



Production of Bio Gas Oil Containing Diesel Fuel with Upgraded Cold Flow Properties by Co-processing

Csaba Tóth*, Péter Baladincz, Jenő Hancsók

University of Pannonia, Department of MOL Hydrocarbon and Coal Processing, Egyetem street 10, H-8200 Veszprém, Hungary
tothcs@almos.uni-pannon.hu

The aim of our experimental work was to investigate the applicability of a catalyst bed compiled of various compositions of hydrogenation catalysts to produce bio-component containing diesel fuel by co-processing of gas oil with vegetable oil. We investigated the heterogeneous catalytic transformability of gas oil fractions with 0, 5, 15, 25 % sunflower oil content at 50-80 bar pressure, 300-380°C temperature (LHSV = 0.75-3.0 h⁻¹ and H₂/HC ratio 600 Nm³/m³) on catalyst systems containing only the main catalyst and the three catalyst layers as well. In case of both catalytic systems and under the favourable operational conditions (360 - 380 °C, P = 80 bar, LHSV = 0.75-1.0 h⁻¹, H₂/HC=600 Nm³/m³) the main properties of the high-yield products made from maximum 0-15 % vegetable oil containing feedstocks satisfy the requirements of standard EN 590:2009+A1:2010. The amount of vegetable oil higher than 15 % reduced the desulphurisation efficiency. By using the catalyst bed prepared of the three catalysts products with CFPP value reduced by 3-4 °C could be produced as in case of using only the main catalyst.

1. Introduction

Long-term forecasts show a tendency toward increasing energy consumption thus the use of engine fuels increases because of the growing population and its increasing mobilization. The depletion of oil stocks, the dependence on oil and import energy sources, and the need of the reduction of environmental pollution turned the attention to alternative energy sources. Within this the development of energy sources from biological origin and their application have become necessary (Wenzel, 2009). Currently, the continuous research and application of the second-generation biofuels produced from renewable sources can certainly contribute to these demands.

To meet the requirements of the EU mainly the biodiesel (FAME) is used as a blending component in the diesel fuels. The biodiesel has more unfavourable properties (e.g. poor thermal and oxidation stability, and thus poor storage stability caused by high unsaturated content, corrosion problems caused by high water content, sensitivity to hydrolysis, unfavourable cold flow properties, less energy content, etc.); so a wide range of (intensive) research has begun to replace it. One of the possible solutions is the heterogeneous catalytic hydrogenation of the triglycerides (e.g. vegetable oil, fats, wastes, etc.), during which the so-called bio gas oil (mixture of i-, and n-paraffins in gas oil boiling point range) can be produced (Hancsók et al., 2012; Kovács et al., 2010; Krár et al., 2010; Mikulec et al., 2009). The bio gas oil is a full value bio blending component, its quantity is not limited by the current diesel fuel standard EN 590:2009+A1:2010 against the biodiesel (up to 7 v/v%).

The hydrogenated vegetable oil (HVO) is used in several countries (Finland, Germany, Austria etc.) as a blending component, but only one company (Neste Oil) produces the largest quantities of the product

(capacity: ca. 2 million tons/year) (NesteJacobs, 2012). In addition, several research groups work on the development of the co-processing of triglyceride and gas oil mixtures as well (Bezergianni et al., 2009; Huber et al., 2007; Melis et al., 2009; Tóth et al., 2010, 2011). In this case, fuels can be produced usually only with unfavourable cold flow properties against the properties of products made by blending of isomerised HVO (Hancsók et al., 2007a,b, Kasza et al., 2011; Krár et al., 2011). To achieve better properties the quality of the full amount of products made by co-processing should be improved by high scale additivition, or catalytic processes. It is therefore necessary to investigate the preparation of a catalyst system and selecting the process conditions to produce bio-component containing diesel fuel with decreased cold flow properties by co-processing of gas oils with triglycerides.

2. Experimental

According to the above mentioned facts, the aim of our experimental work was to investigate the applicability of a catalyst bed compiled of various compositions of hydrogenation catalysts to produce bio gas oil containing diesel fuel with decreased cold flow properties by co-processing gas oil with vegetable oil. The complete conversion of the vegetable oil part, and also the deep desulphurization, the reduction of nitrogen and aromatic content of the feedstocks were expected.

