RESEARCH ARTICLE

Investigation on the Feasibility to Produce Jet-A1 Aviation Fuel by Co-hydroprocessing Petroleum Kerosene with POME and Cardanol

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Abstract

Petroleum kerosene (SRK) and its blends with the bio-components palm oil mill effluent (POME) and cardanol in amount of 2 and 5% were hydrotreated on commercial Co-Mo catalyst in a laboratory trickle bed reactor at temperature of 290°C, liquid hourly space velocity (LHSV) of 1.28 h^{-1}, total pressure of 3.0 MPa, H_2/Oil ratio of 290 Nm^3/Nm^3 to simulate co-processing aiming at production of sustainable aviation fuel (SAF) in the existing hydrotreating technology employed to manufacture petroleum based Jet-A1 aviation fuel. It was found that increased hydrogen consumption during co-processing bio-feeds was mainly related to hydrodeoxygenation reaction leading to production of H_2O. Cardanol, and POME, however exhibited different behavior concerning production of propane (C_3) and $CO+CO_2$ with much lower production from Cardanol implying that it contains less free fatty acids, and less lipids than POME. The higher content of nitrogen (50 times in POME, and 100 times in Cardanol) in bio-feeds inhibits the HDS of petroleum kerosene decreasing the amount of H_2S generated and leaving higher sulfur content in hydrotreated jet product. POME was found unsuitable for production of jet fuel by co-processing due to the inability to meet the specification of maximum -47°C crystallization temperature. The hydrotreated liquid products from the bio-feeds were found highly corrosive, while the mixtures of hydrotreated SRK with untreated cardanol displayed lack of corrosivity suggesting that the unconverted oxygen containing substances in the liquid co-processed product are more corrosive that the original ones present in the bio-feeds.

Keywords: sustainable aviation fuel, co-processing, corrosion.

1 Introduction

The aviation industry generates 4.1% of global GDP and 87.7 million jobs across the globe, and contributes about 2.4% of global carbon dioxide (CO_2) emissions [1, 2]. It is developing faster than road, rail and shipping transport and is considered as one of

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the most difficult to decarbonize, mostly because of its reliance on energy-dense liquid fuels [1, 3]. The most perspective manner to decrease CO_2 emissions in the aviation industry is to employ sustainable alternative aviation fuels (SAF), which the International Air Transport Association (IATA) has estimated could reduce emissions by 65% [4, 5]. ASTM D7566 – 21 [6] specifies the allowable origin of SAF as follows:

1) Fischer-Tropsch Hydroprocessed Synthesized Paraffinic Kerosene (FT-SPK) – up to 50%v/v;
2) Synthetic Paraffinic Kerosene from Hydroprocessed Esters and Fatty Acids (HEFAs) – up to 50%v/v;
3) Synthetic Iso-Paraffins from Hydroprocessed fermented sugars – up to 10%v/v;
4) Synthesized Paraffinic Kerosene with Aromatics Derived by Alkylation of Light Aromatics from Non-Petroleum sources (SPK/A) – up to 50%v/v;
5) Alcohol-To-Jet Synthetic Paraffinic Kerosene (ATJ SPK) – up to 50%v/v;
6) Synthesized Kerosene from Hydrothermal Conversion of Fatty Acid Esters and Fatty Acids (catalytic hydrothermolysis jet – CHJ) – up to 50%v/v;
7) Synthesized Paraffinic Kerosene from Hydroprocessed Hydrocarbons, Esters and Fatty Acids (HC-HEFAs) – up to 10%v/v;
8) Alcohol-To-Jet Synthetic Paraffinic Kerosene with Aromatics (ATJ SPK).

