Production of Diesel Fuel via Hydrogenation of Rancid Lard and Gas Oil Mixtures

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For the second generation bio-fuels the most promising product mixtures are the bio gas oils and diesel fuels containing bio gas oils. These products are in the gas oil boiling point range and made by catalytic hydrogenation of pure triglycerides or triglyceride-gas oil mixtures. The bio gas oil product is a mixture of n- and i-paraffins.

During the experimental work our aim was to investigate the heterogeneous catalytic hydrogenation of rancid lard and its 50% mixtures of gas oil fraction on sulphided $CoMo/Al_2O_3$ catalyst. During a series of experiments we studied the effects of the different feedstocks (lard content of 50-100%) and the process parameters (temperature: 300-380 °C, pressure 40-80 bar, LHSV: 1.0-2.0 h^{-1}, H_2/feedstock rate: 600 Nm^3/m^3) on the yield and quality of the products. We assessed that in the course of the heterogeneous catalytic hydrogenation the deoxygenation of the triglyceride part of the feedstock occurred while the removal of the sulphur and nitrogen content and the saturation of the aromatic content took place with a high degree as well. In the course of the experiments we managed to make excellent quality products, which are suitable for the use in Diesel-engines.

1. Introduction

In the near past, in the whole world research has started for the development and utilization of cleaner and more available energy sources. Among these alternative fuels, there are the renewable, agricultural-derived fuels from biomass and amongst them the bio-derived motor fuels (agro-motor fuels). Because of environmental considerations and its intense rely on import energy sources (>55%) the European Union treats the research of agriculture derived, renewable energy sources with great attention and urges their utilization in greater volumes, besides attending the agricultural production too. Before the worldwide economic crisis, the tendency of the automotive fuel market in the European Union showed a probable increase in the demand for diesel fuels and this tendency will restore in contempt of the feasible spread of hybrid vehicles. Therefore the research and development of the agriculture derived bio motor fuels is coming to the front.

1.1 Biodiesel

Nowadays, the agriculture derived bio motor fuel and bio blending component that is produced and utilized in the greatest volume is the FAME (fatty-acid-methyl-ester) or biodiesel from the first generation biofuels. This is made by the catalytic transesterification of vegetable oils and other fats. However the biodiesel-producing technologies and the product itself also have numerous disadvantages:

- high unsaturated content (causing bad thermal-, oxidation-, and thus storage stability),

- high water content (corrosion problems)
- high sensitivity of ester bonds to hydrolysis (poor storage stability),
- methanol content (toxic),
- reactive OH-group (corrosion of coloured metals),
- low energy content which results high fuel consumption (~10-15%),
- unfavourable cold flow properties (cold-start and pulverizing, CFPP)
- high production costs compared to the applicational value, etc.

1.2 Bio gas oil

One of the nowadays strongly researched alternatives to produce such a product rich in iso-paraffins on triglyceride base is the catalytic hydrogenation (Figure 1) and if necessary, a further isomerization step. In this case the conversion of triglycerides to a product rich in iso-paraffins is recommended by multistage catalytic process (hydrodeoxygenation, and after it isomerization).
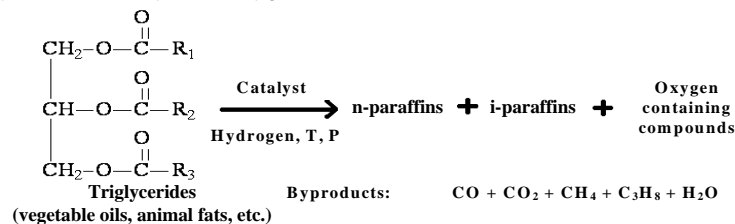
$$CH_2-O-\overset{\overset{O}{\|}}{C}-R_1$$
$$CH-O-\overset{\overset{O}{\|}}{C}-R_2 \xrightarrow[\text{Hydrogen, T, P}]{\text{Catalyst}} \text{n-paraffins} + \text{i-paraffins} + \begin{array}{c}\text{Oxygen}\\\text{containing}\\\text{compounds}\end{array}$$
$$CH_2-O-\overset{\overset{O}{\|}}{C}-R_3$$

Triglycerides
(vegetable oils, animal fats, etc.)   **Byproducts:** $CO + CO_2 + CH_4 + C_3H_8 + H_2O$

Figure 1.: The reaction pathway of the bio gas oil production (R_1, R_2, R_3: carbon chains with C_{11}-C_{23} carbon number)

