CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci

Application of sunflower oils with high oleic acid content and their derivates as fuels for Diesel engines

Ádám BECK, Jenő HANCSÓK*, Márton KRÁR
University of Pannonia, Department of Hydrocarbon and Coal Processing, Hungary, H-8201 Veszprém, P.O. Box 158. Phone: +36 88 624313; *email: hancsokj@almos.uni-pannon.hu

During our research work the possibilities of the direct blending of deeply refined conventional and oleic acid rich (>85 %) sunflower oils and their transesterified derivatives into Diesel fuels in different concentrations was tested. The maximum content of vegetable oil derived components was 5 %. The prepared blends have met the requirements of the established quality standard (EN 590:2004). Considering 5 % of vegetable oil derived components, the most advantageous results were obtained by combining the use of deeply refined sunflower oils rich in oleic acid and their transesterified derivates.

1. Introduction

Application of transportation fuels containing biomass-derived components has emerged into focus in the last years. The main reason of this tendency is the energy policy of the European Union, declared in Directive 2003/30/EC of the European Council and Parliament. A major recommendation of this Directive is that member states are encouraged to ensure that a minimum proportion of biofuels and other renewable fuels are blended into transportation fuels. This proportion is proposed to be 2 %, calculated on the basis of energy content of all gasoline and diesel fuel for transport purposes placed on their markets by 31 December 2005. The proportion of biofuels shall be increased to 5.75 % by 2010 (Tippe, 2005).

One of the solutions can be the direct blending of the refined and pretreated vegetable oils with high oleic acid content and/or their trans-esterified derivates into Diesel fuels and their use in Diesel engines. The recommendations of this Directive can be satisfied with any kind of biofuels, however the blended fuels have to fulfill the requirements of the established standard, and the content of more than 5 % of bio-component have to be indicated at the fuel stations. However we mention that the EN590:2004 standard permits the blending of FAME in 5 v/v%.

The demand for Diesel fuels in the European Union increases continuously (figure 1), satisfying the actual European Union Directive the amount of bio-components used in Diesel fuels will be around $6.73*10^6$ t/year, so there is need for the research of biofuels and the examination of their blending.

Detailed evaluations showed that application of only 0.5-1 % of biodiesel increases well the lubricity of Diesel fuels (Geller and Godrum, 2004), but over 10 % of biodiesel blending significantly less improvement of lubricity was found (Rebis et al., 2006). According to our knowledge only few investigations were carried out on the combined application of both vegetable oils and biodiesels. Therefore we wanted to examine the effect of their joint blend. Based on the European Union directive 2003/30/EC and on literature data, a value of 5 % was selected as the maximum concentration of bio based components in our tests.

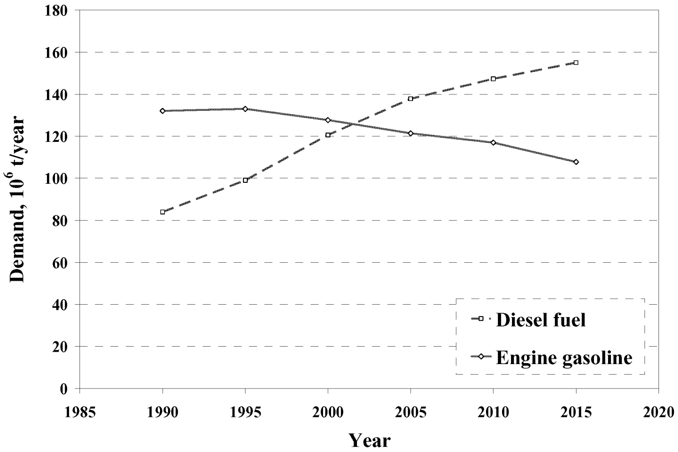

Figure 1. Trends in the quantity of diesel fuel and engine gasoline demands, EU15

2. Experimental

During our research work we tested the possibilities of the direct blending of the refined and appropriately pretreated conventional and oleic acid rich (>85 %) sunflower oils and their transesterified derivatives into diesel fuels in different concentrations. Biodiesels were produced by enzyme catalytic technology by the use of *Candida antarctica* lipase enzyme (Kovács et al, 2003) with quality characteristics according to the EN 14214:2004 standard. In our tests the effect of blending vegetal oils and biodiesels was examined according to the specifications of the EN 590:2004 standard. The Diesel fuel blends consisting of sunflower oil rich in oleic acid (SO-2) and its biodiesel derivative (SOME-2) were compared to those prepared from a conventional sunflower oil (SO-1) and its biodiesel derivative (SOME-1). The effect of the ratio vegetable oil to biodiesel on the quality of the Diesel fuel blends was investigated.

