

Hydrocracking of Atmospheric Residue from Tsagaan-Els Oil, Mongolia

Myagmargerel Bayanmunkh¹, Byambajav Ganbold²,

Narangerel Janchig¹, Gantsetseg Byambasuren¹, Khulan Bayasgalan^{1,*}

¹ Institute of chemistry and chemical technology, Mongolian academy of sciences Peace Avenue, Bayanzurkh district, Ulaanbaatar, 13330, Mongolia

² Agilent Demo Center, Medimpex, Mongolia

*Corresponding author. Email: khulanb@mas.ac.mn

ABSTRACT

Cracking is the complex physical and chemical process of converting high molecular hydrocarbons into valuable products such as gasoline fraction and light fuel fraction. There are several oil fields in Mongolia and three large deposits already are being exploited. The crude oil was classified as high-paraffinic crude oil because of its high viscosity and low yield of fuel fraction. The contents of asphaltenes and resins in the oil were low. Therefore, the cracking process is necessary to convert the paraffinic Mongolian crude oil to lighter distillates for the production of transportation fuels and chemicals. In this work, we studied the hydrocracking process of atmospheric residue (>350°C) to produce fuel fractions from high paraffin Tsagaan-Els oil of Mongolia. The hydrocracking experiment was carried out with and without a catalyst at temperature 450°C for 1-3 h under a hydrogen pressure of 5 MPa. Commercial Ni-Mo/Al₂O₃ catalyst (Ni 3%, Mo 15%) was used in the hydrocracking experiments for 1 and 2 h. The yields of light and middle distillates obtained by hydrocracking of the atmospheric residue for 3 h without catalyst were 15.8 and 17.7 wt.%, respectively. The effect of catalyst was tested in the experiments for 2 h. By the hydrocracking with catalyst, the yield of light distillate has increased 4.5 wt.% in comparison with the yield of light distillate obtained from the experiment without catalyst. In this study, we report that the atmospheric residue in the Tsagaan-Els oil could be liquefied by thermal cracking at 350°C to increase the yield of gasoline and diesel fuel.

Keywords: Crude oil, Residue, Cracking, Distillation, Fraction

1. INTRODUCTION

Nowadays global development is moving towards clean energy but petroleum still plays an important role in the transportation, heating, and raw materials of the chemical industry. Unfortunately, the world's light crude oil production approaches a limit and resource is decreasing rapidly so the attention is focused on refining heavy crude oil. The main technologies for deep refining of heavy oil are thermal and catalytic cracking processes. Catalytic cracking is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a

mixture of more useful products such as petrol and light fuel oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat and pressure, in the presence of a catalyst [1]. There are some deposits of crude oil in our country. Out of them, three large deposits are being exploited. The Tamsagbulag deposit is located in the Matad area of Dornod province, Mongolia. Other deposits such as Zuunbayan and Tsagan-Els are situated in the Zuunbayan area of Dornogovi province, with 332.7 million tons of total proved reserves and 43.25 million tons of total proved recoverable reserves [2, 3].

The Mongolian government is building a crude oil refining facility with a capacity of 1.5 to 2 million tons. Our country imports 1.5-1.8 million tons of petroleum products annually, and diesel fuel accounts for 60-70% of all imported petroleum products. Diesel fuel is mostly used in the agriculture and mining industry. Therefore, if Mongolia's refining plant is fully up and running, it will cover the country's petroleum products consumption while helping to develop the chemical industry. Therefore, the study of deep refining and increasing the yield of petroleum products of Mongolian crude oil is very innovative and very practical.

Previously, we studied the physicochemical properties of petroleum and hydrocarbon composition of Mongolian crude oils. Based on the previous report, the crude oil of Mongolia was determined as heavy oil with high viscosity. The oil has a low yield of light and middle distillates, high content of heavy paraffin [4-6]. In the case of the heavy oil industry, the main problem is low flow quality through the reservoir and pipeline. Therefore, upgrading refers to the breaking down of heavy oil into light and low-weight hydrocarbons. In the last years, research related to the development of new technologies for the production of heavy hydrocarbons, such as heavy and extra-heavy oils, natural bitumens, oil sands has been extensively conducted [7]. However, the study of liquefaction and the thermal cracking of high-paraffin, viscous oils is almost non-existent.

