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Upgrading the Light Cycle Oil by the Use of Acetonitrile with Both Single-Stage and Multi-Stage Extraction

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Abstract

It is known that Europe lacks automotive diesel fuel. Cracked gas oils from catalytic cracking processes, like light cycle oil (LCO), have very poor ignition quality characteristics and are not proper for use as automotive diesel fuel. The upgrade of LCO by solvent extraction, a method known in the refining industry is under investigation. Preliminary outcomes have shown that the raffinate of LCO extraction with acetonitrile as solvent has better properties compared to the initial LCO. In this study, a series of experiments of solvent extraction was performed in an LCO sample that was provided by a refining company in Greece. Acetonitrile was used as an extraction solvent since it has a significantly lower boiling point from the LCO boiling range, therefore it is easy to recover the solvent by distillation. The extraction was studied at various solvent/oil ratios and as a multi-stage process, where the raffinate of the extraction step was fed on the next extraction stage. Mass yield on the extraction products was measured in order to evaluate the efficiency of acetonitrile for the extraction of LCO. Apart from that, key properties of the LCO, raffinate fractions and extract fractions were measured in an attempt to evaluate if the extraction products have properties that can make part of the diesel fuel pool. Some of the properties that were measured include density, viscosity, sulfur content, aromatic hydrocarbons content, and cetane number.

Keywords: *LCO; Extraction; Acetonitrile; Multi-stage; Petrochemicals.*

1. Introduction

It is a reality that in the next years the presence of diesel fuel in the European Union transport sector will be augmented and will play a leading role because of both ecological and finance issues. Diesel engine is more competent than a gasoline engine and due to strict environmental laws nowadays (Euro 4 and Euro 5 emission bounds) has a crucially smaller amount of pollutant emissions in comparison with previous types of diesel engines. Automotive diesel is approximately twice as the motor of gasoline in the European Union states [1]. The standard properties of automotive diesel fuel, are presented in the EN 590 European standard [2].

Light Cycle Oil (LCO) is a side product of the fractionation of fuel catalytic cracking (FCC) reactor liquid waste. Two of the characteristics of LCO, viscosity, and distillation are in the fuel range but due to not good fuel blending component, it has a low cetane number, high density, and high nitrogen-sulfur content. The main behavior of LCO is to work as a viscosity cutter for decreasing the ultimate value of viscosity of heavy residual fuel. LCO is not easy to be upgraded by the use of conventional hydrotreating units, consequently, hydrocracking units with high-pressure values have been used to crack LCO into lighter products and naphtha [3-9]. On the other hand, light cycle oil products comprise useful saturated and aromatic hydrocarbons after their’s graduation and they have the characteristic of a diesel fuel component [10]. Furthermore, disunion and recovery of the aromatic components from LCO can procure significant raw materials for polymer and plastic production. The standard method for upgrading LCO in a refinery is the use of high-pressure hydrocracking units for low sulfur and high cetane diesel production with the essential limitation is firstly the cost and secondly the high amount of hydrogen and the catalyst deactivation during the process [11-13]. Acetonitrile will be used in the extraction of light cycle oil as a solvent. This study examines the effect of solvent/oil ratios and as a multi-stage process, where the raffinate of the extraction step will be fed on the next extraction stage, on the properties.

2. Materials and experimental methods

2.1. Experimental procedure

Light cycle oil (LCO) was collected from the fluidized catalytic cracking unit of Greek refinery, St. Theodore Motor Oil Hellas. The feed is to be considered referring to the fuel LCO, while as solvent the polar compound acetonitrile (CH_3CN) was used.

The laboratory experiments conducted were based on the principle of extraction. Two experimental tests were applied. The first test examined the impact of different feed/solvent ratios on the LCO properties. The fuel and the solvent were mixed based on predetermined feed/solvent ratios of 1:1, 1:1.5, 1:2 and 1:2.5 (based on volume). The second experimental test examined the impact of multi-stage extraction in LCO quality. The multi-stage extraction was facilitated for feed/solvent ratios of 1:1 (based on volume). The final raffinate of each stage was used as feed in the next stage (Figure 1). The experimental procedure is carried out in a total of four such stages to finished products ie FR4 and FE4. The mass balances are given in Table S - 1. The final product of the whole process is the Final Raffinate 4, which is greatly improved in its properties from the original LCO and free of heavy aromatics.