Table 1. contains the main properties of the sulfur-free, summer grade base diesel fuel, the sunflower oils and their biodiesels derivatives. It was found, that the biodiesel sample SOME-2, which was prepared from the sunflower oil SO-2, has a lower cold filter plugging point (CFPP), than that of the biodiesel SOME-1 which was prepared from the conventional sunflower oil SO-1. This was caused by the higher oleic acid content of the sunflower oil SO-2.

Table 1. Main properties of the used blending components

	d_{15}, g/cm^3	KV_{40}, mm^2/s	CFPP, °C	Acid number, mg KOH/g	Sulfur content, mg/kg
GO	0.8353	3.171	-7	0.06	5
SO-1	0.9218	31.220	+33	0.68	2
SO-2	0.9145	39.117	+28	2.26	1.5
SOME-1	0.8932	4.059	-3	0.09	1
SOME-2	0.8855	4.326	-8	0.17	1

Blends containing biodiesel (in 0-5 % concentration), sunflower oil (in 0-5 % concentration) and diesel fuel were prepared from sunflower oil SO-1 and biodiesel SOME-1, as well as from sunflower oil SO-2 and its transesterified derivative SOME-2 biodiesel.

3. Results and Discussion

The density measured at 15 °C of the vegetable oil – biodiesel – diesel fuel blends was between 0.8353 and 0.8392 g/cm^3, their kinematical viscosity at 40 °C varied between 3.178 and 3.541 mm^2/s. The blending of the sunflower oil derived components increased the density and kinematical viscosity according to their blending ratio, however, these properties always satisfied the requirements of the established standards: density at 15 °C maximum 845 kg/m^3, kinematical viscosity at 40 °C minimum 2 and maximum 4.5 mm^2/s.

Examining the blended diesel fuel samples prepared from the SO-1 sunflower oil and its enzyme catalytically transesterified derivate (SOME-1) it was found that the acid number is mainly affected by the concentration of sunflower oil(figure 2.). It was expectable, because the acid number of the vegetable oil was greater than that of the biodiesel produced from it. The same effect was experienced in case of the sunflower oil and biodiesel with high oleic acid content, but the acid numbers were relatively still low.

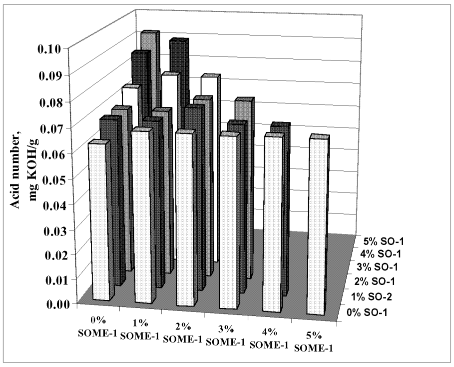

Figure 2. Acid number of blends containing sunflower oil SO-1 and biodiesel SOME-1

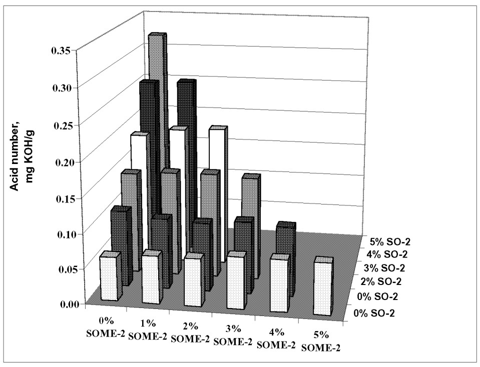

Figure 3. Acid number of blends containing sunflower oil rich in oleic acid (SO-2) and biodiesel SOME-2

After the Engler-distillation of all the blended samples it was found that the shape of all distillation curves were similar to that of the base diesel fuel. The initial and end boiling points did not vary much either.

