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Fuel Obtained from Used Lubricating Motor-Oils by Utilizing Mild Catalytic Hydro-Cracking Process

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Abstract This study aimed to make useful fuel cuts from used lubricating motor-oils by utilizing mild catalytic hydro-cracking process. This research is considered to be the first of all after reviewing both the literature and previous studies. Materials and Methods: In this research, we applied sufficient quantity of different types of used lubricating motor-oils which were collected directly from gasoline, diesel and hydraulic motor-oil service stations. These collected used lubricating motor-oil samples were mixed together very well and considered as typical raw samples for our studies. Industrial catalysts of both MHC 10 and HTH 548 were also used in our experiments and tests. Programmed experiments were adapted using Box-Hunter methods to determine the necessary minimum number of experiments and to define the range of tried parameters. We also used different standard analysis methods, techniques and equipments to determine composition and properties of collected gas and liquid samples including Gas Chromatography Mass Spectrometry (GC-MS). Our studies showed that fuel gas can be obtained at (3.3 wt. %) yield, and useful fuel liquid cut yields such as Naphtha (10.4 wt. %), Kerosene (11.2 wt. %), Gas oil (24 wt. %), and Fuel oil as residuals at (31 wt. %). After studying properties and characteristics of the main liquid and gas products, we found that all high quality products can be marketed directly without any further treatments, or can be mixed directly with similar fuel cuts. Naphtha cut was rich in aromatics at (19 vol %).

Keywords Gas oils, Lubricating, Fuel, Catalysts, MHC 10, HTH 548, Naphtha cut, GC-MS

Introduction

The process of recycling used engine-oil and other lubricating oils has more than five decades. Due to the increasing need of environmental protection and strict legislation, disposal and recycling of waste oils become very important. The recycling of waste lubricating oils can be accomplished through different methods [1,2,3].

Recently, it has been reported the increase of engine and other industrial oils worldwide, and it is expected the increase will continue to rise in the near future due to the increasing incursion of motorization and industrialization. Therefore, the selective collection and recycling of used lubricating oils have been inspired in the last decade all over the world. Under this inspiration more than 40% of different used oils are being recycled, and it is expected that this percentage will increase in the future as essentially necessitated by the accomplishment of selective collection [1, 3-9].

The technology of modern used oil recycling is the re-refining with such process, high quality base oil blending components can be produced with satisfactory requirements of standards [10-14].

The used of lubricating motor oils is a valuable source of different types of hydrocarbons which consist of complex compounds containing (20-60) carbon atoms of (300-750 kg/k.mol) molecular weight, boiling points (300-650 °C), linear and iso-paraffin's, naphthenic hydrocarbons having (5-6) rings in paraffinic chains of different length in series, aromatic- naphthenic rings having side paraffinic chains, beside the additives compounds [15-19].

In recent years, following to the surge in prices of petroleum and its products, energy resources have become the fundamental requirements that should be secured, a fact which prompted interest in the logical utilization of used oils being a source rich in valuable hydrocarbons. The hydrogenation processes might spread in a wide extent due to the increasing demand for modern, high performance group III oils [20-23].

The aim of this research is to perform mild catalytic hydro-cracking process which represents one of good solutions to ensure environmental protection and introduce new opportunities to produce high value products, by transforming the essential hydrocarbons to a valuable fuel cuts while optimizing performance and makes more returns from investments.

Materials and Methods

In our studies, we used lubricating motor-oils samples, which were brought from car service stations, these samples were mixed very well and then its main properties were determined as shown in table (1) [4-7]. After that the used oil samples were treated by settling to allow the separation of a part of water and heavy materials as sediments, deposited and separated, at the bottom of the bowl assembly. The sample then subjected to:

- atmospheric distillation by heating the oil sample up to 200 °C, thus the sample became free of water and light fuel.
- vacuum distillation under low pressure (10 mmHg), using a vacuum distillation automatic steel unit.
- recovered used oil sample cut was obtained, representing (80 wt. %) and considered the raw sample which will be used in subsequent tests and catalytic mild hydro-cracking experiments. Its properties and characteristics were shown in Tables (2,3) and figure (1).