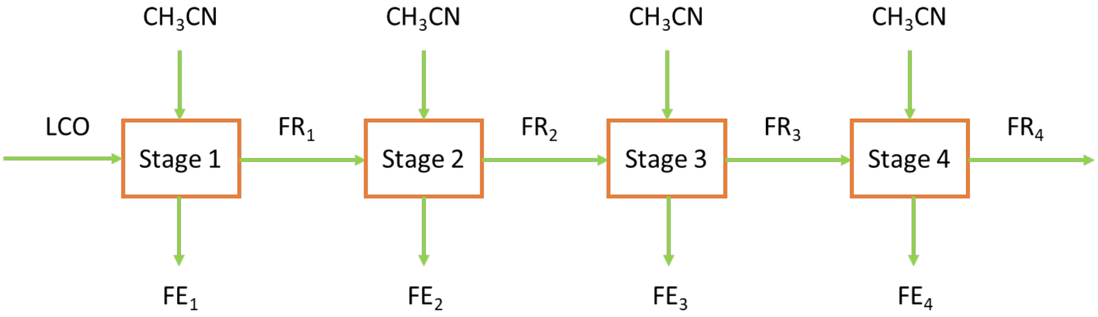

Figure 1 Flowchart of the multi-stage extraction.

Two phases were created after mixing and vigorous agitation. The raffinate and extract phases were collected separately with the raffinate (lower phase) contains solvent, mono-aromatic compounds, and paraffins and the extract (upper phase) will be free from heavy aromatics and has a minimum amount of solvent (Figure S1). Then, the two layers are subjected to atmospheric distillation for evaporation and recovery of the solvent, as well as to obtain the most two samples free from solvent (final raffinate/extract). The evaporation of the solvent is a simple process that can be easily applied in the case of ACN due to the low boiling point. The following condition will be applied and used as the separation condition:

$$[\text{density of raffinate}] < [\text{density of sample}] < [\text{density of extract}] \qquad (1)$$

From the masses of the final products, the reaction yield and the performance of the experimental procedure of extraction will be determined as:

$$a = \frac{m_{raf \cdot f}}{m_{sample}} \qquad (2)$$

where $m_{raf \cdot f}$ is the final mass of raffinate and m_{sample} is the mass of the sample.

Finally, the properties of all the samples obtained at each stage and the original LCO, measured according to standard methods, as the viscosity, density, sulfur content and the content of aromatics, and calculated the index cetane and compared the end as between the and the specifications for diesel.

2.2. Analytical methods

The measurements of the viscosity of the light cycle oil, raffinate and extract were facilitated with a viscometer (Anton Paar SVM 3000) according to the standard methods ASTM D445. A mid-FTIR gasoline analyzer (IROX Diesel Grabner Instrument) was employed to determine the cetane number and total aromatics and total polyaromatics. The ignition delay (ID) was estimated based on the formula:

$$CN=171/ID \tag{3}$$

where ID the ignition delay and CN the cetane number.

3. Results and discussion

3.1. Viscosity and density

According to the outcomes, it's obvious how far are the properties of the original sample of LCO from the standard specifications of diesel (Table S1) and useful conclusions can be deduced about the effect of the extraction with acetonitrile solvent on the LCO properties. Essential outcomes are incurred for both the quantitative efficiency of the extraction process and the quality characteristics of the samples (density, viscosity, cetane number and content in aromatics). Both, the viscosity and density of LCO were reduced with the elevation of temperature.

Table 1. Light Cycle Oil's properties identification

Property	LCO	
T (^oC)	15	40
μ (mPa*s)	4.5188	2.4094
v (mm^2/s)	4.8281	2.6140
ρ (g/cm^3)	0.9359	0.9182

Tables 2 and 3 show that the density and viscosity of each blend LCO/acetonitrile (1:1, 1:1.5, 1:2, 1:2.5) decrease, as the temperature rises from 15^{o}C to 40^{o}C. As the solvent fraction increases, viscosity is elevated by 23.8% and 19.9 % at 15^{o}C to 40^{o}C equivalently.

Table 2. Results of density and viscosity of extract in 15 and 40^{o}C in single stage.

