



THE EFFECT OF BIOFUEL ADDITION TO FLIGHT KEROSENE ON A RUBBER GASKET

Milan Olšovský¹, Marián Hocko²

¹Dept of Chemical Engineering and Environmental, University of Alexander Dubček in Trenčín,
I. Krasku 491/30, 020 01 Púchov, Slovakia

²Dept of Aeronautics, Technical University in Košice, Rampová 7, 041 21 Košice, Slovakia
E-mails: ¹olsovsky@fpt.tnuni.sk (corresponding author); ²marian.hocko@tuke.sk

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Abstract. This paper solves a problem of using unconventional fuels for driving jet engines. The carried out experiments were aimed at assessing the possibilities of using various contributions of MERO (methyl esters of rapeseed oil) biofuel mixed with Jet A-1 aircraft fuel and for analyzing the influences of using an alternative fuel exerted upon the selected parts of the jet engine. The authors of the article compare the effect of adding bio-ingredients (MERO) to Jet A-1 aircraft fuel on the properties of rubber sealings used in the aircraft engine. The physical properties of MERO bio-ingredients and Jet A-1 aircraft fuel are very similar. The conducted research has discovered additional options of mixing MERO biofuel and Jet A-1 aircraft fuel and demonstrated that the total concentration (0–100%) of MERO bio-fuel in Jet A-1 aircraft fuel reaches a process of creating of a homogeneous mixture without sediments or coagulants. The evaluated results indicate that the appendage of the methyl esters of rapeseed oil in Jet A-1 aircraft fuel give out a relatively large slump in physical-mechanical properties within the period of a few days. The raising content of MERO in aircraft fuel is bulking samples and makes itself felt by increasing the weight of the samples.

Keywords: biofuel, flying kerosene, rubber gasket, methyl esters of rapeseed oil.

1. Introduction

Chemical treating is used in a refinery plant for naphtha and kerosene fractions to jet fuel production. It is often necessary to meet acidity, mercaptan and other specifications required for upgrading these fractions and taking into account jet fuel products. One of the fastest growing demands for the refinery product market is jet fuel, often called turbine fuel. Air travel is projected to continue growing in popularity in the years to come and the refinery that produces jet fuel at the lowest cost will be in the best position to supply this market. A refiner that produces high quality jet fuels can find attractive markets for their product throughout the world. Jet fuels must meet very stringent regulations, because they are used by different airlines worldwide and fly to the countries where jet fuel is produced. As is readily apparent to those familiar with caustic treating, some of these specifications are not affected in any way since the compounds affecting the specifications are not caustic extractable (Gary, Handwerk 2001; Meyers 2003).

The refinery production of jet fuel varies from simply withdrawing a side-stream product from the crude oil fractionator that requires no additional treating or

cleanup to withdrawing a side-stream product that requires only minimal cleanup such as clay filtration or a side-stream product that requires caustic treating followed by water washing, salt drying and clay filtration, and finally, to withdrawing a side-stream product that must be hydrotreated before it can meet jet fuel specifications (McKetta 1992). Hydrotreating involves much greater capital investment (from 10 to 20 times) and requires much higher operating costs (from 20 to 50 times) than 'wet treating' which is the phrase often used to denote caustic treating with the attendant cleanup processes. For these reasons, refineries avoid hydrotreating whenever possible. However, hydrotreating can produce jet fuel from most crude oils, whereas wet treating is limited to jet fuels, which already meet the specifications not affected by caustic treating.

Recently, the research and production of biofuels is in the focus of mankind due to the nonuniform distribution and depletion of crude oil reserves, the periodically and rapidly changing prices of crude oil, the utilization of renewable energy sources, the substitution of polluting fossil energy sources replacing import energy carriers, reducing import dependence, political potential to support rural population, moderating agricultural over-

production crises, the utilization of fallow lands, lower lifecycle carbon-dioxide emission and contribution to the protection of soil and water sources (Hancsók *et al.* 2004; Krahl *et al.* 2003).