Two different types of solid refinery hydrogenation catalysts having same chemical composition (Ni Mo / Al_2O_3 SiO_2), but different physical properties and consequently different activity, were used in laboratory steel pilot plant mild hydro-cracking experiments. The first catalysts type is MHC 10 (American made UOP company), the second Industrial catalysts type is HTH 548 (manufactured by French Axens company). The characteristics of both catalysts are shown in Table (1). These two catalysts were activated according to the manufacturer instructions by Pre-wetting the catalyst via exposing the dry catalyst by liquid hydrocarbons at nitrogen atmosphere. Catalyst sulfurization process is necessary to convert its metals oxide to sulfur oxide form using carbon sulfide (CS_2), added to the liquid gas oil as a catalyst washing agent, so as its proportion not to exceed (2 wt. %) and raising the temperature up to (200 °C), then the unit pressurize by hydrogen to (60 bar), and the temperature raised to (230 °C) and then to (290 °C) at the same previous heating rate. The sulfurization process is stopped when hydrogen sulfide percentage (H_2S) increased in outlet gases significantly, and gas samples are taken periodically for analysis. Then the inlet liquid gas oil can be replaced with raw material, and have to be recycled for 36h before starting the implementation of the required experiments.

Hydrogen produced via naphtha steam reforming in Homs refinery- Syria, was utilized in catalytic mild hydro-cracking experiments and were brought by special gas cylinder. Hydrogen gas composition were determined and shown in table (2).

Operating conditions were chosen according to our experience and in ranges similar to those applied usually in mild hydro-cracking process, taking in consideration that the composition, specific gravity, metals and asphalting contents of the utilized lubricating used oils sample are less than those utilized in hydro-cracking process. Programmed experiments according to Box-hunter method were performed, based on the defined operating conditions [8,9]. Hydrogen gas flow rate was controlled at volumetric ratio [$Nm^3/m^3HC = 339 – 340$]. The chosen conditions were: Temperature: (350 – 430°C); Pressure: (35– 70 bar); LHSV: (0.5 – 2.5 h^{-1}); H_2/HC ratio: 339 – 340 (Nm^3H_2 / m^3HC).

In another set of experiments, a purified recovered used oils sample was used as feedstock, and catalytic hydro-treating laboratory steel pilot plant to perform all programmed mild hydro-cracking experiments. The solid catalyst was loaded to the reactor, and operating conditions such as temperature, hydrogen pressure, and space velocity were monitored and the impact of those variables were studied. Programmed experiments were performed, according to the defined operating conditions. Hydrogen gas flow rate was controlled at volumetric ratio 339–340 (Nm^3/m^3HC).

After implementation of several experiments for each catalyst, gaseous samples were taken from the reactor outlet, and liquids products samples withdrawn and collected from the bottom of the cylindrical condenser and all samples subjected to routine tests and analysis for each experiment to determine its composition and properties, according to standard methods of analysis by using GC-MS techniques. Yield and hydrogen chemical consumption were calculated for each experiment.

Both catalysts (MCH-10, HTH-548) were used in the catalytic mild hydro-cracking experiments at the above mentioned conditions. The collected liquid samples were fractionated according to ASTM D- 86 method and the distillation curve was drawn. Each liquid sample was separated, according to market desire boiling range, into different several cuts. The chemical composition and properties of each cut were determined, and a material balance was calculated for all experiments.

Results and Discussion

The chemical composition and properties of each cut were determined, and a material balance was calculated for all experiments. Tables (4, 5 and 6) illustrate the results for one experiment as an example for the catalyst MHC 10.

