contained in the feedstock. The phenomenon is caused by the formation of paraffins as the result of fatty acids chain isomerization (Fig. 1).

Analysis of the fractional composition of the obtained hydorraffinates showed that the initial boiling point of the

Table 5. Examples of cloud points of hydorraffinates obtained as the result of hydroconversion of mixtures containing kerosene and 20 vol. % of natural oil modified by initial processing in various temperatures or unmodified (hydorraffinate obtained from reference feedstock) waste natural oil. Hydroconversion parameters: temperature 593 K, LHSV 1 h^{-1} , pressure 3 MPa, $H_2/\text{feedstock}$ ratio $300 \text{ Nm}^3/\text{m}^3$.

Zeoforming temperature	LHSV [h^{-1}]	
	1.0	3.0
	Cloud points of hydorraffinates, K	
523 K	265.1	264.9
573 K	262.8	262.2
Cloud point of reference feedstock (not zeo-formed)	267.2	

hydroraffinate derived from the feedstock containing modified waste natural oil is not lower than the initial boiling point (IBP) of the hydroraffinate from the reference feedstock without such a modification. Distillation characteristics of both types of hydroraffinates are practically identical.

In comparison to the previous results concerning an initial zeoforming of rapeseed fresh natural oil [5, 11, 12], it can be concluded that the use of waste natural oil as a potential feedstock leads to similar effects on the final hydroraffinates. Cloud points of all investigated hydroraffinates containing fresh or waste natural, initially zeoformed, oils were about 4-5 K lower in comparison to the hydroraffinates obtained from the feedstock of non-zeoformed natural oils (Table 5). Moreover, other properties, like density and distillation characteristics, practically do not differ. In the case of both investigated varieties of feedstock (kerosene with zeoformed fresh rapeseed oil or waste natural oil), the amounts of paraffins transformed from n- form to iso-paraffins were comparable. Analyzing the n-paraffin contents (Table 4), it shows that over 10% of the n-paraffins were transformed into the iso- form [6].

Finally, it is worth mentioning the typical problem connected with the zeoforming process: deactivation of the HZSM-5 catalyst by coking. Solving this problem was not the main priority in the laboratory tests; nevertheless, some significant observations had been made. In laboratory tests (the process described in the article) a significant loss of the HZSM-5 catalyst activity was not observed during a period of 120 hours. It should be noted, however, that in the case of classical zeoforming of the paraffinic fractions a loss of the HZSM-5 catalyst activity within the same period is observed [14]. It may be caused by the temperature differences – zeoforming of paraffins usually occurs at 633-733 K, whereas triglyceride zeoforming was tested within the range of 473-573 K.

Conclusions

The obtained results suggest that the zeoforming of the natural oils (the waste natural oils as well as fresh ones) may be an interesting alternative solution to improve low temperature properties of the paraffinic biocomponents. Nevertheless, the catalyst deactivation by coking must be taken into consideration.

The process runs without hydrogen feed and under relatively mild technological parameters (pressure about 1.7 MPa). Processing of natural oils understood as triglyceride decomposition and relatively small modification of their structure may occur within a low temperature range (523-573 K) but with relatively high feedstock rate (LHSV 3 h⁻¹). The product loss is relatively low (below 1 wt %). The hydroraffinates obtained from waste natural oils modified by processing and then used as co-processing feedstock have better low temperature properties (cloud points) than the hydroraffinates derived from non-modified waste natural oils.

The chromatographic analysis of the hydroraffinates reveals that isomerization of fatty acid chains occurs

(branched chains are formed) and this reaction affects the hydroraffinate properties. Their cloud points diminish with increasing temperature of the waste natural oil processing, therefore deeper modification of the fatty acid triglyceride structure gives better results.

Relatively high acid numbers of processed oil also indicate that such decomposition of triglycerides into free fatty acids occurs.

The results obtained until today allow making the claim that the described process may be an interesting alternative for the low temperature properties improvement of the HVO biocomponents obtained as the result of fatty oils hydroconversion.

Acknowledgements

The initial zeoforming of triglycerides by the hydroconversion process is an innovative technology (Patent pending No. P.396590) and has been awarded at:

- International Salon of Inventions and New Technologies – NEW TIME, 27 – 29.09.2012 in Sevastopol, Ukraine – GOLD MEDAL
- 6th International Fair on Innovation, Eco Ideas, Products and Technologies in Agriculture and Food Industry, AGRO ARCA, 30.08-01.09.2013, Biograd na Moru, Croatia – GOLD MEDAL.
- International Warsaw Invention Show, IWIS 2012, Warsaw, Poland, 19.10.2012 – BRONZE MEDAL.
- Salanul International de Inventică – PRO INVENT, 19 – 22.03.2013, Cluj-Napoca, Romania – BRONZE MEDAL.

