



Production of Pure Biofuel and Some Chemicals From Waste Soap Stock



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Abstract

The non-esculent soap stock oil was employed for producing some rare chemicals, along with certain fractions of biofuels akin to those engendered from petroleum sources. This inexpensive feed stock was hydrotreated using NiMo/Al₂O₃ in the sulfided form as a catalyst. The applied process was accomplished in a continuous micro-reactor, under high pressure of hydrogen. The hydroprocessed oil was treated chemically for separating its liquid hydrocarbons from the fatty acid constituents. The fatty acids were esterified to be transformed to the corresponding methyl ester. The products were identified via the gas chromatographic technique. The results reflect that the acquired hydrocarbons are clean and free from oxygenated compounds, in addition to sulfur, which has an adverse impact on the environment and on the performance of engines, so it can be used as a high – grade biofuel and also as pure chemicals. Furthermore, the prepared fatty acids are characterized by their low molecular weight, with carbon numbers in the range of C₅ to C₂₂, including those with odd carbon numbers that regarded as very rare components in nature. Hence this work offers the ability for obtainment precious products from a cheap material.

Key words: Biofuel, esterification, fatty acids, hydrotreating process, soap stock, vegetable oils.

1. Introduction

The hasty exhaustion of petroleum crude oil providences that conduced to deprivation of substantial energy sources, and owing to the perpetual exigency for chemicals indispensable for industries, researchers have motivated to find means for producing renewable and attractive fuels, in addition to engendering some valuable chemicals from wastes, and inexpensive materials [1–8]. Recently, biofuels derived from vegetable oils, which composed of triglycerides and glycerol, are receiving a great attention as alternative energy sources[9–15]. Transesterification of plant oils is currently the prevalent route for biodiesel production [16–19], however it exhibit numerous disadvantages. Among these, the poor storage and low stability owing to the double bonds involved in the issuing molecules, beside the high oxygen content that minimizes the quality and efficiency of the produced fuel [20]. Lately, some modern technologies such as thermo-

catalytic processes are arose with the intention of producing oils with better fuel characteristics than those obtained via transesterification[21–27].

In a previous work, by applying the hydrotreating and hydrocracking processes we succeeded to eliminate or even to reduce the majority of the above mentioned drawbacks, through the hydroconversion of some non-edible vegetable oils to paraffin rich mixtures of hydrocarbons, which are more expedient to be used in transportation engines[28,29]. Further amelioration of the properties of these fuels aside from acquisition of some chemicals demanded for consequential industries, are the main target of this study.

We focused on the exploitation of soap stock oil as an inexpensive material, for producing more precious matter including pure hydrocarbons completely free from oxygenated constituents, which can also be employed as a high-grade biofuel, along with generating certain valuable chemicals comprising low molecular weight fatty acids, embracing those

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characterized by their odd carbon numbers, that regarded as a very rare components in nature.

2. Experimental

2-1 Feed:

2.1.1 Crude soap stock feed:

Is natural fatty acids from which soap is made. It is a cheap material, produced as a by – product in the course of refining some vegetable oils, such as sunflower and soybean oils. It was employed in this study as a starting feedstock.

2.2. Methods

2.2.1 Degraded soap stock

It was attained by applying the novel catalytic hydroprocessing technique. The soap stock feed was hydrotreated in a fixed – bed micro reactor, using a sulfide NiMo/Al₂O₃ catalyst [29] The reaction was accomplished at 5 h⁻¹ LHSV, 2.5 Mp hydrogen pressure and 450 °C reaction temperature. The apparatus and procedure were fully described in our previous work, that published before [30].

2.2.2 Characterization of crude and hydrotreated soap stock oil:

The acquired hydrotreated product was evaluated on the basis of its fuel characteristics according to different standard ASTM methods, including density (D-1298), viscosity (D-445), sulfur content (D-1552), pour point (D-97), molecular weight (D-2502), calorific value (D- 240), refractive index (D-1747), ash content (D-482), flash point (D- 93)and saponification number ASTM D-5558. These results were compared with those achieved for the crude feed.