The product of the reaction is the so called bio gas oil, of which according to its definition, the bio gas oil is a mixture of n- and i-paraffins in the gas oil boiling point range, made with specific catalytic hydrogenating process of raw materials with high triglyceride content (vegetable oils, animal fats, used frying oils, brown greases of sewage works etc.). This process is very promising, because the most suitable for the utilization in Diesel engines and the most valuable compounds of the fossil derived gas oils are the normal- and isoparaffins with high cetane number and with good cold flow properties. For the production of bio gas oil and bio gas oil containing gas oils, there are two main technological methods (Figure 2.).
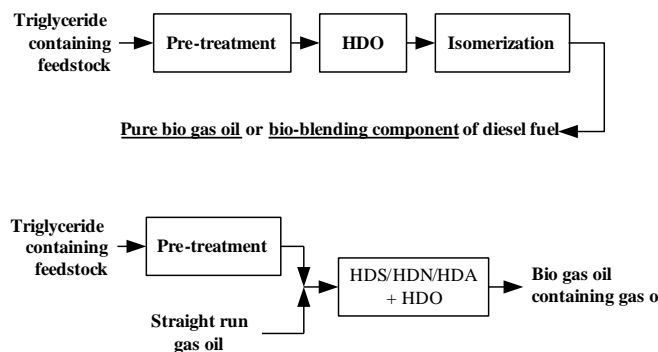
Figure 2.: Possible technological solutions to produce bio gas oil

2. Experimental

During the experimental work our aim was to investigate the heterogeneous catalytic hydrogenation of rancid lard as a model compound and its 50 % mixtures of gas oil fraction on sulphided $CoMo/Al_2O_3$ catalyst. During a series of experiments we studied the effects of the different feedstocks (lard content of 50-100 %) and the process parameters (temperature: 300-380 °C, pressure 40-80 bar, LHSV: 1.0-2.0 h^{-1}, H_2/feedstock rate: 600 Nm^3/m^3) on the yield and quality of the products.

2.1 Experimental equipment

The experiments were carried out on experimental equipment with a tubular reactor of 100 cm^3 active volume capacity. The experimental work was carried out in continuous mode. The equipment contains all of the main apparatus of a heterogeneous catalytic hydrogenation plant.

2.2 Applied feedstocks and catalysts

As the base stock of the heterogeneous catalytic hydrogenating experiments we used 100 % rancid lard (Table 1. and 2.) furthermore a deep desulphurized gas oil (Table 2.) obtained from Russian crude (MOL Plc.). As feedstocks we used pure lard, pure gas oil and their mixtures of 50 %. During the experiments, the sulphur content of the feedstock was adjusted to 1000 mg/kg with the use of sulphur containing chemical (dimethyl-disulphide, which is easily degradable at the investigated process conditions) to preserve the sulphide state of the catalyst.

Table 1.: The typical fatty acid composition of the applied rancid lard feedstock

Fatty acid*	Rancid lard
C14:0	1.19
C16:0	21.35
C16:1	2.04
C18:0	11.54
C18:1	45.40
C18:2	12.50
C18:3	0.78
C20:1	1.06
C22:2	0.67

*CX:Y, where
X: carbon number of the fatty acid,
Y: number of the unsaturated bonds in the fatty acids.

Table 2.: The heteroatom and aromatic content of the feedstocks

Properties	Deep desulphurized gas oil	Rancid lard
Sulphur content, mg/kg	5	20
Nitrogen content, mg/kg	<1	61
Aromatic content, %	22.5	0
Polyaromatic content, %	2.4	
CFPP, °C	-1	~40

2.3 Process parameters

The series of experiments were carried out at process parameters based on previous experimental results with triglycerides: T: 300-380 °C, P: 40-80 bar, LHSV: 1.0-1.5-2.0 h^{-1}, H$_2$/feedstock ratio: 600 Nm^3/m^3. The H$_2$/feedstock volume ratio were chosen regarding the necessary amount of H$_2$ for the saturation and heteroatom removal reactions.

2.4 Analytical methods

The properties of the feedstocks and the products were specified according to the specifications of the valid EN 590:2009+A1:2010 diesel fuel standard, and with standardised calculation methods. The obtained composition of liquid organic product was detected by high temperature gas chromatography.