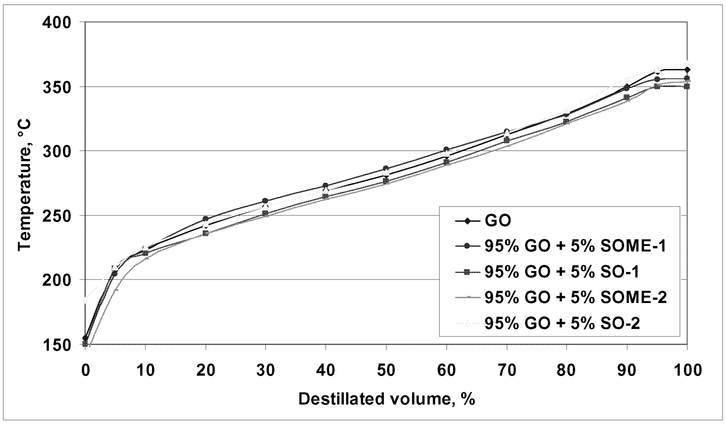

Figure 4. Engler-distillation curve of the base diesel fuel, the blends containing 5 % vegetable oil and blends containing 5 % biodiesel

All samples met the requirements of the EN590:2004 standard (the distilled fraction should be max. 65 v/v% up to 250 °C, min. 85 v/v% up to 350 °C, and the temperature of the distillation at 95 v/v% should be maximum 360 °C). In figure 4 only the most important distillation curves were plotted as examples: distillation curve of the base diesel fuel, blends containing 5 % vegetable oil and those containing 5 % biodiesel.

For the evaluation of the cold properties we investigated the cold filter plugging point and the cloud point of the 0-5 % biodiesel and 5 % total vegetable derived component containing blends (figure 5. and 6.).

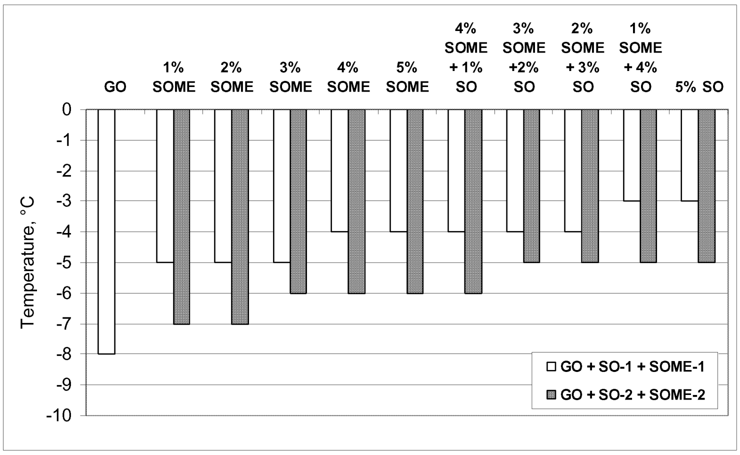

Figure 5. Cold filter plugging point of the examined samples

We found that the samples containing the sunflower oil rich in oleic acid and/or the biodiesel prepared from it had in any case lower CFPP and cloud point, which is more advantageous by the point of view of automotive application. This was caused by the higher oleic acid content of sunflower oil SO-2 and its biodiesel derivative. These samples satisfied the requirements of the standard of summer grade diesel fuels. Using winter grade diesel fuel as the base fuel of the blends flow improver and paraffin dispersing additives will probably be needed in order to meet the requirements of the standard of winter grade diesel fuels.