Therefore, the study of cracking of high paraffinic Mongolian oil with unique characteristics is very novelty. The research is aimed to increase the yield of low molecular weight hydrocarbon content in high paraffin oil using thermal and hydrocracking with

catalyst. The Tsagaan-Els deposit has high paraffin content and is not easy to produce liquid products.

In this work, we studied to establish a suitable cracking process for Mongolian high paraffin's crude oil residues to increase the yield of light fraction and deep refining of heavy crude oil.

2. EXPERIMENTAL

2.1. Materials

Experimental samples were from crude oil from the XIV block of Tsagaan-Els deposit in 1120-1130 m depth, which is located at Zuunbayan, Dornogovi province, Mongolia.

2.2. Experimental procedures

Physical characteristics such as density, viscosity, and flash point and fractional composition were determined according to Petroleum Analysis standard methods [1, 8, 9]. Saturates, aromatics, resins, and asphaltenes (SARA) analysis was performed using the ASTM-D-4124 and SARA methods [10, 11].

Through forming a complex of urea, solid paraffin was extracted from the atmospheric residue (>350°C) under the condition of oil fraction: iso-octane 1:5, oil fraction:urea 1:4, urea: activator (ethanol) 1:4 [8, 9]. The hydrocarbon composition of the obtained paraffin was studied by Gas chromatography-Mass spectrometry as Thermo Scientific-Trace 1310 GC with the detector of TSQ 8000-triple Quadrupole MS and column of DB5MS 30 m x 0.25 mm (D=0.25 μm). The carrier gas was helium with 1.5 mL/min flow [12, 13].

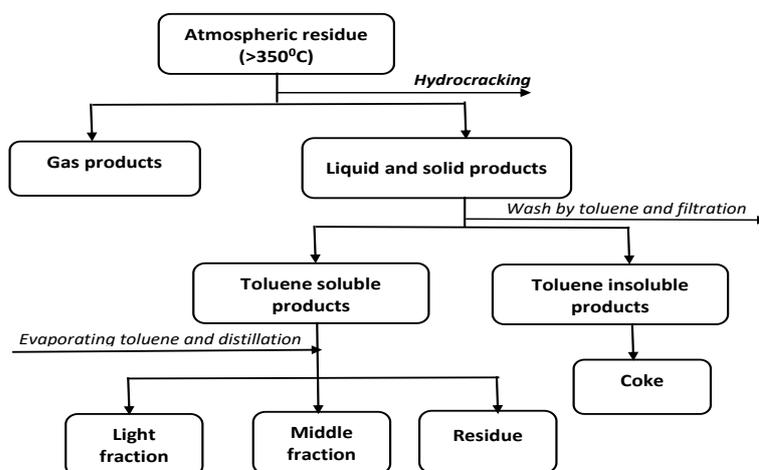


Figure 1. Product separation method of atmospheric residue hydrocracking

The total content of sulfur in the obtained liquid fraction was studied by instruments as Antek Multi Tek. The hydrocracking experiment was carried out with and without a catalyst at temperature 450°C for 1 h, 2 h, 3 h under a hydrogen pressure of 5 MPa. Commercial Ni-Mo/Al₂O₃ catalyst (Ni 3%, Mo 15%) was used in the hydrocracking experiments for 1 and 2 h. Around 15 g of >350°C residues was charged into a 50 mL reactor, along with 1 wt.% Ni-Mo/Al₂O₃ catalyst and 1 wt.% sulfur.

The hydrocracking products were separated as shown in Figure 1. The toluene insoluble product was extracted from the cracking products. The toluene soluble fraction was recovered after solvent evaporation, then fractionated into two fractions by the distillation method.

3. RESULTS AND DISCUSSION

The physical and chemical characteristics, group composition, and content of the fraction of the oil of Tsagaan-Els and its atmospheric residue (>350°C)

have been studied. The physical and chemical characteristics of the samples are given in Table 1.