2.2.3 Extraction of fatty acids

The oxygenated compounds, particularly the fatty acids included in the hydroprocessed sample were extracted according to the following procedure.[31]:

- 1- Saponification of the investigated specimen by 0.7 N solution of NaOH, to get the sodium salts of its hydrolysed fatty acids.
- 2- The acquired alkaline solution was dissolved in excess warm water, stirred for 15 minutes, and the arised hydrocarbon layer was separated.
- 3- The produced hydrocarbons were analysed using FTIR and gas chromatographic techniques.
- 4- A concentrated hydrochloric acid (34%) was added drop wise to the saponified layer till the solution becomes acidic.

- 5- Addition of diethyl ether to this solution creates an ethereal layer embracing the formed fatty acids that separated, washed with distilled water and dried overnight using anhydrous Na₂SO₄.
- 6- Decantation and distillation were performed for dispelling Na₂SO₄ and diethyl ether, consecutively from the fatty acids derived from the assayed sample, afterwards, it was weight and esterified.

2.2.4 Esterification of the fatty acids.

This reaction was carried out in a glass reactor immersed in a water bath, fitted with a reflux side tube, containing a few of anhydrous Na₂SO₄for adsorbing the ensuing water. The fatty acids of the feed and that extracted from the hydrotreated sample were loaded individually in the reactor and refluxed for one hour with methanol and p-toluene sulphonic acid that utilized as a catalyst. After one hour left from the time of reaction, the reactor left to cool and the constituted esters were extracted by diethyl ether. The ethereal layer was separated, washed by distilled water, dried overnight with anhydrous Na₂SO₄ and heated on a water bath at 50 – 60 °C, to get the prepared fatty acid esters.

2.2.5 FTIR Analysis.

FTIR analysis was performed to analyse the feed and the hydrotreated samples as well as the prepared hydrocarbons, employing Nicoletis -LOFT- IR, Nicolet IS-10 apparatus.

2.2.6 Gas chromatographic analysis.

The gas chromatographic apparatus, Agilent 6890, equipped with flame ionization detector (FID), has been employed for identifying the constituents and concentrations of the hydrocarbons acquired from the hydrotreated sample. Separation was performed on a HP.60 column with 30 meter length and 0.25 mm ID. Nitrogen was used as a carrier gas at a flow of 2 ml / min. The temperature of the injector and detector were set at 300 °C.

The hydrocarbon gases evolved during the hydrotreating process were identified using Piona column. The elution of the injected sample was achieved at temperature programmed from 80 °C to 180 °C with an increasing rate of 2 °C/min.

The prepared fatty acid esters were also analysed using INNO wax column with 60 meter length and 0.32 mm ID. The injector and detector temperature were 250 and 280 °C, respectively.

3. Results and Discussion

The soap stock feed was subjected to hydrotreating process. The physicochemical characteristics of the achieved product as well as the virgin oil were determined and the obtained data are summarized in table 1. Evaluation of the quality of the hydrotreated product has been accomplished on the basis of its fuel properties compared with those of the raw soap stock. The exposed information reveals the explicit contradiction between the original oil and its hydroprocessed yield. A distinct improvement in the quality of the acquired outputs has been occurring as evidenced from the substantial drops of density, molecular weight, pour point and viscosity values of the treated oil in relation to those of the corresponding genuine feed. These mainly imputed to the degradation and hydrogenation of the virgin molecules that transformed to lighter – saturated components during the reaction execution. Furthermore, the calorific value of the handled sample is somewhat increased comparable with its analogous heavy crude oil, that principally ensued from the deficiency of oxygen content as a consequence of its treatment in H₂ atmosphere. The decrement in the oxygenated constituents can be pursued from the IR results, declared in figures (1A and B). Accordingly, the applied hydrotreating process succeeded in improving most of the important properties of the raw soap stock to become suitable for utilization as a biofuel. However, due to the acidic feature of the original feed, some oxygenated constituents were still remaining in the hydroprocessed specimen as reflected from the IR spectrum in figure 1B. This leads to certain impact on the specifications of the product, particularly the calorific value (CV) which seems to be, somewhat, lower than that derived from petroleum sources.