The catalyst bed contained three catalysts layers with different activity: protection/prehydrogenation, hydrodesulphurisation/hydrodeoxygenation and isomerisation. During our experiments we investigated the heterogeneous catalytic transformability of gas oil fractions with 0, 5, 15, 25 % sunflower oil content at 50-80 bar pressure, 300-380°C temperature (LHSV=0.75-3.0 h⁻¹ and H₂/HC ratio 600 Nm³/m³) on catalyst systems containing only the main catalyst and the three catalyst layers as well. The selection of the operating parameters was based on the results of our previous experiments and taking into account the physical and chemical properties of the gas oil and the vegetable oil.

We investigated the effect of the catalytic system, the process parameters and the vegetable oil content of the feedstocks on the yield, the physical, chemical and application properties of the main product.

2.1 Experimental Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm³ effective volume. It contains all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic hydrogenation plant. The experiments were carried out in continuous mode.

2.2 Materials and methods

As the feedstocks for the heterogeneous catalytic hydrogenation experiments mixtures of properly prepared Hungarian origin sunflower oil and gas oil with different (0, 5, 15, 25 %) sunflower oil content were used (Table 1). In case of the pure vegetable oil feedstocks the sulphur content was set to 1000 mg/kg – mixing of an easily degradable sulphur compound - to preserve (maintain) the catalytic activity of the sulfide state catalyst.

Three commercial transition metal/Al₂O₃ catalysts with different composition were used expediently chosen according to our pre-experiments.

The properties of the feedstocks and the products were specified as the specifications of the EN 590:2009+A1:2010 standard, relevant for Diesel-fuels and with standardised calculation methods.

3. Results and discussions

The products obtained from the heterogeneous catalytic conversion of the different feedstocks were separated into a gas phase, a water phase and an organic liquid phase. The gas phase separated in the separator unit of the experimental equipment contained (besides of hydrogen) carbon-monoxide and carbon-dioxide forming in the deoxygenation reactions (hydrodeoxygenation, decarbonylation, decarboxylation), propane forming from the triglyceride molecule, hydrogen-sulphide and ammonia forming in the heteroatom removing reactions from the gas oil part of the feedstock, and in addition it contained light hydrocarbon by-products (C₁-C₄) forming in the cracking reactions (as a valuable by-product). The liquid phase contained water (forming in the reduction of triglycerides), hydrocarbons and

different oxygen containing compounds. After the splitting of the aqueous phase, we separated the main product fraction (gas oil boiling point range fraction – mainly C₁₁-C₂₂ hydrocarbons till boiling point of 360 °C) and the residue from the organic phase via vacuum distillation. In all cases the products contained components below the boiling point of 180 °C (gasoline) in less than 1%. The incidentally obtained residual fraction contained the not converted triglycerides, the formed or rather not converted di- and monoglycerides, and hydrocarbons with higher carbon numbers originating from the feedstock or being intermediates, and also carboxylic acids and esters.

Table 1: Properties of feedstocks

Properties	Gas oil (GO)	95 % GO +5% SO	85 % GO +15 % SO	75 % GO +25 % SO	Sunflower oil (SO)
Density (15.6°C), g/cm ³	0.8609	0.8635	0.8697	0.8756	0.9226
Viscosity (40°C), mm ² /s	4.81	6.14	8.75	11.39	31.11
Acid number, mg KOH/g	0.03	0.03	0.04	0.05	0.08
Iodine number, g I ₂ /100 g	1	7	19	31	122
Aromatic content, %					
monoaromatic	27.41	26.00	23.30	20.59	0.00
diaromatic	15.83	14.98	13.46	11.93	0.00
total	43.24	40.97	36.75	32.51	0.00
CFPP, °C	3	3	4	6	20
Sulphur content, mg/kg	5748	5460	4888	4314	1000
Nitrogen content, mg/kg	228	217	195	173	7
Oxygen content, %	10 mg/kg	1.11	2.75	5.85	11.5
Flash point, °C	79	80	80	81	>300
Distillation characteristics					
IBP	215	215	216	216	*
10 v/v%	284	286	289	292	*
50 v/v%	318	321	325	331	*
90 v/v%	346	355	369	*	*
FBP	364	*	*	*	*

* cannot be measured because of the thermal decomposition of sunflower oil
CFPP: Cold Filter Plugging Point

In this publication the change of the product yields and main quality properties are presented only in case of products obtained with the utilizing of the composite catalyst bed. The change of the cold filter plugging point - which was the aim of our scientific work - is of course described and compared in case of products obtained with the usage of the one and the three catalysts containing reactor as well.