Tsagaan-Els crude oil has a medium-density, a high viscosity, and a high flash point, as seen in Table 1. The crude oil has high oil content as well as a high atmospheric residue (73.64%). The atmospheric residue has a low content of high molecular hydrocarbons (asphaltene-resin), a high content of oil fractions (lub. oil-83.84%). Also, the content of n-alkanes in the oil fraction is very high (92.2%). The viscosity of the residual oil is also high (6.43 mm²/sec at 75°C) and the flash temperature in the open crucible is relatively high (184°C) due to the high paraffin content. Due to the obvious high paraffin content, the viscosity and freezing points are correspondingly high.

The solid paraffin was extracted from the Tsagaan-Els crude oil and its atmospheric residue by urea complex formation. The content and distributions of the n-alkanes of paraffin, separated from their samples were determined by gas chromatography and are shown in Figure 2.

Table 1. The physical and chemical characteristics of Tsagaan-Els oil

№	Characteristics of crude oil	Sample	
		Tsagaan-Els oil	Atmospheric residue (AR)
1	Appearance	thick and black color	thick and black color
2	Specific gravity, 20°C, kg/m ³	831.0	890.7
3	Kinematic viscosity, mm ² /sec	40.16 (50°C)	6.43 (75°C)
4	Flashpoint, in open crucible, °C	58	184
5	Freezing point, °C	29	34
6	Group composition, wt.%		
	Resins	8.51	14.97
	Asphaltenes	0.99	0.52
	Oil (hydrocarbons)	88.69	83.84
	n-alkane in the oil	89.05	92.12
7	The yield of fuel fraction, %		
	Boiling point, °C	38	
	Gasoline (Start boiling to – 200°C)	11.635	
	Diesel (200–350°C)	14.725	
	Oil (Lub) fraction (350-450°C)	21.935	
	Vacuum residue (>450°C)	51.705	-

The paraffin extracted from Tsagaan-Els crude oil contains 89.05% n-alkanes with carbon atoms ranging from C17 to C33, particularly n-alkanes with carbon atoms ranging from C21 to C28 predominate.

The paraffin in atmospheric residue contains alkanes of 92.12% with carbon atoms in the range of C17 to C32, as well as predominate light alkanes with carbon atoms in the range of C18 to C23 in this AR. It is possible that during the heating and distillation of the oil, long-chain alkanes decompose to form small-molecule alkanes.

The yield of hydrocracking products is shown in Table 2. When the investigated oil residue was

exposed to a catalytic thermal breakdown procedure at 450°C during with a reaction time of 1-3 h, gaseous, liquid, and solid fractions were produced. The yield of the gaseous product increases as the thermal breakdown period of oil residue increases, whereas the yield of the ensuing liquid product decreases, according to experimental data.

Cracking the atmospheric residue of the Tsagaan-Els oil in 1% NiMo/Al₂O₃ catalyst and a two-hour catalytic cracking process at the temperature of 50°C was produced a high yield of liquid product (80.72%) and the lowest gas output (6.78%).

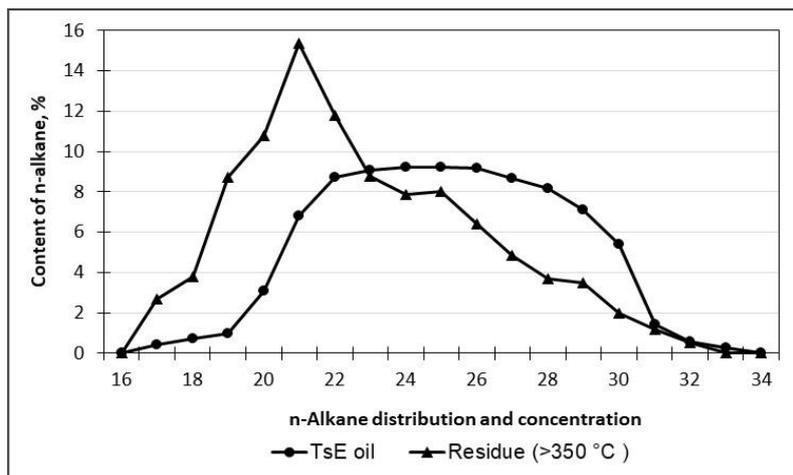


Figure 2. n-Alkane distribution of Tsagaan-Els crude oil and atmospheric residue

The production of gaseous products was lowered by 1.7 times and the yield of liquid products was reduced by 1.5 times after continuing the experiment for 1 h under the same conditions. The preceding experiments showed that the ideally suited condition