Our experiments also showed that as temperature and pressure are increased and space velocity speed decreased, naphtha, kerosene gas oils yields increased and achieved highest values at optimum conditions, but the residuals yield was less for the catalyst MHC-10. Other properties are also affected by the operating conditions, and best liquid products properties were obtained at optimum conditions for both catalysts, as shown in table (7). Similar results were also found for both catalysts with difference in products quality and properties. Catalyst (HTH-548) showed appropriate products yields and properties values at lower temperature and pressure, in comparison with the other catalyst (MHC-10) due to its physical characteristic. Highest yields and the best liquid products properties and quality were obtained using solid catalyst MHC-10, and HMH548 at optimum operating condition. The whole mild hydro-cracking process was summarized in figures (1, 2), and figure (3) which show a proposed schematic flow sheet for the mild hydro-cracking process of used-motor oils.

By analyzing catalytic hydro-cracking products, we can conclude that obtained gases can be used directly as a fuel, or mixed with LPG refinery products. Naphtha is rich in aromatics and have the appropriate boiling range and can be used either by direct mixing with benzene fuel cut streams or as solvent without any further treatment, or for other petrochemical purposes. Kerosene, gas oil and residuals also have similar properties of refinery products, and can be used directly as fuel or by mixing with kerosene or jet fuel cuts streams. Gas oil is the main products and have same boiling range and better properties, compared with standards specification, such as sulfur content, smoking point, pour point, diesel index and cetan index, so we found that no need for further treatment and that gas oil can be used as a diesel fuel, or can be mixed with other treated diesel fuel cuts streams shown in table (8) for both catalysts.

Table 1: Catalyst properties used in mild hydro-cracking experiments

Property	**HTH 548 (Axens)**	**MHC 10 (UOP)**	**Unit**
Form	Cylindrical extrudate	Cylindrical extrudate	-
Diameter	1.2		mm
Average length	5		mm
Loss on ignition at 550 °C	2 max		Wt.%
Sock loading density	0.75	0.685*	kg/l
Dense loading density	0.86		Kg/l
Bulk crushing strength	1.5		MPa
Surface area	160	213*	m^2/g
Bulk density	0.71		

Pore volume	1.58	-	cm^3/g
NiO	2.9	-	wt.%
MoO_3	16.5	-	wt.%

Note: * means that the value has been determined experimentally for the lack of information. Surface area (BET) was measured using a Gemini III 2375 Instrument.

Table 2: Hydrogen gas composition used in all experiments

Compound	**% Vol.**
H_2	80.9
C_1	8.9
C_2	6.9
C_3	2.4
i-C_4	0.5
n-C_4	0.3
i-C_5	0.1
n-C_5	–

Table 3: Liquid products obtained in fractionating process

Cut	**Naphtha**	**Kerosene**	**Gas oil**	**Residuals**
Boiling range, °C	(C_5 – 200)	(200 – 260)	(260 – 360)	+360

Table 4: Material balance for inlet and outlet, and chemically consumed hydrogen utilizing catalyst MHC-10

Inlet			**Outlet**		**Reaction products**	
Substance	**Vol. ml**	**Weight, gr**	**Substance**	**Weight, gr**	**Weight, gr**	**Y, wt%**
gas	49910	14.937	gas	16.339	2.691	2.602
Raw substance	119.1	103.406	Naphtha	8.217	8.217	7.946
H_2 $Nm^3/HC\ m^3$	339.0	-	Kerosene	9.932	9.932	9.605
-	-	-	Gas oil	26.439	26.439	25.568
-	-	-	Residuals	57.417	57.417	55.526
Total inlet substance		118.343	Total outlet substance	118.344	104.695	101.247
-	-		Chemically consumed Hydrogen		1.289	1.247

Table 5: Ranges of optimum operating conditions, yields for mild hydro-cracking utilizing catalyst MHC-10