The requirement of Regulation 2023/2405 of the European Parliament (ReFuelEU Aviation) that aviation fuel producers must include sustainable aviation fuel (SAF) in their products with a minimum of 2% SAF content by 2025, increasing to 70% by 2050 [7] makes petroleum refiners search for cost effective and sustainable ways to manufacture aviation fuel that contains SAF. Co-processing is an alternative to produce aviation fuel meeting the requirements of ASTM D7566 while using the existing refining, transport, and storage facilities, if 5% approved renewable feedstocks together with petroleum streams are hydrotreated together [8, 9]. The superiority of co-processing is due to its cost-effectiveness, as it avoids the need to build new specialized processing units, resulting in savings in both capital and operating costs [10]. However, there is a question whether the existing refinery hydrotreater with the typical catalyst and operating conditions availed to produce 100% Jet A1 aviation fuel based on petroleum kerosene can be employed directly for co-processing without any modifications in the catalyst, operating conditions and equipment used. The aim of this study is to answer this question.

2 Materials and Methods

The following materials were used in this study: petroleum straight run kerosene (SRK), palm oil mill effluent (POME) and cardanol, obtained from cashew nut shell liquid (CNSL) by vacuum distillation. Their properties are summarized in Table 1.

Table 1. Raw material properties.

Feedstock		SRK	POME	Cardanol
Density 15 °C, g/cm^3		0.8056	0.9264	0.9352
Viscosity 50 °C, cSt		-	35.922	17.976
MCRT, wt.%		-	0.49	0.49
TAN, mg KOH/g		0.0013	3.91	1.05
H_2O content, wt.%		0.0189		0.0313
Pour point, °C		-52		
Freezing point, °C		-50		
Elemental analysis, wt.%	C	85.5	75.1	83.8
	H	14.0	11.8	10.9
	N	0.0003	0.0162	0.0284
	S	0.228	0.0043	0.0016
	O (by difference)	0.20	13.1	5.3
Simulated Distillation - ASTM D-6352	IBP	101	331.4	178.8
	5%	150	398.6	394.8
	10%	165	417.6	396.6
	30%	189	529.6	400.6
	50%	210	541.8	403
	70%	229	594.6	404.8
	90%	251	608	408.4
	95%	256	616	426.6
	FBP	275	724.6	440.4

The following feeds were used in the hydrotreating experiments:

1) 100% SRK;
2) 98% SRK + 2% POME;
3) 95% SRK + 5% POME;
4) 98% SRK + 2% Cardanol.

The catalyst for this study was pre-sulfided fresh Co-Mo catalyst TK-576 Brim. A pilot scale unit with a fixed bed reactor and a product separation system running at temperature of 290°C, liquid hourly space velocity (LHSV) of 1.28 h^{-1}, H_2/Oil ratio of 290 Nm^3/m^3, total reactor pressure of 3 MPa was availed in this research. These are the typical operating conditions and the catalyst employed to produce Jet

Table 2. Product yield structure from hydrotreating experiments.

Feedstock		HT SRK*	2% POME	5% POME	2% Cardanol
Normalized yield, wt.% on feed	C_1	0.000	0.000	0.011	0.000
	C_2	0.034	0.011	0.011	0.000
	C_3	0.019	0.063	0.105	0.012
	C_{6+}	0.002	0.000	0.000	0.000
	CO_2	0.000	0.014	0.061	0.001
	CO	0.000	0.013	0.056	0.001
	H_2S	0.241	0.237	0.217	0.218
Total Gases		0.296	0.338	0.461	0.232
Water		0.000	0.256	0.369	0.226
Organic Liquid		99.704	99.406	99.17	99.542