Ratio	15^{o}C			40^{o}C		
	μ (mPa*s)	v (mm^2/s)	ρ (g/cm^3)	μ (mPa*s)	v (mm^2/s)	ρ (g/cm^3)
1:1	5.3391	5.4377	0.9819	2.7367	2.8414	0.9632
1:1.5	5.2506	5.3401	0.9832	2.6876	2.7865	0.9645
1:2	4.9114	5.0178	0.9788	2.5454	2.6507	0.9603
1:2.5	4.9944	5.0884	0.9823	2.6621	2.7625	0.9636

Table 3. Results of density and viscosity of raffinate in 15 and 40 ^{o}C in single stage

Ratio	15^{o}C			40^{o}C		
	μ (mPa*s)	v (mm^2/s)	ρ (g/cm^3)	μ (mPa*s)	v (mm^2/s)	ρ (g/cm^3)
1:1	4.0705	4.4868	0.9072	2.2495	2.5312	0.887
1:1.5	4.3882	4.8860	0.8981	2.3962	2.7206	0.8808
1:2	5.0936	5.7201	0.8905	2.6668	3.0536	0.8733
1:2.5	5.0373	5.7165	0.8812	2.6968	3.1245	0.8631

Tables 4 and 5 present the results of density and viscosity from the multi-stage experimental procedure. It is noticeable that the extractions at various stages affect the viscosity of the samples. As the stages increase density is reduced and viscosity augments. The viscosity of the raffinate showed an increment of 19.1 % and 15.9 % and after a quadruple extraction at 15^{o}C and 40^{o}C respectively (Table 5). The density lessening of 6.3 % and 6.5 % at 15^{o}C and 40^{o}C respectively is attributed to the continuous removal of the heavy aromatic compounds from the successive extraction.

From the other side, the extracts comprise more aromatic compounds compared to the raffinate resulting in a higher value of density.

Table 4. Results of density and viscosity of extract in 15 and 40 oC in the multi-stage procedure

Stage	15^{o}C			40^{o}C		
	μ (mPa*s)	ν (mm^2/s)	ρ (g/cm^3)	μ (mPa*s)	ν (mm^2/s)	ρ (g/cm^3)
1st	4.9858	5.0794	0.9816	2.5894	2.6895	0.9628
2nd	5.1524	5.2463	0.9821	2.6470	2.7475	0.9614
3rd	5.0804	5.2055	0.9760	2.5967	2.7165	0.9559
4th	5.1360	5.3164	0.9661	2.6496	2.7968	0.9474

Table 5. Results of density and viscosity of raffinate in 15 and 40 oC in the multi-stage procedure

Stage	15 ^{o}C			40 ^{o}C		
	μ (mPa*s)	ν (mm^2/s)	ρ (g/cm^3)	μ (mPa*s)	ν (mm^2/s)	ρ (g/cm^3)
1st	4.5303	4.8512	0.9359	2.4234	2.6389	0.9183
2nd	4.6522	4.8844	0.9115	2.4637	2.6918	0.8930
3rd	5.2924	5.9303	0.8924	2.7582	3.1523	0.8750
4th	5.3920	6.1559	0.8759	2.8106	3.2740	0.8585

3.2. Aromatics and cetane number

The aromatic content of diesel is very important. Elevated content of aromatics influences negatively both density and cetane number. The concentration of aromatics is also an intrinsic quality characteristic of the fuels. In the single-stage procedure, the more solvent (acetonitrile) has been added to the blend the higher cetane number the raffinates have. Specifically, as oil – solvent ratio decreased from 1:1 to 1:2.5 the cetane number increased from 23.7 to 36.2 (Fig. 2A).

In contrast, the multi-stage procedure resulted in augmentation of the cetane number while the experimental procedure progresses. The quality of the raffinate improved as the number of stages increased with the cetane number to increase from 26.3 to 42.3 (Fig. 2B). The removal of the aromatic compounds is due to the sequential repetitions of the extraction procedure. A reduction of 47.6 % is noticed between the original sample of LCO and the final raffinate (FR4). In the case of single-stage, raffinate's quality improved as the oil – solvent ratio decreased.