The calorific value is an important parameter in connection with the output power. The high CV point out to the enhancement in the power magnitude of the prepared fuel, which can be produced from an engine. This can be ascribed to the scarcity of the amount of the oxygenated compounds of the employed oil. Consequently, the removal of the residual oxygen from the prepared fuel, as far as possible, is required [32]. Therefore, better traits of the achieved hydroprocessed product can be realized through the elimination of the fatty acids from the investigated sample, to get high – grade biofuel composed essentially from clean hydrocarbons. Then, it becomes also competent for utilization as a pure chemical, that considered as one of the main targets in this study.

To remove the residual oxygen from the hydroprocessed soap stock, the sample was treated chemically for separating the liquid hydrocarbons from the incorporated fatty acids constituents

according to the method pointed out in the experimental section. The acquired products were then subjected to FTIR and gas chromatographic analyses.

Table 1: The main physicochemical characteristics of crude and hydrotreated soap stock oil.

Characteristics	Method	Crude Soap stock	Hydrotreated soap stock
Density g/ml at 20 °C	ASTM D- 1298	0.9278	0.8983
Kinematic viscosity, cSt at 40°C	ASTM D- 445	37.178	15.939
Sulfur content, wt%	ASTM D- 1552	0.0654	0.033
Pour point, °C	ASTM D- 97	24	-12
Molecular weight	ASTM D- 2502	421	233.29
Calorific value, j/kgm	ASTM D- 240	44737	44933
Refractive index, at 20 °C	ASTM D- 1747	1.45095	1.45076
Ash content, wt %	ASTM D- 482	Nil	Nil
Flash point, °C	ASTM D- 93	177	-

3.1 Infrared study.

The Fourier Transform Infrared (FTIR) inspection for the soap stock feed before and after subsection to hydroprocessing and chemical treatment, was performed in the wave number region of 500- 4000 cm⁻¹ the obtained spectra are exposed in figure 1.

The recorded spectrum of the crude feed evidenced the predomination of the oxygenated constituents as revealed from figure 1A. The main absorbance bands associated with these components are conspicuously obvious in as much as the appearance of several bands characteristics of fatty acids and triglyceride in the range of 1285-939 cm⁻¹ and 1711.4 cm⁻¹ that attributed to the stretching vibration of C-O and C=O groups, respectively.

Feeble diffused signals emerged at the high wave number in the region of stretching vibration of OH group at 3750 cm⁻¹, besides; weak peaks could also be recognized at 2672 cm⁻¹ that designated to OH carboxylic acid.

Moreover, IR profiles exhibit two strong signals connected with asymmetric and symmetric stretching vibration of methyl and methylene groups at 2926-2857cm⁻¹ region. In addition, the appearance of several bands around 1456 cm⁻¹ and 1377 cm⁻¹ are arised from aliphatic C-H bonding of methylene and methyl groups.