2.5 Obtaining the main product fraction

The fractionation of the product mixture was carried out as it can be seen in Figure 3. In the course of the experiments, the product mixture was separated into gaseous and liquid phase in the separator unit of the experimental equipment. After separating the water from the obtained liquid product mixture, we separated the light, C$_5$-C$_9$ hydrocarbon products by distillation up to 180 °C from the organic liquid phase. The fraction above the boiling point of 180°C was separated to gas oil boiling point range main product (C$_{10}$-C$_{22}$ hydrocarbons up to the boiling point of 360 °C) and to residual fraction by vacuum-distillation. All product yields are based on the amount of the feedstock.
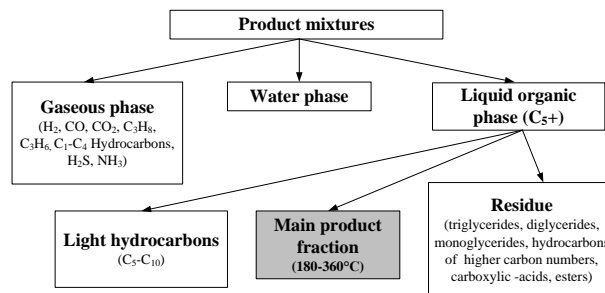
Figure 3.: The method of the product fractionating

3. Results and discussion

The gaseous phase besides hydrogen, contained carbon-oxides which were formed during the deoxygenation, propane originated from the triglyceride molecule, hydrogen sulphide and ammonia formed in the course of heteroatom removal and a very small amount of lighter hydrocarbons (C_{4-}) originated from the hydrocracking reactions. The slightly increasing amount of the lighter hydrocarbons (C_{4-}) in the gaseous phase and mainly the amount of the fraction below boiling point of 180 °C (C_5-C_{10}) showed, that the hydrocracking activity of the applied catalyst increased with the temperature. With increasing temperature, the yield of the main product fraction slightly increased (Figure 4.). The cause of this was that at higher temperatures, the reaction rate was higher, so the conversion of triglycerides of the lard slightly rose in case of both feedstock. In the case of 50 % feedstock the obtained yields were higher, because the feedstock already contained 50 % gas oil boiling point range hydrocarbons. In the case of pure lard, the highest main product fraction yields (46-53 %) were obtained at 340-380°C, however did not reach of the theoretical yield of 80-85 % calculated from the fatty acid composition of the triglycerides. As a function of the pressure – in the investigated process parameter range – there were no definite trends in the case of pure lard, 60 bar pressure proved to be favourable and on the other hand in the case of mixture feedstock 40 bar proved to be favourable. The decrease of the LHSV favoured the triglyceride conversion to paraffin with both of the feedstocks, as the yield of the main product fraction increased with the higher retention time (lower LHSV) (Figure 5.).
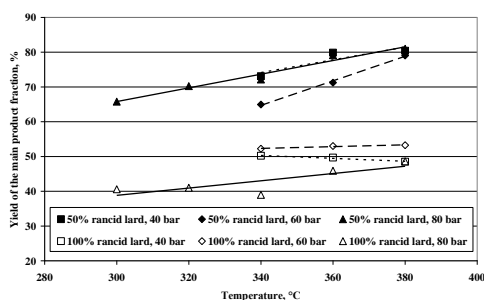

Figure 4.: Yield of the main product fraction (LHSV=1.0 h^{-1})
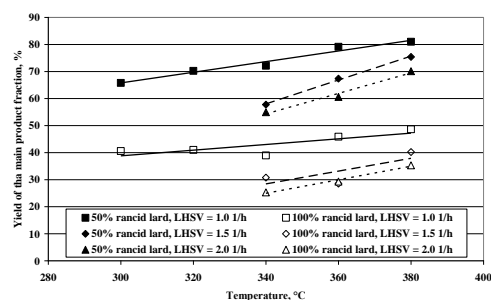

Figure 5.: Yield of the main product fraction (P=80 bar)

Based on the results of the experiments, we investigated the ratio of the oxygen removal reaction pathways of the triglycerides. As the gas oil contains several compounds besides normal and isoparaffins, the concentration of the forming C_{15} and C_{16} or rather the C_{17} and C_{18} paraffins was determinable only in the case of pure lard feedstock. The quantity of these compounds increased in the liquid product mixture with increasing the temperature. The ratio of the conjugate and the singular hydrocarbons namely the ratio of the hydrodeoxygenating (HDO) and the decarboxylation/decarbonylation (DCO) reactions decreased with increasing the temperature (Figure 6.). The application of lower pressures also favoured the DCO reaction pathway. By changing the LHSV – in the investigated parameter range – in the point of the HDO/DCO ratio (Figure 7.), there

were no definite trends either, so this parameter did not influence the formation of the conjugate/singular hydrocarbons.
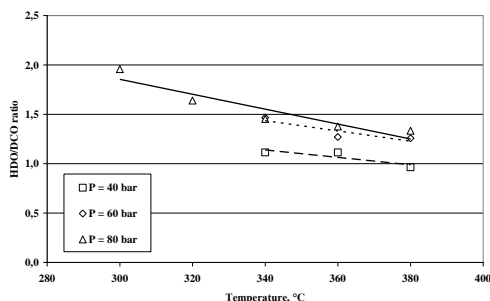