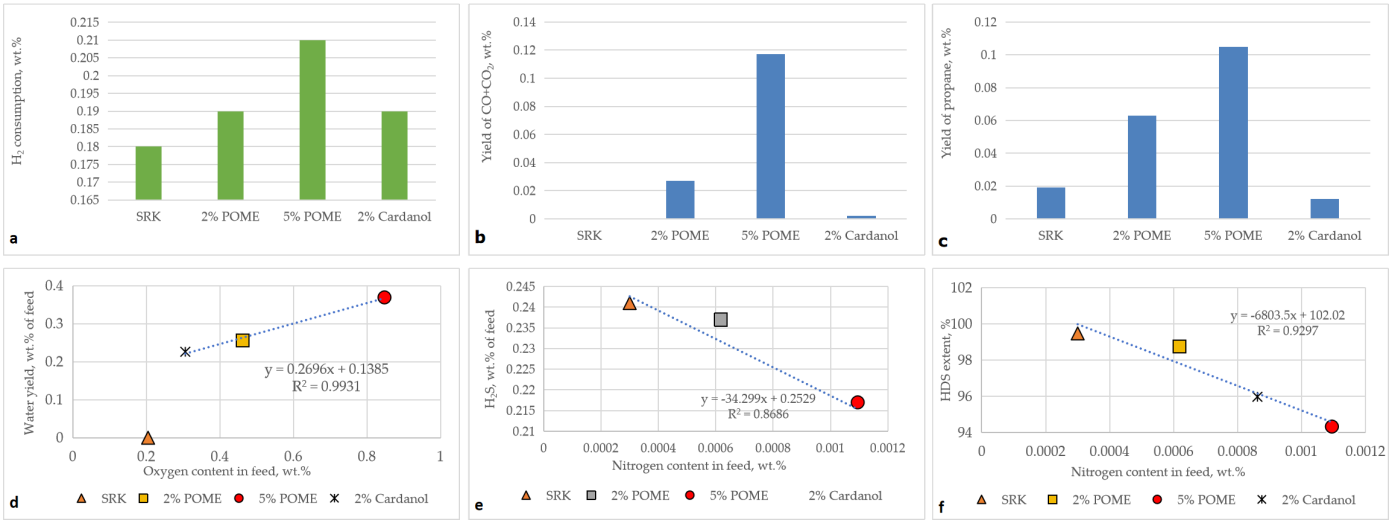

Figure 1. Hydrogen consumption (a) and yield of products: $CO+CO_2$ (b), propane (c), water (d), H_2S (e), and hydrodesulfurization extent (HDS) observed during hydrotreatment of the four feeds.

A1 aviation fuel based on 100% petroleum kerosene feed in LUKOIL Neftohim Burgas refinery.

3 Results and Discussion

The data in Table 1 indicate that POME exhibits distillation characteristics typical for a petroleum atmospheric residue (50% VGO and 50% VR), while Cardanol demonstrates distillation characteristics of VGO. The content of oxygen in POME is the highest among the three examined materials.

Table 2 and Figure 1 present the product yield structure, hydrogen consumption, and hydrodesulfurization extent (HDS) obtained during hydrotreatment of the four examined feeds mentioned above.

The feeds containing bio-components exhibit higher consumption of hydrogen mainly due to the reactions of hydrodeoxygenation leading to production of H_2O (Figures 1 (a) and (d)) [11]. Cardanol, and POME, however exhibit different behavior concerning production of propane (C_3) and $CO+CO_2$ with much lower production from Cardanol implying that it contains less free fatty acids, and less lipids than POME (Figures 1 (b) and (c)). The higher content of nitrogen (50 times in POME, and 100 times in Cardanol (see Table 1)) in bio-feedstocks inhibits the HDS of kerosene (Figure 1 (f)) decreasing the amount of H_2S (Figure 1 (e)) generated and leaving higher sulfur content in hydrotreated jet product (Table 3).

The data in Table 3 indicate a decrease in density for the feeds containing POME, suggesting that they contain a higher amount of paraffinic components, while the cardanol-containing feed exhibited higher density that is in line with its higher content of aromatic compounds [12]. Pour point and freezing point linearly decreased with enhancing content of POME (Table 3 and Figure 2), confirming the presence of linear high melting point paraffin containing structures in POME, while the feed blend containing cardanol did not show impairment of the cold flow properties

Table 3. Properties of hydrotreated products obtained from the four feeds.