The yield of the liquid organic product decreased with increasing temperature and pressure as well as with decreasing LHSV in case of gas oil and vegetable oil feedstocks. This was caused by the higher conversion of vegetable oil – while water, CO₂, CO and lighter products formed, decreasing the yield of the liquid product – and on the other hand the hydrocracking of the hydrocarbons. By using gas oil feed the liquid product yield was higher than 96% in every case. With vegetable oil feed, the organic liquid product yield was between 81-94 %. Therefore during the processing of vegetable oil fewer products are formed than in case of gas oil feed. For these reasons, and the knowledge of theoretical yields it is reasonable that the higher vegetable oil content in the feed causes lower yield of the organic liquid products.

At mild reaction parameters, the products from pure vegetable oil contained a high amount of residual fraction. In case of stricter reaction parameters, a higher quantity of products was formed in the gas oil boiling point range, which means that with increasing the temperature and pressure, and decreasing the LHSV the yield of the main product increased.

In case of pure gas oil feed, the yield of the main products is almost equal to the yield of the organic liquid product, because of the low rate of cracking reactions. The yield of the main product decreased with the tightening of the reaction parameters.

In the case of mixture feedstocks, the yield of the main product shaped in a very complex way. At strict reaction parameters (LHSV=0.75 h⁻¹, P=80 bar) with increasing vegetable oil content, the curve – it is decreasing with the temperature - of the products formed from pure gas oil feed is shifted to a maximum-curve (Figure 1 "A"). The yield of the main product decreased with the increasing vegetable oil content. At mild reaction parameters (LHSV=3.0 h⁻¹, P=50 bar) from setting out the decreasing curve of the main product obtained from pure gas oil, the tendencies of the curves shifted to continuously increasing (Figure 1 "B"). At these reaction parameters the vegetable oil conversion is still incomplete. With increasing temperature, the conversion increased as well as the yield of the main product. At rigorous reaction parameters, from 340 °C the entire vegetable oil content was converted. With further increasing temperature, the yield of the main product decreased, because of the cracking reactions. That phenomenon only occurs over 15 % vegetable oil content, because a lower content cannot compensate the decrease of the product yield from the gas oil feed share. With blending vegetable oil to gas oil the product yield is less in every case than in the event of pure gas oil feed.

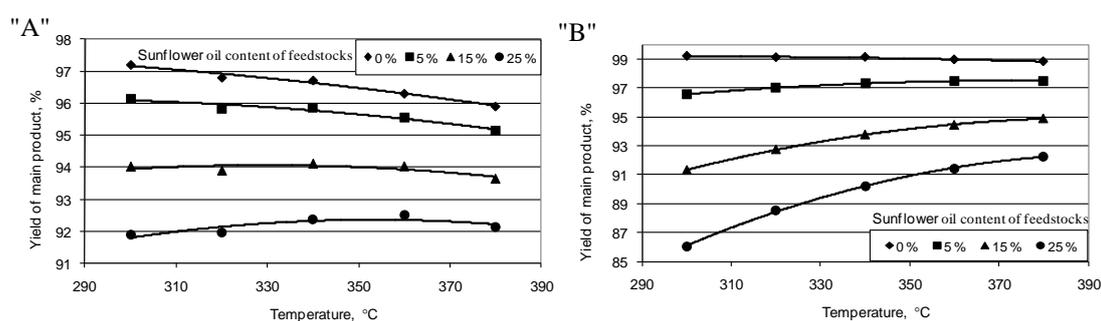


Figure 1: The yield of the main product as a function of the temperature and the vegetable oil content of the feedstocks ("A": LHSV= 0.75 h⁻¹, P=80 bar) ("B": LHSV= 3.0 h⁻¹, P=80 bar)

In the following the major properties of the main products are presented only in case of space velocity (LHSV= 0.75 h⁻¹) and pressure (P= 80bar) found the most favorable to avoid the wordiness.

The aromatic content of the main products changed as a minimum curve as a function of the temperature, its favourable range was around 360 °C (Figure 2 "A"). By increasing the vegetable oil content of the feedstocks the aromatic content of the products decreased, partly because of the aromatic hydrogenation reactions, and partly because the feedstocks had inherently less aromatic content. (This turn was caused by the mixing of sunflower oil.) The lowest aromatic content achieved was 27 %.

During the investigation of the sulphur content of the main products we concluded that the sulphur content decreased very significantly by the increasing severity of the operational parameters (Figure 2 "B"). At the same time, by increasing the vegetable oil content of the feedstocks the sulphur content of the products increased, however, the feedstock with originally higher vegetable oil content had a lower sulphur content. The reason of this effect was that during the hydrogenation of vegetable oil part of the feed the oxygen content (11.5 %) of the triglycerides inhibited the removing of the sulphur content (0.574 %) of the gas oil part, because both heteroatom removing reactions could be performed on the same active sites of the catalysts.