Operating conditions	**Value**
Temperature, °C	405 – 415
Pressure inside the reactor, bar	58 – 70
h^{-1} Space velocity, (LHSV)	1.15 – 1.25
Hydrogen partial pressure, bar	46.9 – 56.6
H_2 , $N\ m^3/HC\ m^3$	339 - 340
Temperature, °C	405 – 415
Yield	**Value, Wt%**
H_2S	0.5
$C_1 – C_2$	0.5
$C_3 – C_4$	3.6
Naphtha	12 – 13
Kerosene	13 – 14
Gas oil	29 - 30
Residuals	39.8 – 42.7
Total	**101.3 – 101.4**
Hydrogen wt % Chemically consumed	1.3 – 1.4

Table 6: Properties of main products from mild hydro-cracking of used motor oils (the catalyst MHC-10)

Products properties	**Value**
Naphtha	
Specific gravity, d_4^{15}	0.753
Boiling range, (°C)	50 – 200
Sulfur content, (ppm)	14 max.
P/N/A (%vol)	68.5/12.5/19
Kerosene	
Specific gravity, d_4^{15}	0.830
Boiling range, (°C)	200 – 260
Sulfur content, (ppm)	30 max.
Smoking number. (mm)	19 – 20
Sat./Ar. %vol.	75/25
Gas oil	
Specific gravity, d_4^{15}	0.855
Boiling range, (°C)	260 – 360
Sulfur content, (ppm)	0.012 – 0.025
Poure point. (mm)	– 10
Viscosity at 37.8°C, cSt	5.8 – 6
Diesel index. DI	54 – 58
Cetane index. CCI	58 – 60
Residuals	
Specific gravity, d_4^{15}	0.875
Sulfur content, (ppm)	0.045 – 0.085
Poure point. (mm)	– 6
Viscosity index, VI	113 – 116

Table 7: Used lubricating oil properties and a comparison between yields and properties values of vacuum distillation and hydro-cracking products, utilizing two types of solid catalysts

Used Lubricating oils Properties, wt%	100	
Specific gravity, d_4^{15}	0.8933	
Properties of Vacuum distillation products	**Value**	
Yield, wt%	80.0	
Specific gravity, d_4^{15}	0.8815	
Distillation, (ASTM D1160), (°C)		
5 %	360	
50 %	481	
95 %	555	
Catalyst used in Mild Hydro-cracking	**HTH 548**	**MHC- 10**
Operating conditions	**Values**	
Temperature, (°C)	412 – 430	405 – 415
Pressure inside the reactor, (bar)	60 – 63	58 – 70
Partial pressure of hydrogen, (bar)	48.5 - 55	46.9 – 56.6
Liquid hourly space, LHSV, h^{-1}	1.0 – 1.3	1.15 – 1.25
H_2 , N m^3/HC m^3	339 – 340	339 – 340
Yield, (wt%)	**Values**	
H_2S	0.4	0.4

$C_1 - C_2$	0.32	0.4
$C_3 - C_4$	2.24	2.88
Naphtha	8 – 9.6	9.6 – 10.4
Kerosene	8.8 – 10.4	10.4 – 11.2
Gas oil	22.4 – 24	23.2 – 24
Residuals	32.08 – 36.96	31.8 – 34.2
Total	80.88 – 80.96	81.04 – 81.12
Hydrogen chemical consumption	0.88 – 0.96	1.04 – 1.12
Products properties	**Values**	
Naphtha	0.755 -0.7575	0.753
Boiling range, (°C)	50 – 200	50 – 200
Sulfur content, (ppm)	20 max.	14 max.
P/N/A (%vol)	69/13/18	68.5/12.5/19
Kerosene specific gravity,d_4^{15}	0.830	0.830
Boiling range, (°C)	200 – 260	200 – 260
Sulfur content, (ppm)	50 max.	30 max.
Smoking number, (mm)	20 – 21	19 – 20
Sat./Ar.(%vol.)	73/27	75/25
Gas oil, specific gravityd_{15}^{15}	0.845 – 0.855	0.855
Boiling range, (°C)	260 – 360	260 – 360
Sulfur content, (ppm)	0.022 max.	0.012 – 0.025
Pour point, (°C)	– 8	– 10
Viscosity at 37.8°C ،(cSt)	3.9 – 5.9	5.8 – 6
Diesel index, DI	53 – 58	54 – 58
Cetan index, CCI	56 – 63	58 – 60
Residuals, (+360°C)		
Specific gravity, d_4^{15}	0.874	0.875
Sulfur content, (wt%)	0.045 – 0.085	0.045 – 0.085