Besides, the Directive 2003/30/EC of the European Council and European Parliament (2003), finalized in May 2003 calls for the following: Member States should ensure that a minimum proportion of biofuels and other renewable fuels is placed on their markets, and, to that effect, shall set national indicative targets. A reference value for these targets shall be 2%, calculated on the basis of energy content, of all petrol and diesel fuel for transport purposes placed on their markets by 31 December 2005. The reference value shall be increased to 5.75% by 31 December 2010 (0.75% year increase) for the Member States. The transportation fuels blended with biofuels shall meet the requirements of the valid national and EU standards for engine gasoline (EN 228:2004) and for diesel fuel (EN 590:2004), too; for percentages of biofuels, blended into mineral oil derivatives, exceeding the limit value of 5% fatty acid methyl ester, a specific labelling at the sales points shall be imposed. Member States shall report to the Commission before 1 July each year on the measures taken to promote the use of biofuels, on the national resources allocated to the production of biomass for energy uses other than transport, on the total sales of transpiration fuel and the share of biofuels.

Blending 5 v/v % of biodiesel into diesel fuel is authorized from 1 May 2004, so long as biodiesel is in accordance with all requirements of EN 14214:2003 standard. Vegetable oil fatty acid methyl esters can be produced from vegetable oils, animal fats and used frying oils. The application of the latter two is not so general, because their availability is lower than that of various types of vegetable oils. Animal fats are mainly used to produce fat powder while collection and adequate treatment of used frying oils is not widespread. Although used frying oils are classified as dangerous substances according to the Decree of the Hungarian Government (102/1996. (VII. 12.) Korm. rendelet...), even the great consumers (restaurants, fast food restaurants etc.) return only the half of their used volume to the collecting companies.

The significance of the application of vegetable oils and their derivatives in the above mentioned areas arises from environmental aspects, mainly from their good biodegradability. The most important application area would be utilization as a fuel of internal combustion engines. It is a generally accepted opinion that vegetable oils cannot directly be used in modern engines, only their conversion products, especially mono alkyl methyl esters. The chemical transformation of used frying oils is not possible by the conventional method (alkali catalyst) because of its high free fatty acid content (5÷35%). The alkali catalyst immediately reacts with free fatty acids contained in used frying oils resulting in soaps, and therefore it is not able to catalyse the reaction. A possible way is the conversion of used frying oils with acid catalyst (chlorhydric acid, sulphuric acid, acid ion-exchange resin). A substantial amount of acid catalyst and significantly higher reaction time is necessary for transes-

terification, compared with the alkali catalysed method (Canakci, Van Gerpen 1999). Another option is the conversion of used frying oils by combined acid and alkali catalyzed transesterification. In this process, the free fatty acid content of used frying oils are first pre-esterified in the presence of acid catalyst, then, transesterification is finished by alkali catalyst (Hancsók *et al.* 2004).

The high free fatty acid content of spent frying oils can also be reduced by mixing unused vegetable oil. On the basis of the quality characteristics of used frying oils, the amount of unused vegetable oil to be mixed into the spent oil has to be determined to ensure the suitability of the mixtures for the two step transesterification. The objective of our research work was to determine the favourable ratio of spent frying oil and unused vegetable oil resulting in practically complete conversion during combined transesterification. Besides, our aim was to study the effect of a free fatty acid content of used frying oil and operating conditions of combined transesterification on the yield of methyl esters. During combined transesterification, a solvent is used to increase the rate of reaction at the inter-phase.

2. Experimentation

2.1. Materials

Biopetroleum MERO of the 2nd generation is still at present the only alternative fuel which is generally used for petroleum engines. It even overcomes conventional engine petroleum taking into account its parameters and especially considering the relation to a fuel system and engine wear. As each alternative fuel, biopetroleum has its advantages and disadvantages. Biopetroleum has high lubricant power (it is more lubricant than petroleum), thus it decreases the wear of friction engine parts and prolongs the service life of fuel injection nozzles. The lubricant power of petroleum is extra important because some engine parts are greased directly by fuel rather than by oil. Biopetroleum does not require any special storage conditions and can be stored in the same type of containers used for petroleum storage. Biopetroleum has better burning properties in the burning process, and therefore significantly decreases the effects of engine smoking, the amount of solid parts, sulphur, carbon dioxide, aromatic matters and hydrocarbons in general. Thanks to its structure, biopetroleum is reducible in 21 days, and therefore is suitable for operations where the contamination of soil is caused by fuel, i.e. especially in agriculture and forest production, water utilization protection zones etc. Biopetroleum is considered to be cleaner, as one having power to release carbon and perfectly clean the engine and all fuel systems, thus preventing from the sedimentation of fuel filters. When biopetroleum is stored, it is necessary to insure the clearness of storage space and protect biopetroleum from contact with water. The long-lasting storage of biopetroleum is not recommended since the possibility of the decomposition of its plant parts. It is aggressive towards rubber and easily oxidizing with the following creation of sediments and acid products.