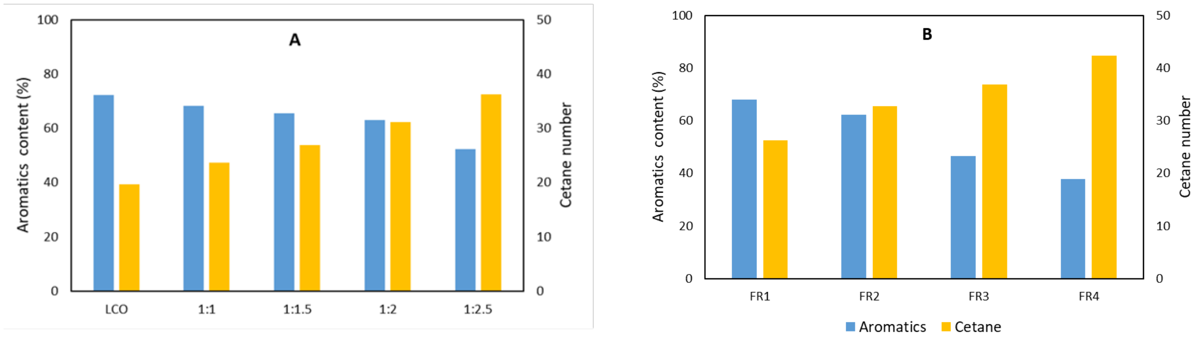

Figure 2. Results of aromatics and cetane number of the raffinate in single (A) and multi-stage (B) extraction.

According to Figure 2, the cetane number increases as the quantity of the solvent (acetonitrile) augments. In single-stage extraction, the cetane number is 26.7 for the blend 1:1 whereas in the blend 1:2.5 the cetane number is 35.4. From the other side, in the final stage of the multi-stage extraction, the cetane number almost approaches (CN=42.3) the standard value of approximately 46 (Fig. 2B). Figure 3 shows the ignition delay during 25 repetitions. Ignition delay was used to determine the cetane number.

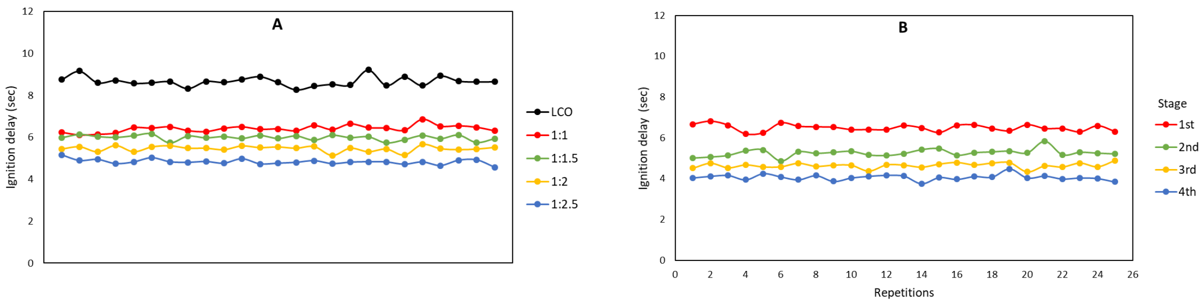

Figure 3. Results of ignition delay of the raffinate in single and multi-stage procedure

As the oil – solvent ratio decreases, the aromatics of extract increased from 55% to 61.6% and aromatics of the raffinate decreased from 68.2% to 52.2% (Fig. 4A). In the multi-stage extraction (Fig. 4B), the content of polyaromatics slightly reduced from 22.1% to 21.8% in the extract and reduced from 26.4% to 16.9% in the raffinate.

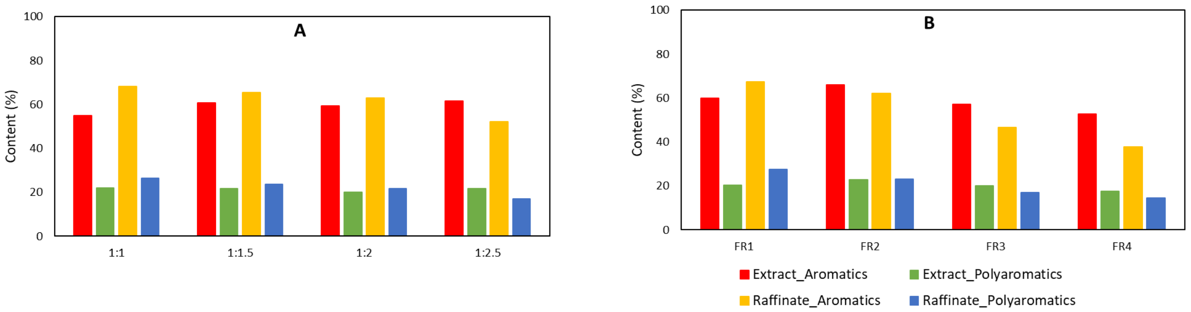

Figure 4. Results of aromatics and polyaromatics in single (A) and multi-stage (B) extraction