Feedstock		HT SRK	2% POME	5% POME	2% Cardanol
Physicochemical properties	Density 15 °C, g/cm^3	0.8026	0.8025	0.8016	0.8037
	H_2O content, wt.%	0.0026	0.0031	0.0020	0.0194
	Pour point, °C	< -52	< -51	-47.0	< -51
	Freezing point, °C	-50.0	-37.0	-27.0	-49.0
Elemental analysis, wt.%	C	85.8	85.8	85.8	85.7
	H	14.0	14.0	14.1	13.9
	N	0.00003	0.00003	0.00003	0.00003
	S	0.0012	0.0028	0.0123	0.0090
	O (by difference)	0.2388	0.2272	0.1677	0.3710

Table 4. Detailed physicochemical properties included in the specification for Jet A1 aviation fuel.

Indices	Method	Dimension	HT SRK	2% POME	5% POME	2% Cardanol
Total acid number	ASTM D 3242	mg KOH/g	0.002			0.012
Distilation	ASTM D 86					
Initial boiling point		°C	160			153
10% (v/v) distilled		°C	181			182
50% (v/v) distilled		°C	204			206
90% (v/v) distilled		°C	230			235
Final boiling point		°C	234			265
Residue		%(v/v)	1.2			1.2
Losses		%(v/v)	1.2			0.5
Flash point	ASTM D 56	°C	49.5	49.0	30.0	44.5
Copper strip corrosion 2 h at 100°C	ASTM D 130	class	2C	3B	4A	4B
Electrical conductivity	ASTM D 2624	pS/m	0			0
Particles	IP 565					
$\geq$4 μm		ISO code	15			16
$\geq$6 μm		ISO code	14			13
$\geq$14 μm		ISO code	12			10
$\geq$21 μm		ISO code	10			8
$\geq$25 μm		ISO code	9			7
$\geq$30 μm		ISO code	7			6
Aromatic hydrocarbons	ASTM D 6379	% (v/v)	16.6			17.7
Viscosity at 20°C	ASTM D 445	mm^2/s	4.399			4.578
Smoke point	ASTM D 1322	mm	25.0			25.0
Net heat of combustion	ASTM D 3338	MJ/kg	43.290			43.272
Thermal stability (JFTOT) at 260 ∘C	ASTM D 3241					
Tube deposit rating (Annex A1-VTR)		class	0			0
Filter pressure differential, mm Hg		mm Hg	0			0
Microseparometer (MSEP)	ASTM D 3948	rating	98			99
Lubricity	ASTM D 5001	mm	0.80			0.64

of the hydrotreated product most probably because of the aromatic character of cardanol. It is noteworthy that the hydrotreated 98%SRK/2%cardanol mixture shows a much higher oxygen content, which may be a result of one order of magnitude higher water content in this product compared to other three feeds.

The detailed physical and chemical properties, which are embraced in the specification for Jet A1 aviation fuel presented in Table 4 show that except the petroleum hydrotreated kerosene all other feeds containing bio-components manifested unacceptably higher values for the copper strip corrosion. A possible reason for this observation could have been the presence of light ends (lower values of flash point), which can comprise H2S that in turn may provoke the appearance of high corrosivity.

For that reason 2 % of the light ends were removed by distillation according to the requirements of ASTM D 86 and the copper strip corrosion was measured again and the results of these measurements are given in Figure 3. While the removal of the light ends improved the corrosivity of petroleum kerosene, it did not affect