Properties: density (15 °C) = 882 kg/m³; acidity number = 0.23 mg KOH/g; inflammation point = 168 °C; sulphur content = 0.1 Mg/kg; kinematic viscosity (40 °C) = 4.5 mm²/s; heating power = 39.0 MJ/kg.

Jet A-1 aircraft fuel is a mixture of liquid hydrocarbons that boil mainly up to a temperature of 275 °C. It is a clear liquid with the typical smell of kerosene. To increase utility features, it embodies special additives. The basic additive package includes antioxidant, anti-static and lubricant additives. The fuel can also include other additives suitable for the operations of aviation technologies and are approved by responsible aviation authorities. Aviation petroleum falls into the 2nd threat inflammable class, can have irritable effects on the human organism and evoke skin changes. It does not vapour under normal temperature but vapours formatted in higher temperatures and have narcotic effects. It also degrades the skin. While trying to manipulate this matter, it is recommended to follow instructions provided in the Material Safety Data Sheets (MSDS).

Properties: density (15 °C) = 810 kg/m³; acidity number = 0.003 mg KOH/g; inflammation point = 64 °C; sulphur content = 0.01 Mg/kg; kinematic viscosity (20 °C) = 5.23 mm²/s; heating power = 43.292 MJ/kg.

The physical qualities of MERO biofuel and Jet A-1 aircraft fuel are very similar (Hocko, Bajusz 2006 and 2007). Investigation into the possibilities of mixing MERO biofuel and Jet A-1 aircraft fuel has discovered that the same mixture without sediments or coagulants is created in all concentrations (from 0% up to 100 %) of MERO biofuel contained in Jet A-1 aircraft fuel. Despite the fact that the created mixtures having various concentrations of MERO included in aircraft fuel did not have, even following a year of investigation, a tendency towards return separation of heavy MERO fuel component ($\rho_{\text{MERO}} = 882 \text{ kg/m}^3$) from easier Jet A-1 aircraft fuel component ($\rho_{\text{Jet A-1}} = 810 \text{ kg/m}^3$), it is necessary to perform durable testing under different temperature conditions.

For rubber sealings, we use a rubber compound employed in the rubber sealing elements of the air turbo-compressor engine gasket (Barlow 1988; Cieselski 1999; Ciullo, Hewitt 1999).

2.2. Methods

The preparation of rubber mixtures was made following two-stage mixing according to Slovak standard STN 62 1425¹⁴. Mixing at the first stage was made at a temperature of approximately 130 °C under laboratory conditions mixing PLASTOGRAF BRABENDER. Mixing at the second stage was made at a temperature of approximately 80 °C applying laboratory double-gear type BUZULUK (with friction 1:1.14).

For preparing samples, we made the vulcanizing characteristics of rubber mixtures at 150 °C during 60 minutes of registration using a Monsanto vulcameter. All vulcanizing curves of rubber mixtures have an increasing torsional moment. The vulcanized mixtures in the forms of plates were stored for 24 hours. Then, cutting was employed to prepare test specimens in the

form of both sides of shovels for tensile tests. For testing hardness, specimens appeared in the forms of rings and 'graves' for designating tear strength. The cut samples were conditioned for at least 16 hours at an examination temperature. Then, mechanical properties have been determined.

To estimate the physical-mechanical characteristics of the samples – tension strength in breakage and elongation were measured according to ISO 37:2005 standard. The INSTRON shredder was used at a laboratory temperature testing a clutch movement speed of 100 mm/min.

The hardness of vulcanized rubber was measured according to STN standard (Vajdová *et al.* 2003) using the IRHD durometer with the precise measurement of ± 0.5 IRHD. The weight of vulcanized rubber was measured according to ISO 1817:2005 standard (volumetric method) under laboratory temperature applying analytical balance MERCK.

3. Results and Discussion

One of the parts of the BIOPAL Project realized under conditions of the Faculty of Aeronautics of Technical University of Košice in cooperation with the Faculty of Industrial Technologies in Púchov have concentrated on the results of a long-lasting influence of various concentrations of the mixtures of MERO biofuel and Jet A-1 aircraft fuel on the sealing elements of the air turbo-compressor engine (ATCE).

