

Diesel production technology from renewable sources – second generation biofuels

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There is a continuous growth in consumption of diesel fuel in Europe and its shortage leads to an increase in its price. New ways of the increase of diesel fuel share at market are searched for. In the field of quality, there is a permanent requirement to reduce the sulphur and aromatics contents in the fuel. Simultaneously, a continuing pressure to reduce regulated emissions is kept.

One of the means of increasing the diesel fuel production lies in the utilization of waste and excess triacylglycerols (TAG) of vegetable and animal origin in a process of catalytic oxygen elimination. To the advantages of the process, the utilization of hydrorefining catalysts and excellent emission profile of the products can be included. As a disadvantage of TAG hydrodeoxygenation, high unit investment costs should be mentioned. Such disadvantages may be eliminated via connecting the process of hydrogenation desulphurisation of gas oil with TAG hydrodeoxygenation by means of technology modification and relatively simple adjustment of the corresponding equipment.

The study is devoted to the issue of direct transformation of vegetable oils and/or animal fats to liquid fuels applying a commercially available NiMo and NiW-based hydrorefining catalysts combined with atmospheric gas oil. Tests of TAG conversion to fuel components were performed and the basic qualitative indicators were evaluated.

During the final stage, a long-term stability test of the catalyst was carried out and a larger amount of the sample for application tests was prepared. Performance and emission measurements were made using a VW Touareg vehicle. The tests documented that even 5% (wt.) concentration of the second generation bio-components reduces the controlled and uncontrolled emissions.

Introduction

The process of the catalytic transformation of triacylglycerides (TAG) on hydrotreating catalyst and in hydrogen atmosphere is one of the possible sources of renewable middle distillates.

In the process, three parallel reactions take place: hydrogenation, hydrodeoxygenation and decarboxylation. In case of hydrogenation-

hydrodeoxygenation, the products are water, propane and *n*-paraffins with even number of carbon atoms, corresponding to the pertinent fatty acids in the treated oils/fats, predominantly *n*-C₁₆ and *n*-C₁₈. In case of hydrogenation-decarboxylation, the products are CO₂, propane and *n*-paraffins with odd number of carbon atoms in the molecule, generally by one carbon atom lower than the number of carbon atoms in acyls of used TAGs, predominantly *n*-C₁₅ and *n*-C₁₇.

A higher selectivity of the generation of liquid hydrocarbons, as well as a higher fuel quality is declared for the above processes. Reaction yield is about 80 % and it is connected with the elimination of oxygen, as the molecules of TAGs contain about 11 % of oxygen. As advantageous features of hydrocracking, exploitation of conventional refinery technology, and hydrotreating catalysts may be mentioned ^[1,2]. In the process, no uncommon byproducts are formed, all of them can be processed in refinery streams. Economy of the process is more acceptable than that of the process of transesterification. It is estimated that the process costs (without costs for input oil) reach 50 % of the costs of transesterification ^[3]. However, the investment costs for facility establishment are higher by 50 %.

Among the certain disadvantages of the product, low-temperature properties caused by a high content of *n*-alkanes C₁₅-C₁₈ can be mentioned, however, catalytic isomerisation in the presence of hydrogen is an appropriate solution of the problem. In the role of catalyst, Pt anchored on Al₂O₃/zeolite HZSM 22 is used ^[5]. The process occurs at temperatures 280 – 370°C, pressures 3.5 – 8 MPa, LHSV 1 – 4 h⁻¹. CFPP of the product ranges from -18°C to -14°C. However, the catalyst is very sensitive and becomes easily deactivated.

At the time being, commercial processes NExBTL of the companies Neste Oil ^[6,7,9] and Ecofinning™, which are offered jointly by UOP and Eni, are available ^[8].

Experimental

Catalytic conversion of triacylglycerides (TAGs) in a mixture (6,5% vol.) with atmospheric gas oil has been investigated with conventional hydrotreating catalysts sulphided NiMo/γ-Al₂O₃, and with NiW/NiMo catalysts prepared on different supports (NaY zeolite, ZrO₂, TiO₂). The target of our research was to prepare renewable biodiesel in one reaction step and with smaller investment costs.

The tests were performed in flow apparatus, in a tubular reactor (the total volume 250 ml) with catalytic bed of 100 ml, feed range 100 – 1 000 ml/h, maximal operation temperature 600 °C, maximal operation pressure 100 bar. The device was equipped with the regulation of pressure, temperature, feed stock loading and reaction products discharging. Feed stock container and pipelines were heated to decrease the viscosity and/or to maintain the possibility of animal fats feeding.

Reaction feed stock is pumped by a piston pump and mixed with reaction gas on the head of the reactor. Formed mixture, depending on the amount of the catalyst, passes through a bed, which is, based on the reaction conditions, placed in the reactor body, where the reaction proceeds. The formed product passes subsequently through a cooler to a separator, where reaction gas is separated from the product.