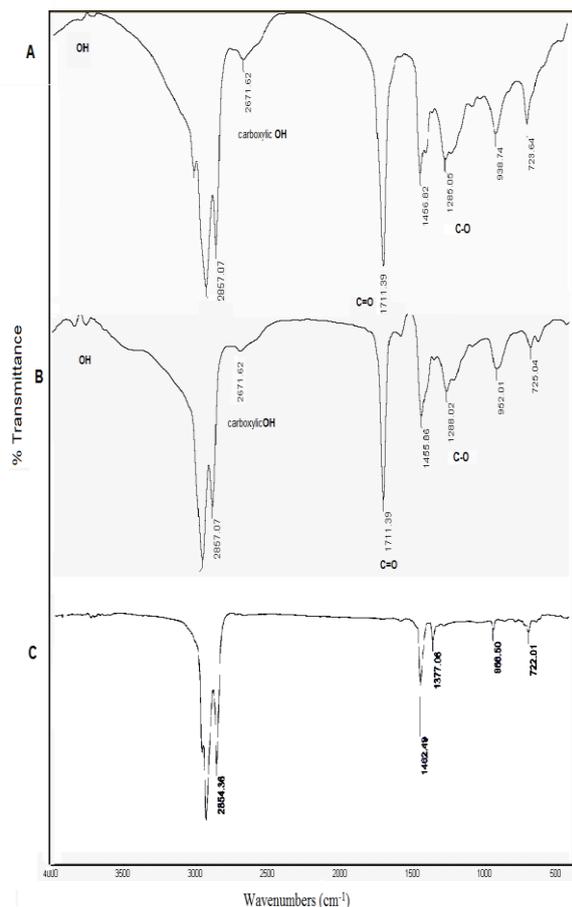


Figure 1: FTIR spectral Analysis of A- crude soap stock, B- hydrotreated soap stock and C- the prepared hydrocarbon

Also, the demonstrated figure reveals moderate absorption peaks at about 724 cm^{-1} which ascribed to the out of plane of alkene.

The spectrum achieved after hydrotreating the soap stock feed using sulfide $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst is declared in figure 1B. The represented FTIR profile sheds light upon the crucial improvement in the quality of the acquired product compared to the crude oil, due to the significant diminution of the oxygen constituent. This can be evidenced through the explicit reduction in the intensities of the characteristic bands of the fatty acids at 1711.4 cm^{-1} , as well as those emerged in the range of $1285\text{--}939\text{ cm}^{-1}$ that related to stretching vibration of $\text{C}=\text{O}$ and $\text{C}-\text{O}$ groups, respectively. This substantiates that deoxygenation has occurred as a result of hydrotreating the oil, and the attained product incorporates relative restriction in the content of the oxygenated components.

In addition, the IR spectrum obtained after processing the crude soap stock with hydrogen indicates a considerable reduction in the height of the peak recorded at the olefin region, at 724 cm^{-1} (figure 1B) compared with its analogous in the spectrum of the virgin oil (figure 1A). The weakness of this signal may be accounted for the saturation of the olefinic bonds existed in the original molecules.

Figure 1 C illustrates the FTIR profile of the chemically treated product of the hydroprocessed soap stock oil. The exposed result indicates that the acquired hydrocarbons, attained after the fatty acids extraction, are very clean and almost completely free from the associated oxygen components as demonstrated from the evanescence, or even the drastic decrement of those signals characteristics for $\text{C}=\text{O}$ and $\text{C}-\text{O}$ groups at 1711.4 cm^{-1} and $1285\text{--}939\text{ cm}^{-1}$ range consequently. The achieved hydrocarbons can be employed as a pure chemical and also as a high – grade biofuel, free from oxygenated components, devoid of sulfur, which has an adverse impact on the environment and the performance of engines.

This conclusion was confirmed through the saponification number determination for the crude and the obtained hydrocarbons which found to be 673.2 and Nil mg KOH/g respectively. These results indicate the absence of carboxylic acid from the hydrocarbon meaning that free from fatty acids.

3.2 Gas chromatographic study

3.2.1 Gas chromatographic analysis of the fatty acid methyl esters:

The fatty acids of the crude soap stock feed and those derived from its hydrotreated product were esterified to their corresponding methyl esters, and analyzed via gas chromatographic technique to investigate their constituents and carbon number distribution. The recorded gas chromatographic profiles and the obtained results are exposed in figure 2 and table 2.

As evidenced from the data, all methyl esters of fatty acid (MEsFA) of the virgin oil are characterized by their even number of carbon atoms. The most prevalent components are methyl esters of octadecanoic (C_{18}) and hexadecanoic (C_{16}) acids, that comprised 75.11 and 17.69 wt %, respectively. The remainders amount to 7.2 wt % represents the higher molecular weight fraction, embracing eicosanoic (C_{20}) and docosanoic (C_{22}) acids.

The information inscribed in table 2 and figure 2 clarify that, the FAMEs prepared from the hydrotreated soap stock are altogether lighter than depicted for those produced from the crude oil.

Table 2: Carbon number distributions of fatty acid esters extracted from crude soap stock feed and its hydrotreated product .