We prepared some samples of the mixtures of MERO biofuel and Jet A-1 aircraft fuel graded to 10%. Classical sealing rings were put in the construction of the fuel sets of ATCE. The samples were being monitored for 12 months. The sizes of the samples were measured and changes in their physical properties were investigated at the intervals of one week. Following one year of various mixtures affecting rubber sealing, the samples and the received results of measurements were sent to the Faculty of Industrial Technologies in Púchov where the detailed analysis of individual samples was accomplished. To confirm the obtained results in the Faculty of Industrial Technologies, testing a long-lasting attack of various concentrations of the mixtures of MERO biofuel and Jet A-1 aircraft fuel on sealing elements was repeated. In the following part of the article, some knowledge gained from the above mentioned long-lasting experiment performed at the Faculty of Aeronautics and a short-lasting experiment performed at the Faculty of Industrial Technologies is described.

Even if in the same cases the tests can simulate operational conditions quite well, we cannot always expect direct connections between lab test results and effect achieved from some practical usage. For testing, we have to take into consideration rubber thickness because the speed of liquid penetration depends on time (Barlow 1988; Mark *et al.* 2005). The inner volume of a product with big thickness can stay unaffected during the whole time of its defined lifetime. It is also known that the liquid affecting rubber, especially in high temperatures, can also be affected by air oxygen (Loadman 1998).

It is definite from the measured values that when the volume of MERO bio-fuel increases, the resistance of the fuel mixture decreases. Resistance decreased practically about 100% in the clear MERO fluid. The hardness of sample 1 (100% Jet A-1) is even higher than the hardness of the standard. Presumably, it is caused by the structure of Jet A-1 aircraft fuel that includes different mixtures of organic adducts. Aircraft fuel does not attack rubber as a plasticizer or diluents but vice versa. The rubber contained in aircraft fuel is reduced and thereby increases its hardness. On the contrary, when an additive to MERO bio-fuel increases, the hardness of the sample decreases. It is caused by the fact that the methyl esters of greasy acids of Coleseed oil affect the India-rubber matrix as an inner plasticizer (increases the mobility of macromolecules). The distances among macro molecules enlarge and thereby the sample resistance decreases.

The analyzed samples were directed especially on the effects of the mixture of MERO biofuel and Jet A-1 aircraft fuel on the physical-mechanical parameters of sealings. The samples of the sealings were exposed to various concentrations of fuel mixtures for 12 months (327 days). Following this time, the samples were taken out of the liquid and their basic physical and mechanical parameters were measured.

It is evident from the chart that the solidity of the samples decreases proportionally to an increasing amount of the content of the mixture of MERO bio-fuel and Jet A-1 aircraft fuel. The values of solidity characteristics decrease more expressively if there is more than 20% of biofuel in the mixture. A decrease in resistance is caused by MERO biofuel attacking India-rubber mixtures and having an effect of a plasticizer. When the samples of mixtures had a higher content of MERO biofuel (more than 50%), the sealings were so damaged by attacking fuel that it was not possible to clamp them into the shredder and measure solidity characteristics.

This is due to the fact that at a lower level of the mixture of MERO bio-fuel and Jet A-1 aircraft fuel, both of the samples got in contact with air oxygen that speeded

up the process of degradation. It has explained why some samples, despite the higher concentration of MERO fuel attacking them, were not that depredated as the samples affected by air oxide.

The measured values shown in Table 1 and Figure disclose that up to 20% of MERO contained in the mixture with Jet A-1 aircraft fuel causes that the weight of the sample decreases comparing with the original state. It is supposed due to the rubber made structure that the rubber matrix has ability to ‘accept’ a certain amount of a plasticizer (MERO). The effects of soaking up and the partial destruction of a rubber sample commence when more than 20% of MERO in the mixture with Jet A-1 aircraft fuel is contained.

Change in sample weight increases practically linearly with an increase in the content of the mixture of MERO bio-fuel and Jet A-1 aircraft fuel (above 20%). An increase in the sample weight of rubber sealings depending on the affecting time of fuel is practically the same after 7 and 14 days (see Table 2). Therefore, change in weight is primarily affected by the structure of MERO biofuel in the mixture.