As a result, products corresponding to the current standard (EN 590:2009+A1:2010) with lower than 10 mgS/kg content could be produced at 80 bar pressure, 0.75 h⁻¹ liquid hourly space velocity and at 360-380°C in case of 0 % and 5 % vegetable oil content of feedstocks and at 380 °C in case of 15 % vegetable oil content.

The cold filter plugging point of the main products decreased by increasing the temperature in case of both catalytic systems. The CFPP value of the main products is clearly increased by increasing the vegetable oil content of the feedstocks because of the large amount of generated n-paraffins (Figure 3). The CFPP value of the products was smaller in all cases obtained by utilizing the three catalysts containing systems than in case of the catalytic system containing only the main catalyst.

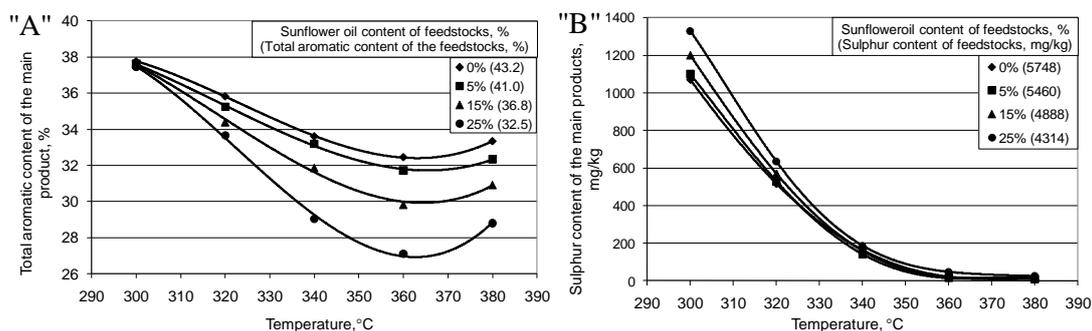


Figure 2: The aromatic ("A") and sulphur ("B") content of the main products as a function of the temperature and the vegetable oil content of the feedstocks ($LHSV= 0.75 h^{-1}$, $P=80 bar$)

The gap between the CFPP values of the two product groups increased by increasing the vegetable oil content of the feedstocks. The reason for this was that from the generated larger amounts of n-paraffins larger quantities of i-paraffins were also formed with good cold flow properties. The CFPP value of the products was reduced with 3-4 °C compared to the products made on the main catalyst only. The difference between the CFPP values of the products made from 5% vegetable oil containing and pure gas oil feedstocks was not significant, because of the limited mixing of the vegetable oil. In case of the catalyst system containing three catalysts, from 360 to 380 °C and up to 25 % vegetable oil containing feedstocks products also could be produced which meet the requirements of the valid standard (summer quality in the temperate zones: up to +5 °C).

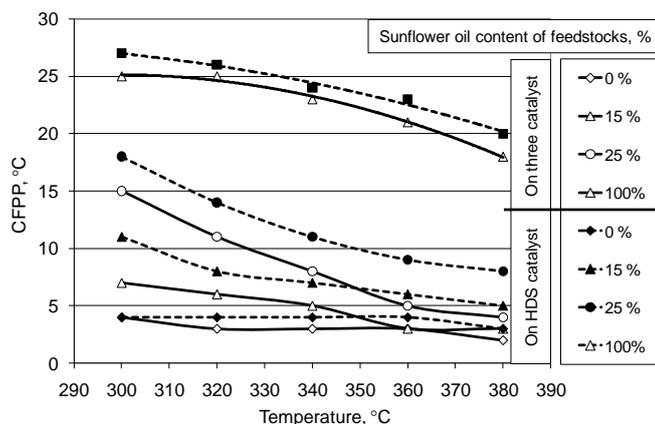


Figure 3: The CFPP value of the main products as a function of the temperature and the vegetable oil content of the feedstocks ($LHSV= 0.75 h^{-1}$, $P=80 bar$)

4. Conclusions

On the basis of the results we obtained that both the vegetable oil conversion reactions (olefinic double saturation, deoxygenation) and gas oil quality improvement reactions (heteroatom removal, aromatic content reduction) took place. In case of both catalytic systems and under the favourable operational conditions ($360-380\text{ }^{\circ}\text{C}$, $P=80 bar$, $LHSV=0.75-1.0 h^{-1}$, $H_2/HC = 600 Nm^3/m^3$) the main properties of the high-yield products made from the maximum 0-15 % vegetable oil containing feedstocks satisfy the requirements of standard EN 590:2009+A1:2010. The amount of vegetable oil higher than 15 % reduced the desulphurisation efficiency, whereas the removal of heteroatoms took place on the same active sites of the catalyst, so the deoxygenation reactions forced back the desulphurisation reactions because of the intake of large quantities of the oxygen with the triglyceride molecule of vegetable oil (oxygen concentration of the feedstocks: 0.001-11.5 %).