Carbon number	Type of fatty acid of ester	Soap stock feed wt%	Hydrotreated product, wt%
C5	Pentanoic acid	-	0.2649
C6	Hexanoic acid	-	0.0942
C7	Heptanoic acid	-	0.5409
C8	Octanoic acid	-	1.3291
C9	Nonanoic acid	-	6.7600
C10	Decanoic acid	-	9.9936
C11	Undecanoic acid	-	16.0855
C12	Dodecanoic acid	-	19.2278
C13	Tridecanoic acid	-	2.5116
C14	Tetradecanoic acid	-	1.1931
C15	Pentadecanoic acid	-	0.9973
C16	Hexadecanoic acid	17.6912	8.3974
C17	Heptadecanoic acid	-	0.4639
C18	Octadecanoic acid	75.1092	30.1776
C19	Nonadecanoic acid	-	0.4395
C20	Eicosanoic acid	2.9684	0.9687
C21	Heneicasanoic acid	-	0.1924
C22	Docosanoic acid	4.2311	0.3626
Others	Tricosanoic, Tetracosanoic acid	0.00001	
Total		100	100

Furthermore, the carbon number distribution are ranging between C₅ and C₂₂ including those with odd and even number of carbon atoms. The weight percentages of esters corresponding to octadecanoic and hexadecanoic acids are intensely diminished from 75.11 and 17.69 wt % to become 30.18 and 8.4 wt% consecutively. This can be attributed to the dissociation of the heavier C₁₈ and C₁₆ molecules to lighter fatty acids during the subsection of the feed to the hydrotreating process. The degraded components are mainly restricted in the range of C₉ and C₁₃, comprising about 54.6 wt % of the cracked fatty acids. It is worth to mention that the fatty acids extracted from the hydrotreated feed are equivalent to 27 wt % of the product. The remainder represents the weight percentage of the hydrocarbon fraction in the sample.

Consequently, this study offers the possibility of generating a variety of fatty acids that have different applications in industry. For instance, C₄-C₆ fraction is appropriate for perfumes, greases and plasticizers manufacture, whereas C₇-C₉ can be utilized for fatty alcohol production. Higher molecular weight fatty acids (C₁₀- C₁₆) are agreeable to making the toilet soap and varnishes, while their esters are available to be used as an economic substitute for diesel fuel [33]. C₁₇-C₂₀ fraction is expedient for manufacturing high grade household soap. Moreover, all of these fatty acids can be used as starting materials for synthesis of other chemical compounds.

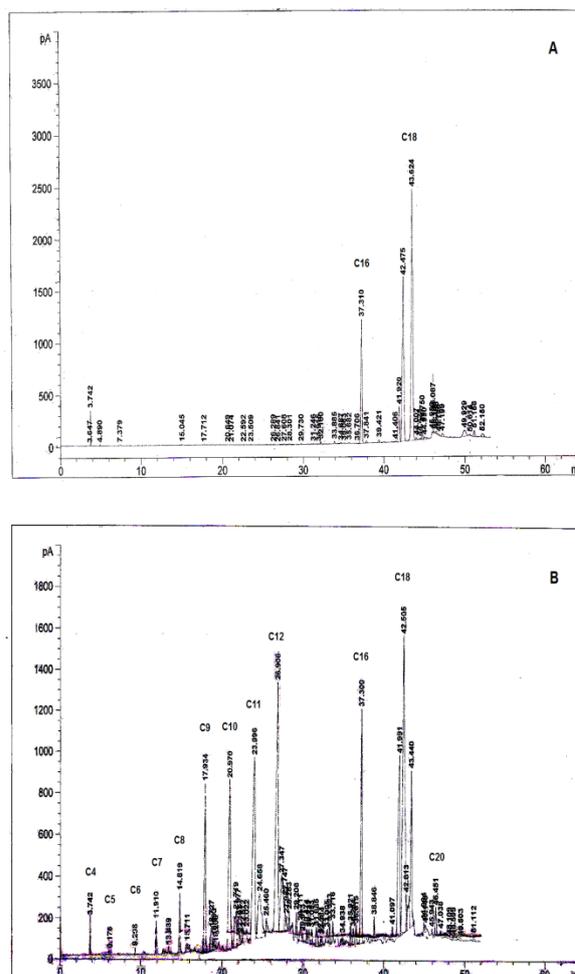


Figure 2: Gas chromatographic analysis of fatty acid esters of A: crude soap stock and B: hydrotreated soap stock.