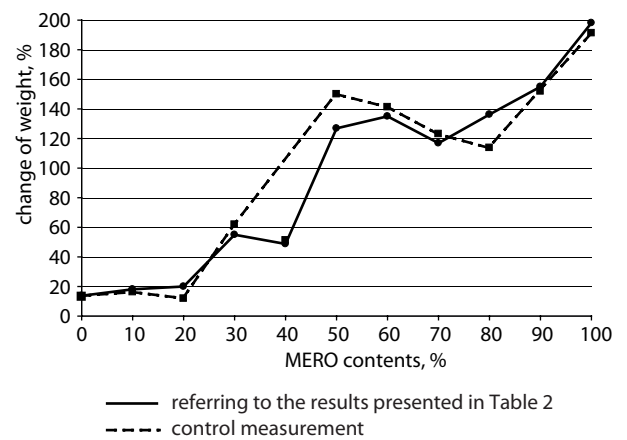


Fig. Changes in the weight samples of fuel content following 327 days

Table 1. Changes in the samples of the qualities of physical-mechanical properties following a 12 month attack of MERO–Jet A-1 mixture

Sample	Solution content MERO/Jet A-1, wt. %	Hardness, IRHD	Elongation, %	Strength, kPa
0	Without solution attack	94.33	81.28	20.5
1	0 : 100	95.33	77.52	19.7
2	10 : 90	90.66	75.52	16.7
3	20 : 80	87.33	73.40	12.4
4	30 : 70	77.00	–	–
5	40 : 60	75.66	17.28	1.8
6	50 : 50	62.33	–	–
7	60 : 40	63.00	–	–
8	70 : 30	50.60	–	–
9	80 : 20	46.00	–	–
10	90 : 10	56.33	4.32	–
11	100 : 0	53.00	2.88	0.7

Table 2. Changes in the weight samples of fuel content (%)

Days/sample	1	2	3	4	5	6	7	8	9	10	11
7	17.8	22.5	19.7	24.8	24.1	0	26.0	28.6	34.5	30.2	46.3
14	24.4	20.3	27.5	30.2	36.9	32.7	39.1	42.4	38.8	36.6	47.8
21	14.7	23.8	34.1	34.5	42.5	44.4	–	47.9	–	–	41.4
28	9.3	17.6	12.8	21.6	–	22.6	25.8	23.2	27.3	31.7	39.3
35	36.0	9.8	10.1	–	21.9	22.2	26.0	23.3	27.3	27.3	38.8
42	7.5	5.2	8.0	–	14.3	18.9	13.9	19.8	24.2	21.0	29.1
49	7.4	7.6	16.5	20.4	17.7	16.3	25.2	12.1	20.3	22.2	37.8
56	11.0	2.6	6.0	16.1	17.7	13.7	22.8	19.8	25.0	30.2	31.1
70	14.6	7.0	–	19.2	11.7	15.9	15.2	26.1	23.3	24.1	40.4
77	13.8	7.4	11.6	12.0	17.9	22.5	24.7	19.9	29.4	29.5	28.3
91	3.8	12.6	11.6	13.2	17.2	13.9	18.4	19.9	28.1	22.6	29.7
98	4.4	3.1	6.1	3.9	12.3	11.3	5.7	17.8	20.6	20.1	26.9
105	11.5	15.5	19.6	25.1	24.5	37.2	27.0	23.5	34.4	28.5	28.7
113	17.5	11.5	25.2	20.1	29.4	30.5	30.0	–	36.7	38.1	50.3
121	17.7	17.6	21.9	25.1	–	11.0	21.7	45.4	39.7	43.8	51.9
128	8.9	15.5	20.6	25.2	25.3	27.8	30.0	34.9	39.0	40.0	43.8
327	13.4	16.1	12.0	62.4	51.3	49.8	141.9	123.4	114.1	152.6	191.3

4. Conclusions

The introduced results of experimental analysis have definitely proved negative effects of the mixture of MERO biofuel and Jet A-1 aircraft fuel on rubber sealings used in the construction of aviation engines. Ignoring the introduced facts can have a significant influence on a safety level in aviation.

The examples from the history of aviation and astronautics (American Shuttle) show that even a crash can be caused by the consequences of damage to such an elementary element as sealing. For this reason, it is very important to properly investigate the effects of biofuels on the individual components of aviation engines and to accept such measures for construction that would limit possible negative results before headless transition to using biofuels in aviation engines.

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