Liquid sample is withdrawn continuously, as this equipment has individual level gauge that enables to set a sample amount.

Reaction gas, after being discharged from the separator, passes through a gas flow meter allowing both controlling and measuring its amount. The products were evaluated according to EN 590 standard.

Catalysts

Commercial NiMo/ γ -Al₂O₃, and NiW/NiMo catalysts prepared on different supports (NaY zeolite catalyst, TiO₂, ZrO₂) in sulphidic form were used. The catalysts were prepared by two step incipient wetness impregnation of the different support. The catalyst was sulphurized directly in the reactor with 5 % solution of dimethyl disulphide in gas oil. It was dried at 120 °C in the stream of nitrogen. Sulphurization was achieved in the stream of hydrogen at pressure 3 MPa. Temperature was gradually increased with the gradient 100 °C/h.

Results and discussion

Vegetable oils and animal fats can act as a significant source of hydrocarbons. In the technological process exploiting hydrogen and conventional hydrorefining catalysts, it is possible to produce raw materials with the cetane number exceeding 80 while hydroisomerisation is needed to reduce low-temperature properties. However, the technology is cost demanding. An addition of vegetable oils/animal fats to gas oil at hydrogenation refining units represents a lower-priced variant, however, it is accompanied by certain restrictions and risks, too.

Vegetable oils/animal fats contain free fatty acids and the impact of their acidity to the reactor and pipes corrosion should be taken into account. Moreover, they contain alkaline metals and phosphorus acting as catalytic poisons cutting down the catalyst activity and lifetime. The water formed during hydrodeoxygenation poses a further problem to the catalyst. Therefore, it is advantageous to perform the reaction in a separate reactor connected in parallel with the main hydrorefining reactor. The issue of the catalyst choking up with alkaline metals and phosphorus can be solved using a catalytic bed filled with a cheaper catalyst trapping the mentioned adverse substances prior to the main catalyst.

Within the experiments performed, a connection of the process of gas oil hydrogenation refining and that of vegetable oil hydrodeoxygenation applying the hydrorefining catalyst in one step was verified. Modifying the catalyst acidity, we tried to adjust the isomerisation and consequently improve the product low-temperature characteristics. A possible adverse effect of the reaction water was suppressed using a TiO₂ or ZrO₂-based supports. For the sake of comparison, zeolite NaY and commercial desulphurising catalyst NiMo/Al₂O₃ were tested too. As metal components, Ni, Mo and W underwent testing.

To atmospheric gas oil produced by crude oil distillation, 5% (vol.) or 6.5% (vol.) of refined rape-seed oil was added. Common hydrorefining and hydrodeoxygenation was carried out at temperature 360°C, pressure 3.5/4.5 MPa, LHSV=1 h⁻¹ and ratio H₂:HC=1000. During the tests execution, the formed hydrogen sulphide was stripped off by nitrogen.

Decarboxylation was favoured at lower pressures and hydrodeoxygenation increased with increasing pressure fig. 1. Decarboxylation results in odd number paraffin (C₁₇)

production and CO₂ formation whereas hydrodeoxygenation results in even carbon number paraffin production (C₁₈); therefore the ratio of nC₁₇ to nC₁₈ is a measure of the decarboxylation/hydrodeoxygenation ratio. The temperature dependence is opposite-tab. 2. Standard hydrotreating catalysts of NiMo, NiW all showed activity for both reactions. The courses of hydrodeoxygenation/deoxygenation were complete using all the catalysts. Gas oil acted as a solvent. Ni W (NiW)-containing catalysts exhibit an extraordinary hydrogenation activity. In case of catalyst supports with low specific surface (ZrO₂), the level of desulphurization was lower when compared to the commercial catalyst. The cetane number increased substantially and reached the value of 56.7. However, lubricating capacity stipulated by standard (541 vs 460 μm) was not achieved. The isomerization does not take place with tested catalyst.

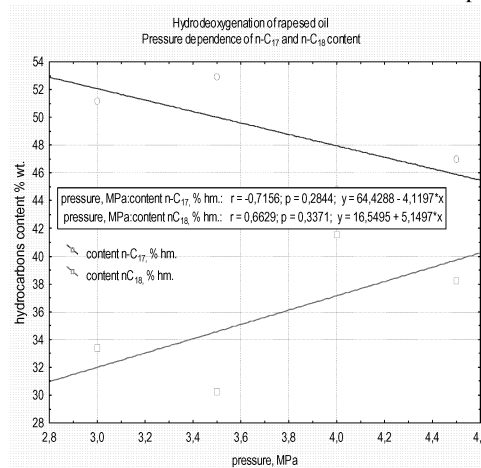


Figure (1) Hydrodeoxygenation of rapeseed oil. Pressure dependence of n-C₁₇ and n-C₁₈ content