3.2.2 Gas chromatographic analysis of the obtained hydrocarbons.

In this respect, it is significant to mention that, some hydrocarbon gases were evolved throughout the performance of the hydrotreatment operation. The derived gases were collected and identified via gas chromatography as declared in table 3. The

demonstrated data substantiate that the carbon number distribution of the generated gases are ranging between C₁ and C₄. The maximum weight percentage is found to be 39.65 % for ethane, whereas the minimum value comprising 6.81wt% is for butanes. Methane and propane are existed with approximately equal concentration (about 26.2- 27.3 wt %). Hence the availability of these hydrocarbons in the gaseous product can be arranged descendingly in the following sequence.

Ethane > propane ≥ methane > butanes

On the other hand, the liquid hydrocarbons acquired after getting out the oxygenated compounds from the processed soap stock feed were also analyzed qualitatively and quantitatively by gas chromatography, the recorded pattern and the obtained data are exposed in figure 3 and table 4.

It is apparent from the depicted results that, the hydrocarbons attained after the fatty acids removal incorporate various fractions, located principally in the gas oil range, in addition to gasoline and kerosene, beside some residues. Their amounts come to 52.8, 21.9, 24.9 and 0.4wt% successively.

Table 3: Carbon number distribution of gases obtained from hydrotreated soap stock oil .

Carbon number	Weight percentages
Methane	26.22
Ethane	39.65
Propane	27.33
Butanes	6.81

Obviously, the carbon number distribution of the lighter cut is ranging between C₅ and C₉. The highest concentrations are found to be 5.2-5.3 wt% for C₉ and C₆, whereas the least values are 2.7 and 4.3 wt % for C₄ and C₅ respectively. So the attained lower molecular weight hydrocarbons is composed principally from gasoline- free from fatty acids

The second cut, which is equivalent to kerosene – like fraction involve hydrocarbons in the range of C₁₀ up to C₁₄. Their amounts fluctuated from 3.7 wt % for decane and undecane to 5.2-5.4 wt % for tridecane and tetradecane, respectively. 6.9 wt% is the highest concentration that inscribed for dodecane.

The demonstrated gas chromatographic analysis of the hydrocarbon components of the heavier cut evidenced that the carbon numbers are principally located between C₁₅ and C₂₂ meaning that it composed essentially from clean gas oil. The most predominant constituents arose from the investigated deoxygenated hydrotreated soap stock in this cut are situated between C₁₅ and C₁₈ that comprised 45.9 wt%. Whereas, the least concentrations were found to be 1.9, 3 and 2 wt% for C₁₉, C₂₀ and C₂₂ consecutively.

Table4: Gas chromatographic analysis of the prepared hydrocarbons obtained from hydrotreated Soap stock oil.

Carbon number	Hydrocarbons, wt%	Petroleum-like fraction
C5	4.3	Gasoline –like fraction
C6	5.3	
C7	2.7	21.9 wt%
C8	4.4	
C9	5.2	
C10	3.7	Kerosene –like fraction
C11	3.7	
C12	6.9	24.9 wt%
C13	5.2	
C14	5.4	
C15	12	Gas oil –like fraction
C16	6.7	
C17	14.5	52.8 wt%
C18	12.7	
C19	1.9	
C20	3.0	Residue 0.4 wt%
C22	2.0	
>C22	0.4	

In view of the obtained results, the cheap- non edible soap stock oil was exploited to produce different types of liquid fuels, including gasoline, kerosene and gas oil like distillates that can be used as high -grade substituents of petroleum fractions, to meet the great demand for refined products and the petrochemical feed stocks.