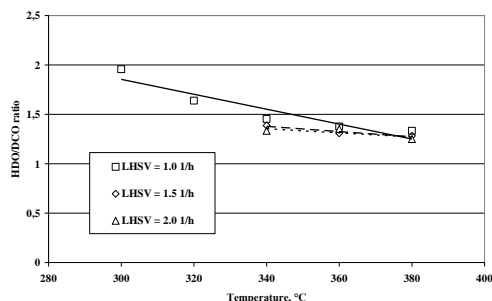Figure 6.: Ratio of the HDO and DCO reaction pathways (LHSV=1.0 h^{-1})

Figure 7.: Ratio of the HDO and DCO reaction pathways (P=80 bar)

To summarize, in the case of the investigated sulphide state CoMo/Al_2O_3 catalyst the HDO reaction pathway take place with higher rate, because normal paraffins forms in 52-66 %. Through the investigation of the isomerisation activity of the sulphide state catalyst was determined that at the applied process parameters, the concentration of the isoparaffins (Figure 8.) increased with increasing the temperature and with decreasing the pressure. The cause of this was, that with the increasing temperature the isomerisation reaction rate increasing as well. We investigated the effect of the LHSV, and we determined, that in the case of higher LHSV which means lower retention time slightly less isoparaffin molecules are formed (Figure 9). At the investigated process parameter range, at the most favourable cases, the main product fraction contained only 3-7 % isoparaffins.
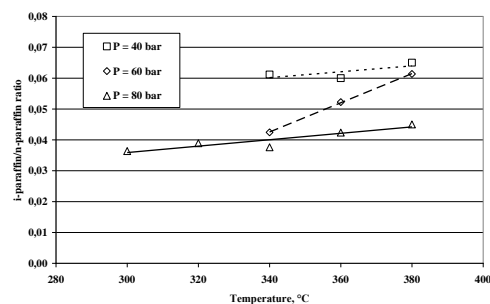

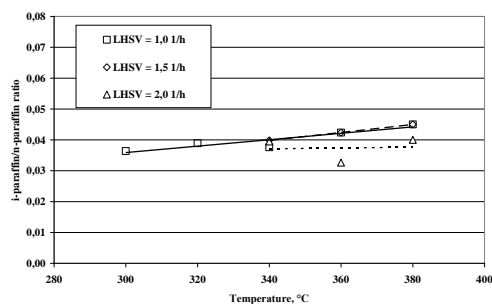Figure 8.: Ratio of the formed iso- and normal paraffins (LHSV=1.0 h^{-1})

Figure 9.: Ratio of the formed iso- and normal paraffins (P=80bar)

4. Conclusion

In this paper we shortly introduced the bio gas oil or bio gas oil containing gas oil producing technologies, respectively. During our experimental work we investigated the heterogenous catalytic hydrogenation of rancid lard, as a renewable agriculture-derived waste feedstock, on sulphide-state CoMo/Al_2O_3 catalyst. During the experimental work our aim was to investigate the heterogeneous catalytic hydrogenation of rancid lard as a model compound and its 50 % mixtures of gas oil fraction on sulphided CoMo/Al_2O_3 catalyst. During our experimental work, we determined, that at the investigated process parameters combinations (temperature: 300-380 °C, pressure 40-80 bar, LHSV: 1.0-2.0 h^{-1}, H_2/feedstock rate: 600 Nm^3/m^3) for the utilisation of pure rancid lard or its 50 % mixture with gas oil stream feedstock, the applied sulphide state CoMo/Al_2O_3 catalyst is not suitable for high conversion. The triglyceride conversion was far from complete (the main product fraction in the case of pure lard was 53% at maximum while the theoretical is 80-85 %) at the strictest process parameters, either. The obtained products could be excellent diesel gas oil blending components, because they have high

cetane number (in case of pure rancid lard feedstock: about 90, in case of 50 % rancid lard containing feedstock: about 75) due to their high n-paraffin content (in the case of pure lard feedstock 93-97% n-paraffin content) and because they have low sulphur-, nitrogen-, and aromatic content. Of course, the residual fraction can be recirculated to the reactor (multiple flow process). To determine the proper recirculation rate of the residual fraction, further experiments are needed. The cold flow properties of the products can be improved by catalytic hydroisomerization of the n-paraffins then with additivation. With this high quality bio-motor fuel or bio-derived blending component for Diesel motor fuel can be obtained.

Acknowledgement

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