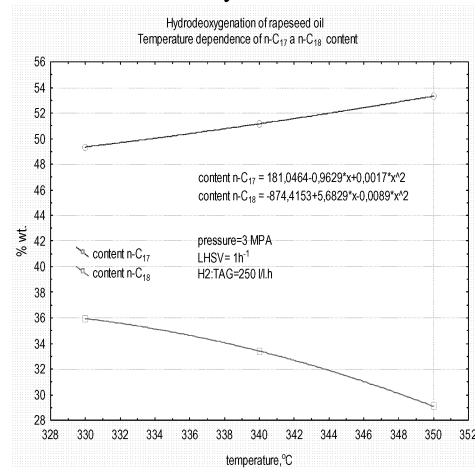


Figure (2) Hydrodeoxygenation of rapeseed oil. Temperature dependence of n-C₁₇ and n-C₁₈ content

The standard refinery distillate hydrotreating units do not appear to be suitable for renewable diesel production in a co-processing scheme, but co-processing of biomasses such as plant oils and/or fats/wastes may be processed in a new refinery distillate hydrotreating unit. Flow scheme is in the fig. 3.

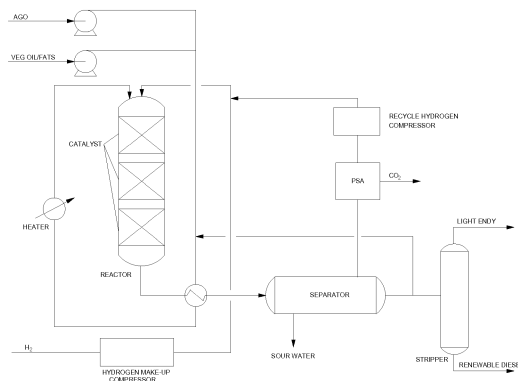


Fig.3 The proposal flow scheme for co-processing atmospheric gas oil with renewable biocomponents

Evaluation of performance and emission characteristics of the diesel fuel containing 5% (vol.) of renewable diesel (prepared rapeseed oil hydrodeoxygenate) and their comparison to diesel fuel class F were done too.

Measurements of the performance and emission characteristics were realized using a vehicle VW Touareg. The engine was equipped with an electrically controlled pump-line nozzle direct injection system, a turbocharger with intercooler and water-cooled exhaust gas recirculation. The exhaust path of engine have diesel oxidation catalyst. Emission measurements were performed with an exhaust gases analyser MAHA MGT5. The measurements were carried out at constant operation parameters, i.e. engine idling and constant speeds 60, 90, or 120 km/h and evaluated as the average of five consecutive measurements.

Along with measurements of regulated emissions, determination of unregulated emissions, namely of VOCs (volatile organic compounds) and carbonyls were performed. VOCs were determined with an analyser Bernath Atomic equipped with a FID detector. Carbonyl content in off-gases was determined using HPLC. Carbonyls in off-gases are trapped and derivatized to carbonyl hydrazones using a sorption tube filled with 2,4-dinitrophenylhydrazine. The trapped carbonyl hydrazones are extracted from the tube by an adequate amount of acetonitrile and the resulted extract undergoes concentrating and analysing by HPLC method.

Table.1 VW Touareg R5; comparison of VOC and NO_x emission diesel vs. diesel+renewable diesel

Fuel	test	VOC mg/kg	C _{org.} mg.m ⁻³	NO _x mg/kg	Carbonyls µg/l
Diesel	idling	4,5	7,23	44,0	0,9
	60 km.h ⁻¹	6,0	9,65	87,6	2,8
	90 km.h ⁻¹	4,0	6,43	294,6	4,8
	120 km.h ⁻¹	14,0	22,51	476,2	0,2
95 % diesel + 5% renewable diesel	idling	2,4	3,86	28,2	0,2
	60 km.h ⁻¹	2,5	4,02	85,6	0,8
	90 km.h ⁻¹	1,9	3,05	288,0	0,8
	120 km.h ⁻¹	2,0	3,22	474,6	0,8

Reduction in CO₂, CO emissions and hydrocarbons content observed in all modes represents a positive effect. NO_x content decreased at engine idling by 50%. Even more important are VOCs and total carbon emission reductions. Analogously, a positive impact concerning carbonyl emission reduction was reached by adding biofuel of the second generation. Their absolute value is, however, very low due to the fact that a vehicle is equipped with an oxidation catalyst.

An addition of the second generation biocomponent to fossil diesel exhibits a significantly positive effect on emissions, those unregulated in particular.

Conclusions

TAG can be converted to the second generation biocomponents in mixtures with atmospheric gas oil from crude oil distillation using a hydrorefining catalyst. Adding 6.5% (vol.) of vegetable oil, gas oil containing 5-5.5% of biocomponent was prepared, characterized with excellent performance and emission parameters. The philosophy of introduction of a second reactor into the existing structure of hydrorefining unit allows to reduce investment cost of biocomponent processing.

Acknowledgement

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