Table 8: Products specifications of resulted cuts for each utilized catalysts

Test	**Syrian Standard**	**Diesel by**	
		Catalyst MHC-10	**Catalyst HTH-548**
Sp. Gr. @ 60/60 °F	0.820–0.850	0.855	0.845 – 0.855
Color	3.0 max.	1 – 1.2	1 – 1.2
Flash Point P.M. Closed	140 min.	-	-
Total Sulfur, %wt	0.5 max.	0.025	0.022
Viscosity @100°F, cSt	1.6 – 6.0	5.8 - 6	3.9 – 5.9
Pour Point, °C	25 / -4 max.	– 10	– 8
Cloud Point, °C	32 / 0 max.	– 6	– 4
Diesel Index	53 min.	54 - 58	53-58
Cetan Index	50 min.	58 - 60	56-63
Conradson carbon, %wt	0.2 max.	0.022	0.020

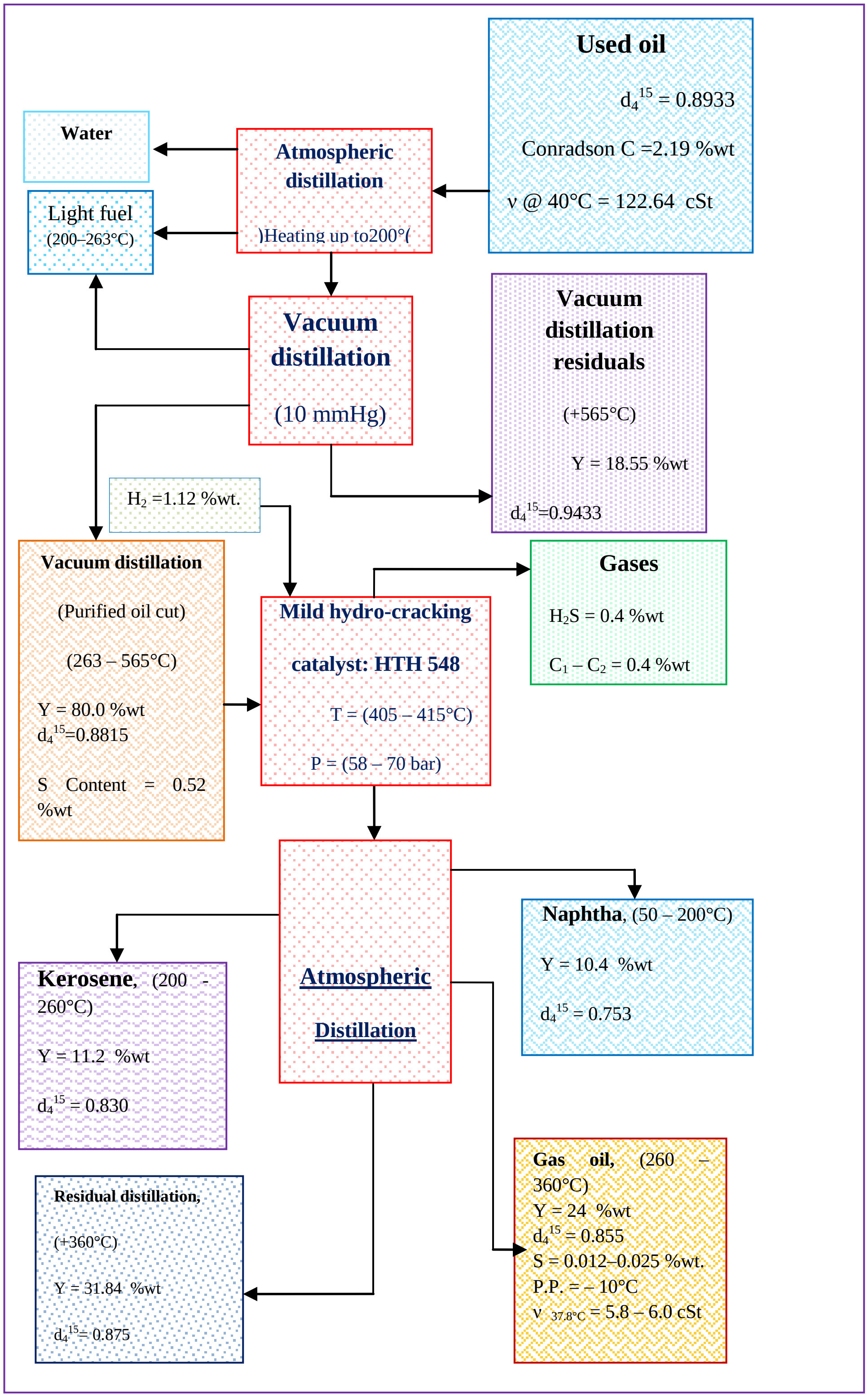

Figure 1: Initial flow sheet for mild hydro-cracking of purified recovered used lubricating motor oils utilizing catalyst (HTH-548) at optimum operating conditions