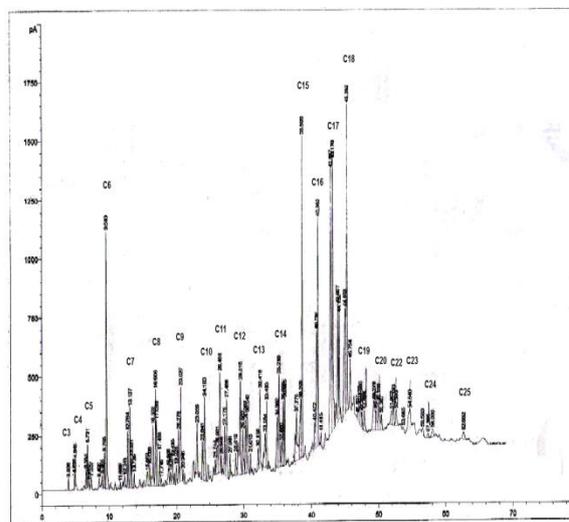


Figure 3: Gas chromatographic analysis of hydrocarbons of the hydrotreated soap stock.

4. Conclusions:

- Hydroprocessing technology was applied to get valuable materials from a non-edible, inexpensive soap stock oil
- Low molecular weight fatty acids have odd number of carbon atoms that considered as a very

rare component in nature can be derived from the acquired product.

- The fatty acids extracted from the degraded soap stock have their significance as a feed for various petrochemical industries, including the manufacture of perfumes, plasticizers, synthetic lubricating oil, fatty alcohols.... etc..

- The achievement of neat hydrocarbons are realized that can be utilized as pure chemicals and also as a clean high grade biofuel characterized by nil sulfur and free from oxygenated compounds.

- The hydrocarbons separated from the hydrotreated soap stock product can be fractionated to light, middle and heavy cuts, corresponding to gasoline, kerosene and gas oil –like fractions, alternative to those engendered from the fossil fuel. .

- The biofuel attained from this study is more advantageous over the regular petroleum as being clean, biodegradable and more environmentally friendly compared to those derived from fossil fuel.

5. Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that “There are no conflicts to declare”.

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الملخص العربي

إنتاج وقود حيوي نقي وبعض الكيماويات من مخلفات مخزون الصابون

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تم تحويل مخلفات صناعة الزيوت و التي تستخدم في صناعة الصابون والغير صالحة للاستهلاك الغذائي في إنتاج بعض الكيماويات النادرة، بالإضافة إلى مقطرات معينة من الوقود الحيوي النقي شبيه بتلك المستخرجة من مصادر بترولية. وقد تم هدرجة هذا الزيت رخيص الثمن بالاستعانة بجهاز الضغط العالي باستخدام النيكل - موليبدينم على الألومينا في صورته الكبريتية كحفاز وذلك في جو من الهيدروجين. وقد عولج المنتج المدرج كيميائيا لفصل الهيدروكربونات السائلة عن الأحماض الدهنية والذي أجريت له عملية الأسترة لتحويله لنظيره من الاستر الميثيلي ليتسنى تعريف مكوناته بتحليله باستخدام تقنية كروماتوجرافيا الغاز.

وأُسفرت النتائج عن إمكانية الحصول على هيدروكربونات نقية وخالية من المركبات الأكسجينية وكذلك الكبريت الذي له تأثير سلبي على البيئة وعلى أداء المحركات. لذا فإنه يمكن استخدامه كوقود حيوي عالي الجودة، وأيضا كمواد كيميائية نقية. علاوة على ذلك، فإن الأحماض الدهنية المحضرة تتميز بأوزانها الجزيئية الصغيرة؛ حيث تتراوح الأعداد الكربونية بها من C₅ إلى C₂₂ بما في ذلك تلك المحتوية على أعداد كربونية فردية، والتي تعتبر مكونات نادرة الوجود في الطبيعة. وبناء عليه فإن هذا العمل يوفر القدرة على إمكانية الحصول على منتجات ثمينة من مواد رخيصة الثمن.