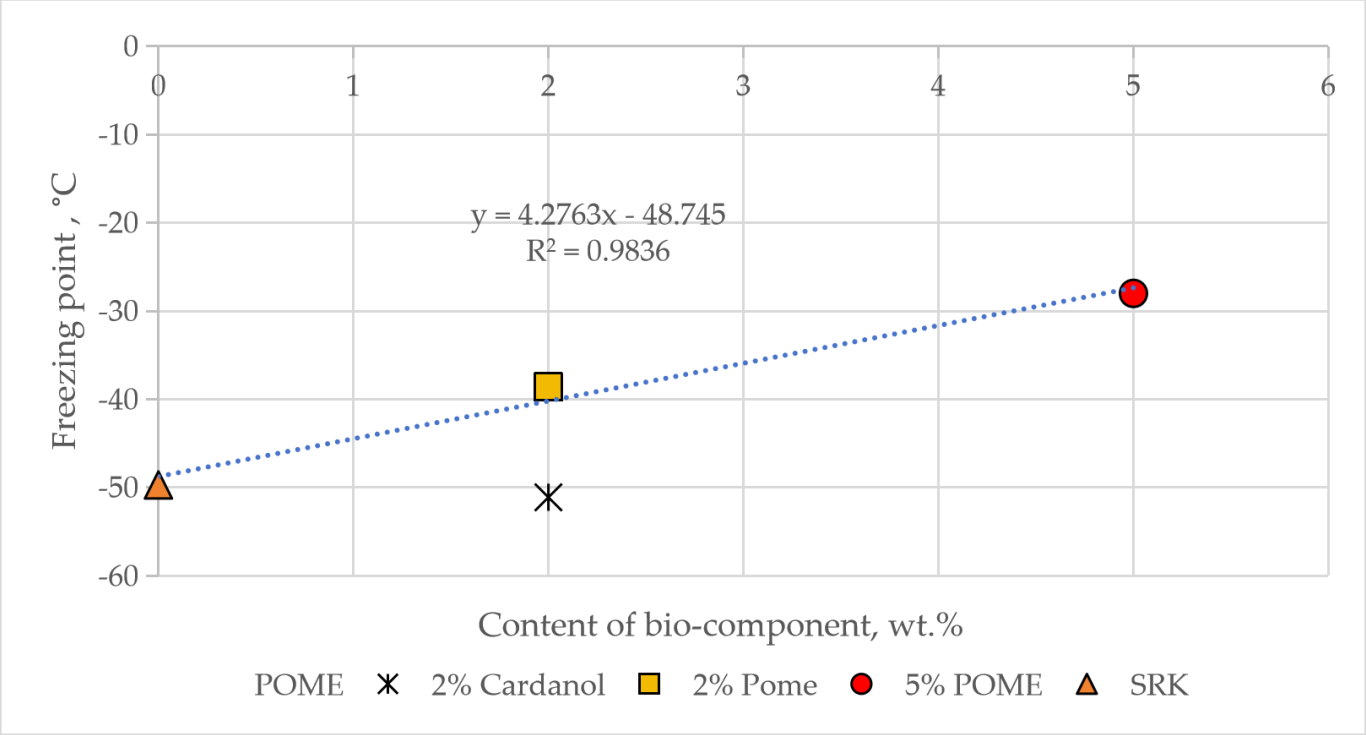

Figure 2. Dependence of freezing point of hydrotreated product on the content of bio-component in the blend SRK-bio-component.

Table 5. Properties of 100% commercial hydrotreated petroleum kerosene and its blends with cardanol.

Properties	Commercial hydrotreating unit petroleum kerosene hydrogenate	2% Cardanol	5% Cardanol	10% Cardanol
Initial boiling point	165.4	168.2	165.5	154.1
10% (v/v) distilled	180.7	181.3	183.3	182.6
50% (v/v) distilled	198.9	199.5	202.3	203.3
90% (v/v) distilled	226.6	228.0	234.8	280.9
Final boiling point	239.2	258.6	264.5	
Residue	1	2.2	3.7	10
Losses	0	2	5	
Freezing point, °C	-50.7	-50.5	-50.5	-50.9
Copper strip corrosion	1B	1A	1B	1A

the values of copper strip corrosion of the blends containing bio-components.