The concentration of aromatics is another crucial factor and is presented in Figures 5 and 6. The aromatic ring is very constant and does not change (decompose) effortlessly in big values of temperature. Then again, condensation and polymerization through the formation of PAH (polycyclic aromatic hydrocarbon) molecules help to the formation of particulate by aromatics [16]. As an alternative of total aromatics, polyaromatics concentration is more important for the regulation of PAH and particulate matter emissions because it is related to these forms of exhaust emissions [17]. The primary reason for solvent extraction was the eclectic elimination of compounds that are miscible to the solvent (acetonitrile). According to Figure 5 aromatic hydrocarbon concentration in raffinate was decreased as the solvent/oil ratio accrued.

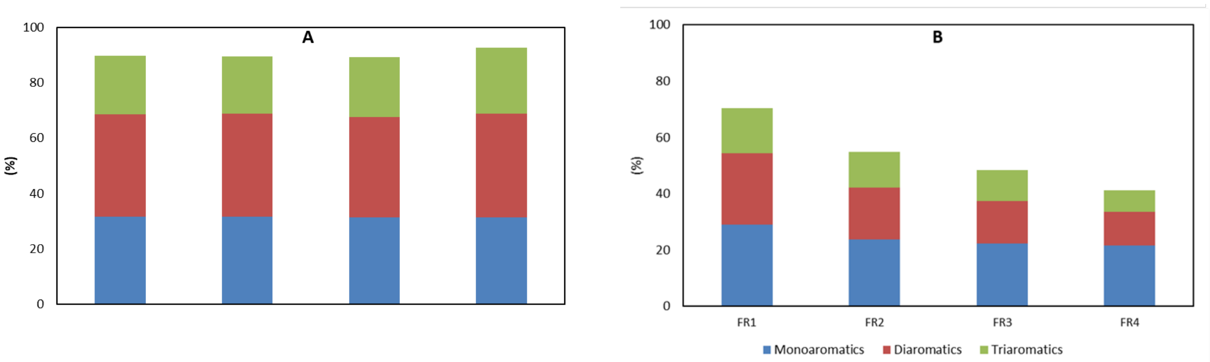

Figure 5. Results of aromatics composition of extract in single (A) and multi-stage (B) extraction

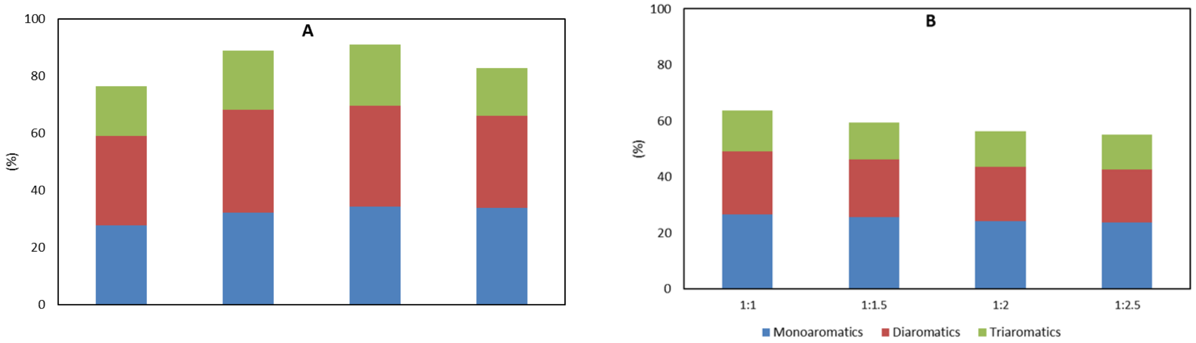

Figure 6. Results of aromatics composition of raffinate in single (A) and multi-stage (B) extraction