We found that by using the catalyst bed prepared of the three catalysts fuel components with (slightly) better cold flow properties could be produced as in case of using only the main catalyst. The CFPP value of the products was reduced by 3-4 °C, but by increasing the isomerisation activity the hydrocracking activity increased, so the yield of the main products (depending on the vegetable oil content) decreased by 2-5 %. The achieved reduction of the CFPP value is not enough to achieve the winter quality, so the cold flow properties of the products should be improved by catalytic isomerisation or additivation.

Based on the results we concluded that an existing hydrogenation plant with a slight modification may be suitable for the processing of vegetable oil and gas oil mixtures. In a single step it can be achieved to improve the quality of the gas oil part and the conversion of vegetable oil part to n- and i-paraffins.

Acknowledgement

This work was supported by the European Union and co-financed by the European Social Fund in the frame the TAMOP-4.2.2/B-10/1-2010-0025 project and we acknowledge the financial support and the feedstock by MOL Plc DS Development.

References

- Bezergianni S., Kalogianni A. and Vasalos I.A., 2009, Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production, *Biores. Tech.*, 100, 3036-3042.
- Hancsók J., Krár M., Magyar Sz., Boda L., Holló A., Kalló D., 2007a, Investigation of the production of high cetane number biogasoil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al₂O₃, *Microporous Mesoporous Mater.*, 101, 148-152.
- Hancsók J., Krár M., Magyar Sz., Boda L., Holló A., Kalló D., 2007b, Investigation of the production of high quality biogasoil from pre-hydrogenated vegetable oils over Pt/SAPO-11/Al₂O₃, *Stud. Surf. Sci. Catal.*, 170, 1605-1610.
- Hancsók J., Kasza, T., Kovács, S., Solymosi, P., Holló, A., 2012, Production of bioparaffins by the catalytic hydrogenation of natural triglycerides, *Journal of Cleaner Production*, DOI: 10.1016/j.jclepro.2012.01.036
- Huber G.W., O'Connor P., Corma A., 2007, Processing biomass in conventional refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures, *Appl. Catal. A*, 329, 120-129.
- Kasza, T., Solymosi, P., Varga, Z., Whál Horáth, I., Hancsók, J., 2011, Investigation of isoparaffin rich alternative fuel production, *Chemical Engineering Transaction*, 24, 1519-1524.
- Kovács S., Boda L., Leveles L., Thernesz A., Hancsók J., 2010, Catalytic Hydrogenating of Triglycerides for the Production of Bioparaffin Mixture, *Chemical Engineering Transactions* 21, 1321-1326.
- Krár M., Thernesz A., Tóth Cs., Kasza T., Hancsók J., 2010, Investigation of catalytic conversion of vegetable oil/gas oil mixtures, *Silica and Silicates in Modern Catalysis*, Transworld Research Network, India Kerala, 435-455.
- Krár, M., Kasza, T., Kovács, S., Kalló, D., Hancsók, J., 2011, Bio gas oils with improved low temperature properties, *Fuel Processing Technology*, 92, 886-892.
- Melis S., Mayo S., Leliveld B., 2009, Vegetable oil co-processing in diesel hydrotreaters, *Biofuels Technology*, 1, 43-47.
- Mikulec J., Cvengros J., Joríková L., Banic M., Kleinová A., 2009, Diesel production technology from renewable sources – second generation biofuels, *Chemical Engineering Transactions*, 18, 475-480.
- NesteJacobs, 2012, <www.nestejacobs.com> accessed 30.05.2012
- Tóth, Cs., Baladincz, P., Kovács, S., Hancsók, J., 2010, Producing Diesel Fuel by Co-Hydrogenation of Vegetable Oil with Gas Oil, *Chemical Engineering Transactions*, 21, 1219-1224.
- Tóth, Cs., Baladincz, P., Kovács, S., Hancsók, J., 2011, Producing clean diesel fuel by co-hydrogenation of vegetable oil with gas oil, *Clean Techn. Environ. Policy*, 13(4), 581-585.
- Wenzel H., 2009, Biofuels: the good, the bad, the ugly-and the unwise policy, *Clean Techn. Environ. Policy*, 11, 143-145.