is the introduction of atmospheric residues of high paraffin oil into a hydrogen cracking process involving 1% NiMo/Al₂O₃ catalyst at 450°C under a hydrogen pressure of 5 MPa.

Table 2. Yield of cracking products of atmospheric residue Tsagaan-Els oil

№	Yield	Condition of experiments, (at 450°C)				
		Non-catalyst			With catalyst (1 wt% Ni-Mo/Al ₂ O ₃)	
		1 h	2h	3 h	1 h	2 h
1	Liquid products, wt.%	56.33	55.19	45.86	80.72	52.28
2	Gas, mL	39.22	35.11	43.75	12.5	37.71
3	Coke, wt.%	4.45	9.7	10.39	6.78	10.01

To determine the fuel fraction yield, the product produced by liquefying the residual oil was further distilled on a vacuum distillation apparatus at temperatures ranging from boiling point to 220°C (gasoline) and from 220 to 350°C (diesel).

According to the composition of the liquid product fraction formed as a result of the thermal and hydrocracking process of the Tsagaan-Els atmospheric residue, the gasoline fraction was 20-35 wt.% and the diesel fraction was 26-39 wt.% (calculated in the liquid products). The highest yield of liquid products was occurred from a one-hour cracking process at 450°C with NiMo/Al₂O₃ catalysts, although the yields of gasoline and diesel fractions were rather low, at 16.72 wt.% and 26.44 wt.%, respectively. The residue yield of >350°C is quite high (56.84%)

As shown in Figure 3, the results indicate that the gasoline fraction was 32-34% and the diesel fraction was 34-39% after 2 and 3 h of the thermal cracking at 450°C and 2 h of evaluation with NiMo/Al₂O₃ catalysts. Based on our experiments and data obtained, the atmospheric residue of Tsagaan-Els oil can be liquefied by catalytic and non-catalytic thermal cracking processes to improve its gasoline yield by 18.13 wt.%, and diesel yield by up to 18.43 wt.%. In this case, long-chain hydrocarbons in oil residue are broken down to simpler molecules as light hydrocarbons, by the breaking of carbon-carbon bonds at results of cracking process. As a result of the cracking process, this residue obtained a fuel fraction [14-16]. In addition, it has been shown that it is possible to increase the fuel fraction yield as a result of the cracking process of high paraffin oil residues in Mongolia.

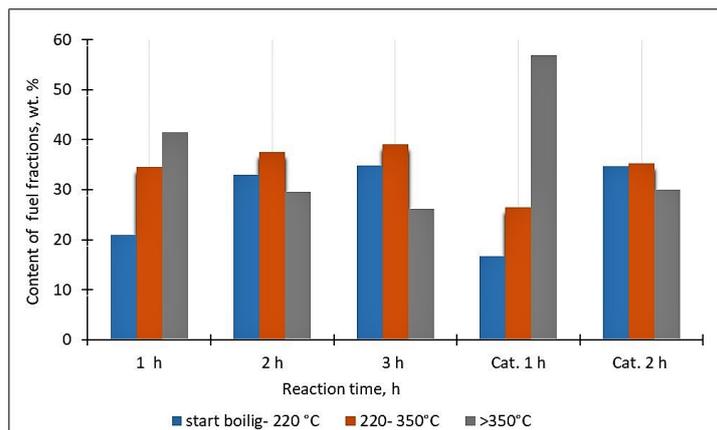


Figure 3. Fractional composition of liquid products after cracking process of Tsagaan –Els atmospheric residues

Figure 4 shows the group composition (SARA-s method) of liquid products produced by thermal cracking at 450°C for 1 and 2 h (non-catalyst) of Tsagaan-Els oil and atmospheric residue.