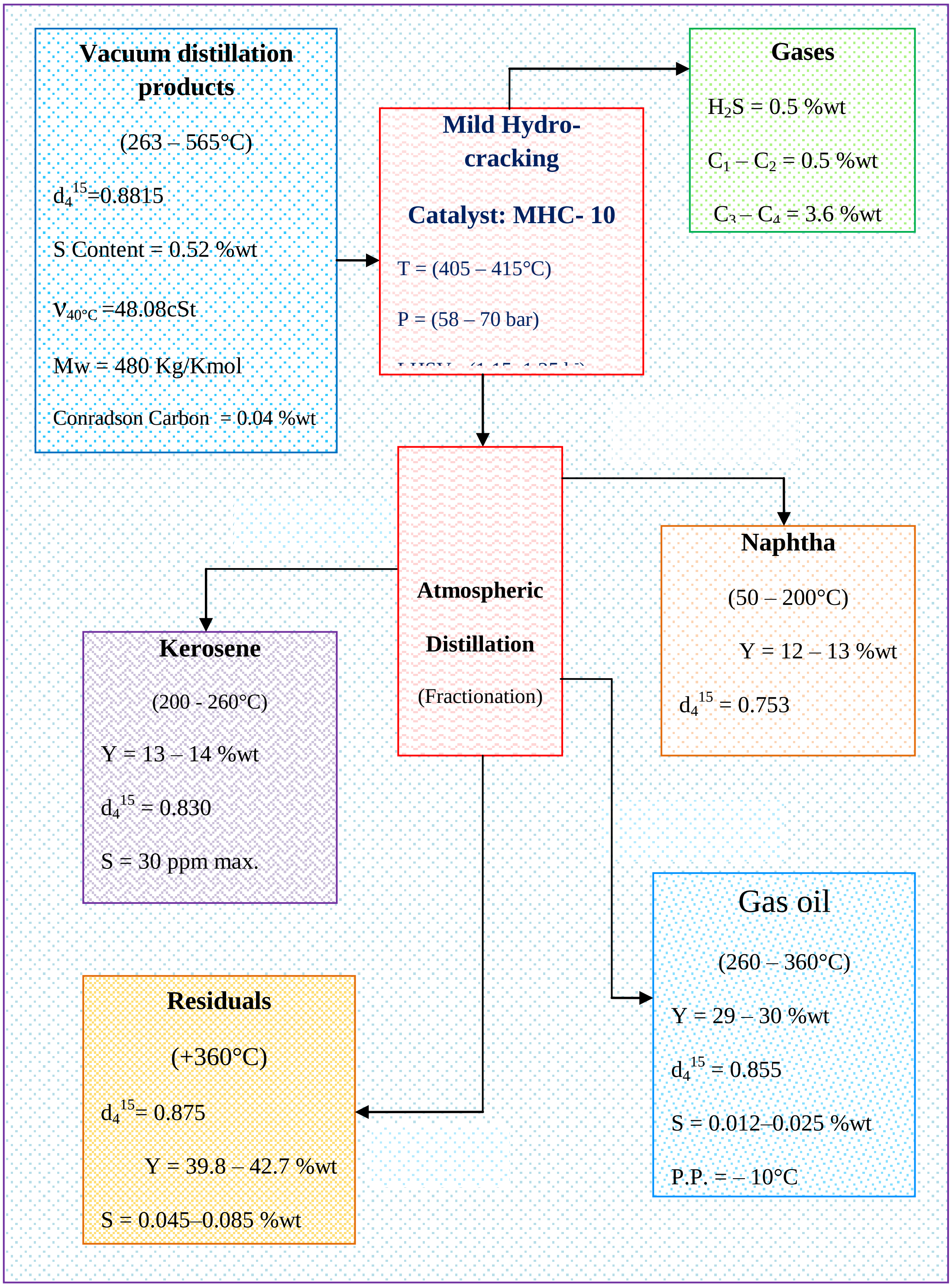

Figure 2: Initial flow sheet for mild hydro-cracking of purified recovered used lubricating motor oils utilizing catalyst (MHC 10) at optimum operating conditions.

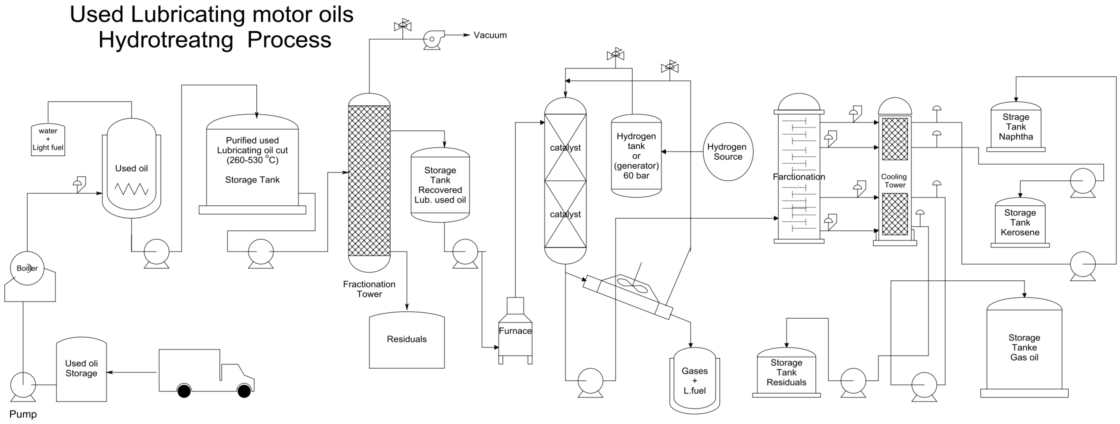

Figure 3: Proposed Schematic flow sheet for the mild hydro-cracking process of used-motor oils

Conclusions

This research is promising and absolutely new. The results from our studies showed that mild catalytic hydro-cracking process of purified and recovered samples resulting from used lubricating motor oils is a solution to meet environmental protection aspects and introduce new opportunities to produce high-value products, by transforming the essential hydrocarbons to valuable fuel products, while optimizing performance and makes more returns. The influence of all parameters such as temperature, pressure, catalyst, and space velocity were all determined. Solid catalysts utilized in hydrogenation of refinery petroleum cuts can be used in mild hydrocracking of used motor oils.

By checking the characteristics of all products, we conclude that they fit local and international standards and they are ready for use without any further treatments.

Compliance with Ethical Standards

This study was not funded by any institution.

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