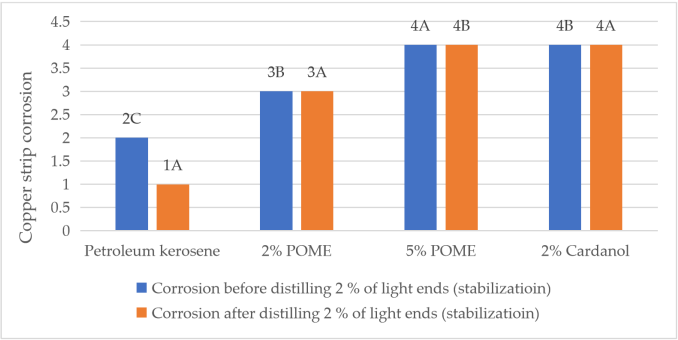

Figure 3. Copper strip corrosion of hydrotreated petroleum kerosene and the blends containing bio-components.

Earlier research has shown that during processing bio-oils the resulting refined products exhibited copper strip corrosion values that exceeded the specified limits for fuels because of the effect of residual oxygen in the liquid product, which is quite high in some cases [13, 14]. In order to understand whether these oxygen containing species are similar to those from the bio-feed, blends of petroleum hydrotreated kerosene sampled from a commercial hydrotreater dedicated to production of Jet-A1 fuel was blended with cardanol with 2, 5, and 10% in the mixture. These mixtures were characterized for their distillation characteristics, freezing point and copper strip corrosion (Table 5). The data in Table 5 indicate that cardanol does not affect freezing point

regardless of its content in the blend with petroleum kerosene. It influences the higher boiling point material in the blends and the residue remaining after distillation increases exponentially with the content of cardanol in the mixture. Interestingly the copper strip corrosion of the blends shown in Table 5 did not demonstrate the high values observed from their co-hydrotreated products. This suggests that in the hydrotreatment environment at the investigated catalyst and operating conditions POME and cardanol underwent chemical transformations leading to the generation of corrosive oxygen containing species different from the original oxygen substances present in the original POME and cardanol, which as shown from the data in Table 5 are not corrosive. The data in Table 4 show that the hydrotreated 100% petroleum kerosene has TAN of 0.002 mg KOH/g, while the hydrotreated 98%petroleum kerosene/2% cardanol has TAN of 0.012 mg KOH/g, that is twice as low as that of the feed blend. This implies that about 50% of oxygen containing acidic species are converted during the hydrotreatment process but the remaining species appear more corrosive than the original ones. Unfortunately, no data have been found in the literature to identify these highly corrosive substances remaining after the refining co-process, most likely due to the high specificity of the specialized analytical methodology it requires. The authors of this research, who originate from Bulgaria, were not capable of finding the required specific analytical technique to identify the corrosive species left after the hydrotreating co-processed products.

4 Conclusion

The production of SAF by co-processing of petroleum kerosene mixed with the bio-feedstocks POME and cardanol in amount up to 5% meeting the requirements of ASTM D7566 using the existing refining hydrotreatment technology seems very challenging. POME due to the poor cold flow properties of the co-hydrotreated product cannot be used for SAF co-processing utilizing the existing hydrotreating refining technology. Cardanol, in turn, does not constrain SAF production by co-processing from the point of view of cold flow properties, but exhibits unacceptably high values of the copper strip corrosion. Both co-processing bio-feeds demonstrated very high values of the copper strip corrosion showing that the unconverted oxygen containing substances are more corrosive that the original ones present in the bio-feeds as the bio-feed mixed with the hydrotreated petroleum kerosene exhibit low values of the copper strip corrosion.

Data Availability Statement

Data will be made available on request.

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Conflicts of Interest

Dicho Stratiev, Rosen Dinkov, Angel Nedelchev, and Ivelina Shishkova are affiliated with LUKOIL Neftohim Burgas, Bulgaria. The authors declare that this affiliation had no influence on the study design, data collection, analysis, interpretation, or the decision to publish. Dicho Stratiev served as an Associate Editor of the *Journal of Chemical Engineering and Renewable Fuels* at the time of manuscript submission. To ensure the integrity of the peer-review process, Dicho Stratiev was not involved in the editorial handling, peer review, or decision-making process for this manuscript, which was handled independently by another editor. The remaining authors declare no conflicts of interest.

AI Use Statement

The authors declare that no generative AI was used in the preparation of this manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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