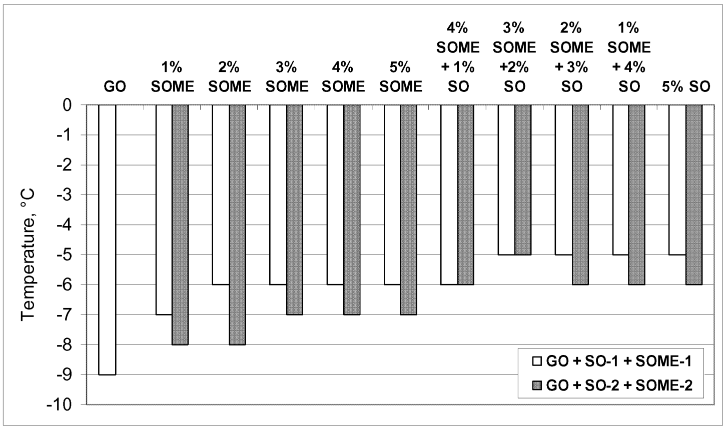

Figure 6. Cloud point of the examined samples

The lubricity of the diesel fuel – sunflower oil – biodiesel blends (containing 0-5 % biodiesel or samples containing 5 % of vegetable oil derived components in total) was tested with the modified Stanhope-Seta four-ball tester. The results of this method correlate well with the high frequency reciprocating rig (HFRR) method (Bubálik et al., 2005). The results (figure 7.) showed that only 1 % of biodiesel already increases the lubricity, but additional concentration of biodiesel SOME-1, had much lower effect on the lubricity. According to our results further increase of biodiesel concentration had little effect on the lubricity.

Figure 7 also illustrates, that by altering the vegetable oil – biodiesel ratio, the lubricity of the samples did not change much. This is true both for the mixture of conventional sunflower oils and their transesterified derivatives, and for the mixture of vegetable oils rich in oleic acid and their derivates.

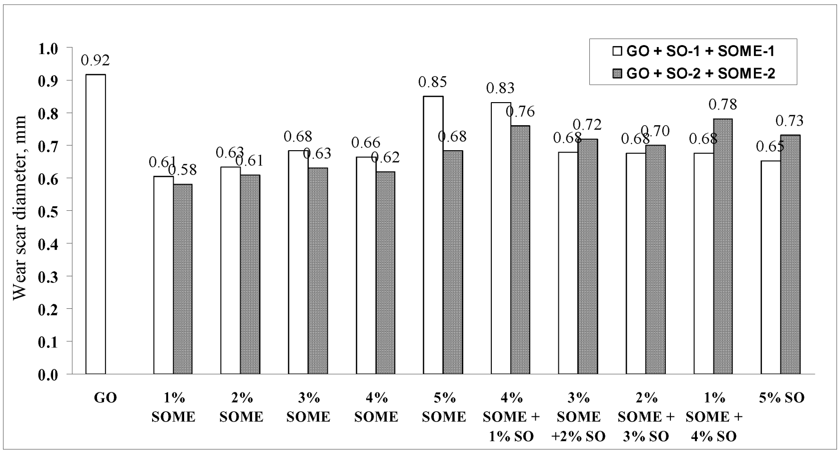

Figure 7. Lubricity of the base diesel fuel, blends containing 5 % vegetable oil and those containing 5 % biodiesel

4. Summary

Diesel fuel containing 5 % of vegetal oil and/or its derivates still maintains its quality to meet the established standards, however 5 % of vegetal oil blended into Diesel fuel increases the kinematical viscosity by 10 % and the cold filter plugging point by 3-5 units. Based on our results it was established that the investigation of the use of these blending components in a concentration of >5 % may not be useful.

Considering maximum 5 % of vegetal oil derived components, the most advantageous results were obtained by using both the deeply refined vegetal oils with high oleic acid content and their transesterified derivates. The cold filter plugging point and the cloud point slightly increased when using both biodiesel and vegetable oil. It is advantageous from economical point of view, because the cost of vegetable oils is significantly lower than that of biodiesels. These blends fulfilled the requirements of the standards for temperate zone grade C diesel fuels. Of course, further investigations are needed by using winter grade diesel fuels as a base fuel for blending.

5. References

Bubálik, M., Hancsók, J., Molnár, I. and Holló, A.: „Characterization of the AF/AW properties of diesel fuel", Fuels **2005**, 5th International Colloquium, 2005. 01. 12-13., Technische Akademie Esslingen

Geller, D. P. and Goodrum, J. W.: „Effects of specific fatty acid methyl esters on diesel fuel lubricity", Fuel, **2004**, 83, 2351-2356.

Kovács, F., Hancsók, J. and Bélafiné Bakó, K.: „Transesterification of Vegetable Oils With Enzymatic Catalysts", Fuels **2003**, 4th International Colloquium, 2003. 01. 15-16., Technische Akademie Esslingen

Rebis, J., Frydrych, J. and Kolodziejczyk, K.: „Tribological properties of diesel oil and FAME blends", Tribology of Alternative Fuels and Ecolubricants, **2006**, Vienna Region, Austria, ISBN 3-901657-21-5, 83-84

Tippe, B.: „Sulfur cuts, European demand growth reshaping diesel market", Oil&Gas Journal. **2005**, 103(46), 18.