3.3. Sulfur content

Particulate matter emissions are affected by sulfur content. Elevated concentration of sulfur in diesel fuel outcomes in higher sulfate emissions that conduce to the total particulate matter emissions [14-15]. Sulfates behave as forerunners for the configuration of the agglomerates that create particular matter. The sulfur content of the raffinate was decreased after solvent extraction procedure compared to base fuel (LCO). The sulfur content reduced in the raffinate and augmented in the extract, as the oil – solvent ratio lessened whereas in multi stage process sulfur content diminishes for both extract and raffinate. Due to the extraction of polar sulfur compounds by the polar solvent, there is a reduction in sulfur content of the raffinate. For the exact word, the sulfur content of the extract augmented and was higher than the sulfur content of the base fuel. On all occasions, the sulfur concentration of the raffinate was big, well above the specification stint for automotive diesel fuel. Figure 7 shows the change in sulfur content for the raffinate and extract samples.

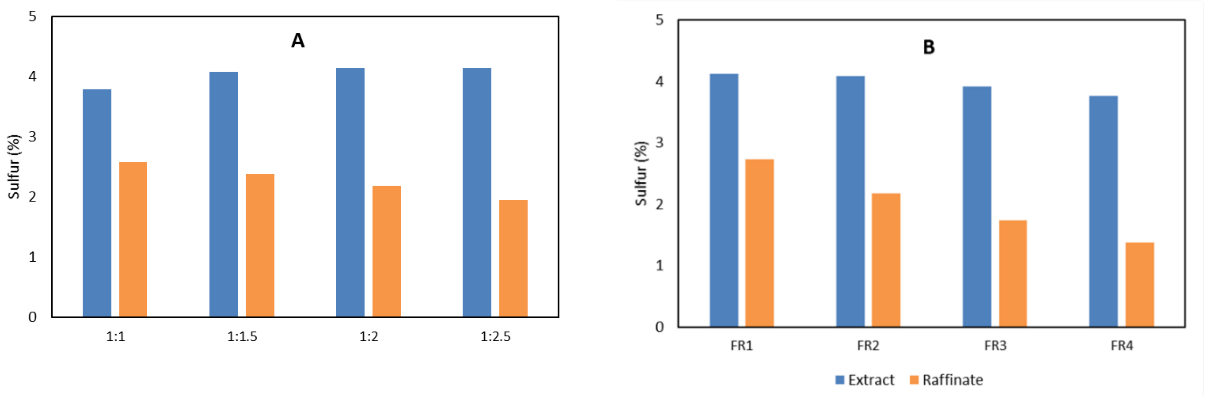

Figure 7. Results of sulfur content in single (A) and multi-stage (B) extraction

In the case of single-stage, the sulfur content in the extract reached 3.79, 4.08, 414 and 4.15 % for ratio of 1:1, 1:1.5, 1:2 and 1:2.5 respectively. Contrarily, the raffinate showed downward tendency reaching 2.58, 2.38, 2.18 and 1.94% of sulfur content for ratio of 1:1, 1:1.5, 1:2 and 1:2.5 respectively. The trend of these results is in good fit with the results of the preceding study of Karnonis *et al.* [8] who reported similar trend. As it is depicted in Fig. 7, multi-stage resulted in reduction of sulfur content for both extract and raffinate. The sulfur content in the extract was reduced by 8.7% (reached sulfur content of 4.12% after the 1st stage and 3.76% after the 4th stage) whereas in the raffinate sulfur content was reduced by 49.5% (reached sulfur content of 2.73% after the 1st stage and 1.38% after the 4th stage).

3.4. Efficiency (a%)

The attribution of the multiple extractions is assessed from the efficiency of each process. The efficiencies of the raffinates are given in Table 6.

Table 6. Efficiency variation in each stage of raffinate products

Stage	Feedstock (g (mL))	CH_3CN (g (mL))	Raffinate (g)	Extract (g)	a_{raf} (%)
I (LCO → FR1)	936 (1000)	750 (1000)	600	1086	68.26
II (FR1 → FR2)	400 (439)	338 (439)	318	420	74.50
III (FR2 → FR3)	200 (224)	169 (224)	174	194	82.50
IV (FR3 → FR4)	100 (114)	89 (114)	90	99	86.00

The measurement of efficiency process is based on the product of raffinate because the raffinate shows improvement in its properties compared to the original LCO. As the experimental procedure progresses, the efficiency of each stage accrues compared to the previous one. This fact was anticipated because as the extraction continues, there are fewer aromatic compounds in every stage compared to the previous one.