References

1. HANCSÓK J. The importance of iso-paraffins in the modern engine fuel production, 8th International Colloquium Fuels Conventional and Future Energy for Automobiles, Esslingen, Germany, 19-20 January 2011, TAE Proceedings, pp. 391-373, **2011**.
2. JAKKULA J., NIEMI V., NIKKONEN J., PUROLA V., MYLLOYA J., AALTO P., LEHTONEN J., ALOPAEUS V. Process for producing a hydrocarbon component of biological origin, Patent EP 1396531 (US 4 230 085), **2004**.
3. JAKKULA J., AALTO P., NIEMI V., KIISKI U., NIKKONEN J., PIIRAINEN O. Fuel composition for a diesel engine, Patent EP 1398364 (US 200455209), **2004**.
4. JAKKULA J., AALTO P., NIEMI V., KIISKI U., NIKKONEN J., PIIRAINEN O. Diesel fuel composition, comprising components based on biological raw material, obtained by hydrogenating and decomposition of fatty acids, Patent WO 2004022674, **2004**.
5. JAKKULA J., AALTO P., NIEMI V., KIISKI U., NIKKONEN J., PIIRAINEN O. Diesel fuel composition, comprising components based on biological raw material, obtained by hydrogenating and decomposition of fatty acids, Patent CN1688673, **2005**.
6. JĘCZMIONEK Ł. Subjects of vegetable oils and animal fats hydroconversion process into HVO hydrocarbon paraffinic biocomponents. Monographic volume, Prace Naukowe Instytutu Nafty i Gazu w Krakowie, 185, Kraków, **2012** [In Polish].

7. JAKKULA J., AALTO P., NIEMI V., KIISKI U., NIKKONEN J., MIKKONEN S., PIIRAINEN O. Fuel Composition for a Diesel Engine, Patent US 7 279 018 B2, **2007**.
8. NAIR P. UOP / Eni Ecofining™ Process Refining Renewable Feed stocks, International Symposium on Biofuels, 25-26 September, New Delhi, India, **2007**.
9. EGEBERG R., MICHAELSEN N., SKYUM L., ZEUTHEN P. Hydrotreating in the production of green diesel, *Petroleum Technology Quarterly*, **Q2**, 101, **2010**.
10. JĘCZMIONEK Ł., LUBOWICZ J. Investigation of rapeseed oil and middle distillate blends in hydroconversion process, *Oil and Gas Institute Issue 2008*, DK-4100-110/08, Kraków, **2008**.
11. JĘCZMIONEK Ł. Zeoforming of triglycerides as a way to improve a low-temperature properties of the second generation fuel biocomponents, *Przemysł Chemiczny*, **1**, 115, **2012** [In Polish].
12. JĘCZMIONEK Ł., PORZYCKA-SEMCIUK K. Triglyceride zeoforming – a method for improving the low-temperature properties of second generation biocomponents obtained from natural oils, *Fuel*, **113**, 17, **2013**.
13. KOVÁCS S., HANCSÓK J. Investigation of the Transformability of Vegetable Oil with Heterogeneous Catalyst, 8th International Colloquium Fuels Conventional and Future Energy for Automobiles, Esslingen, Germany, 19-20 January 2011, TAE Proceedings, pp. 391-373, **2011**.
14. JĘCZMIONEK Ł., LUBOWICZ J., KACZMARCZYK A. The zeoforming process of the naphtha fraction from Fischer-Tropsch synthesis. XV Zeolite Forum, ISBN: 978-83-60514-07-8. Kocierz, Poland, 16-21 June, pp. 213-220, **2008**.
15. JĘCZMIONEK Ł., LUBOWICZ J. Gasoline components via zeoforming of the naphtha fraction from Fischer-Tropsch synthesis, *Pol. J. Environ. Stud.*, **18**, (1B), 56, **2009**.
16. MARTÍNEZ A., PRIETO G. The potential use of micro and mesoporous molecular sieves in the production of liquid fuels from syngas, XV Zeolite Forum, ISBN: 978-83-60514-07-8. Kocierz, Poland, 16-21 June, pp. 13-30, **2008**.
17. BUZETZKI E., ŠVAŇOVA K., CVENGROŠ J. Zeolite catalysts in cracking of natural triacylglycerols, 44th International Petroleum Conference, Bratislava, Slovak Republic, September 21-22, **2009**.