Table 7. Total efficiencies in the multi-stage extraction

Stage	a_{total} (%)
I (LCO → FR1)	68.26
II (LCO → FR2)	50.85
III (LCO → FR3)	41.95
IV (LCO → FR4)	36.07

The total efficiency of the experimental procedure from LCO to the final raffinate FR4 has the smallest value (Table 7). This fact occurs because as the extractions go on, the aromatic compounds are reduced and so the value of the total efficiency decreases.

4. Conclusions

This study examined the influence of different extraction procedures on LCO characteristics. The raffinate (upgraded LCO) exhibited improved properties as regards density, viscosity, and cetane number compared to the original sample LCO. In the case of single-stage, raffinate's quality improved as the oil – solvent ratio decreased. Polyaromatic hydrocarbons content reduced from 68.2 to 52.2%, sulfur content was reduced 2.58 to 1.94%, and cetane number increased 23.7 to 36.2. Multi-stage extraction resulted in an enhanced quality of the raffinate. More specifically, as the stages increase, polyaromatic hydrocarbons content reduced from 67.9 to 37.8%, sulfur content was decreased 2.73 to 1.38%, and cetane number increased 26.3 to 42.3. The final raffinate cannot be accepted in both processes as an automotive fuel. The properties of the extract worsen, as the LCO – solvent ratio decreases. The produced extract has poor properties in order to be used as a diesel blending component. The utilization of extract may have positive effects as viscosity cutter in the production of heavy fuel oil.

From the findings, only the cetane number of FR4 is close to 46 which is acceptable for the Greek market. The FR4 (final raffinate) can be mixed with Gasoil which resulting from the atmospheric distillation. The mixture is fed into the hydrodesulfurization unit to reduce the sulfur content so as to be used both as heating and automotive diesel. It is also obvious in the multi-stage process if there was an additional stage e.g. FR5, its cetane number would be according to Greek market specifications. Solvent-based extraction can be regarded as a low-cost upgrading process of LCO properties maintaining high efficiency.

Supplement

Table S1. Greek diesel fuel's specifications

Property	Value	Property	Value
Density (g ml^{-1}, 15^{o}C)	0.820 – 0.845	Ignition point (^{o}C)	55
Distillation (% v/v)		Cold filter plugging point	-5
Maximum distilled in 250^{o}C	65	Maximum water (mg kg^{-1})	200
Maximum distilled in 350^{o}C	85	Suspended particles (g/m^{3})	24
Maximum distilled in 360^{o}C	95	Carbon residue (% w/w)	0.30
Viscosity (cSt, 40^{o}C)	2 – 4.5	Ash (% w/w)	0.01
Sulphur	0.005	Maximum copper corrosion	3
Cetane index (minimum)	51	Oxidation resistance (g m^{-3})	25
Cetane number (minimum)	46	Maximum aromaticity (% w/w)	11

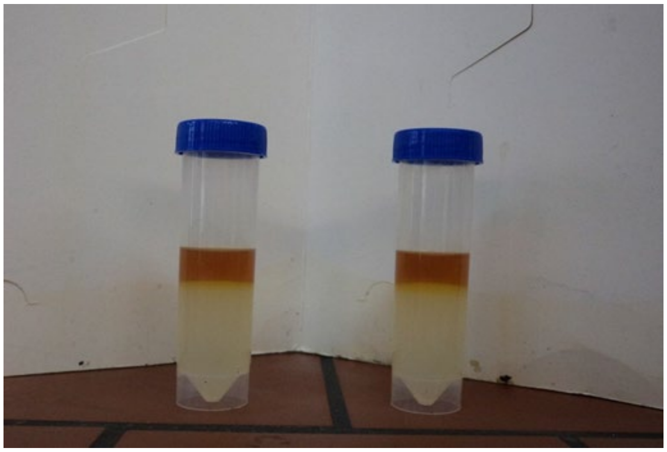

Figure S1. Separation of extract and raffinate from solvent

Declaration

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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