After a 1 h thermal cracking operation, the oil (hydrocarbons) content was reduced while the content of asphaltene-resin compounds increased. This is because thermal treatment converts the aromatic hydrocarbons in the residual oil into resinous molecules.

In comparison to the group composition of AR, the oil content increased, the asphaltene content declined by 2 times, and the resin content decreased by 3 times upon thermal cracking of AR at 450°C for 2 hours. In addition, a large amount of gasoline and

diesel fractions is created in this instance Figure 3. In other words, as asphaltenes and resin in the oil degrade to generate oil fractions, the output of light fractions increases. The thermal decomposition process is directly connected to reaction time, as seen in Figure 4.

In this condition, high-molecular compounds are decomposed into low-molecular ones, resulting in a higher fuel output. By analyzing the composition of the product, it is possible to determine the amount of hydrocarbons in the oil after processing and how the hydrocarbons change during the thermal process of the oil, as well as to liquefy the reaction in the correct direction [16, 17].

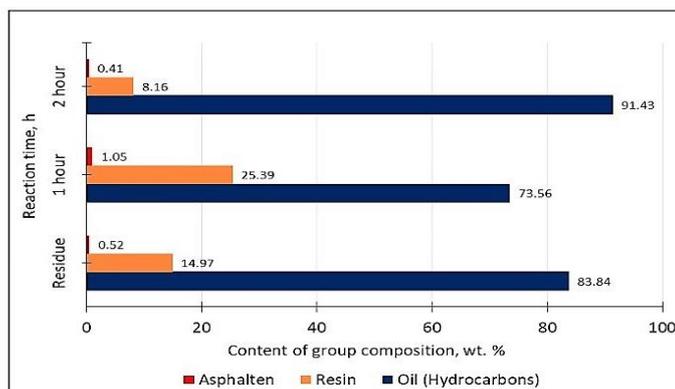


Figure 4. The content of group composition obtained liquid product after thermal cracking of Tsagaan-Els atmospheric residue

Figure 5 shows the total sulfur concentration of the gasoline and diesel fractions obtained from hydrocracking products.

When sulfur-rich diesel is burned, the sulfur reacts with oxygen (SOx) to produce emissions that contribute to poor air quality and have negative

environmental and health consequences. As a result, the amount of sulfur in petroleum products is strictly regulated. According to EN 590:2009, the sulfur level of diesel must be 350 ppm, 50 ppm, and 10 ppm, respectively, for classes K3, K4, and K5. The

gasoline should be 500 ppm for class K2 according to EN 228:2004 [18, 19].

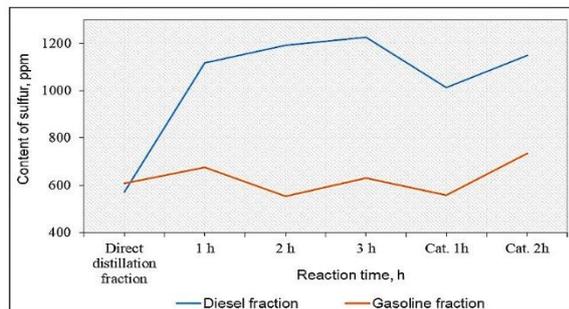


Figure 5. Sulfur content of gasoline and diesel from liquid products after cracking process

After cracking, the sulfur level of gasoline is 573-734 ppm and 608-1149 ppm in the diesel portion from liquid products. The sulfur content of diesel fractions produced by cracking oil residues is nearly twice that of diesel fractions produced by normal distillation. On the other hand, the amount of sulfur in the final gasoline fraction increased just slightly. The sulfur concentration in the gasoline fraction formed during the 2 h at 450°C (non-catalyst) and 1 h at 450°C with catalyst was relatively low when compared to direct distillation gasoline.

The gasoline fractions created by refining the atmospheric residual have a low sulfur percentage, but the diesel fraction has a high sulfur content. According to the research, additional hydrotreating of fuel fractions from liquid products of AR by cracking is necessary to reduce sulfur concentration.

4. CONCLUSION

Our work completed the studies on physical and chemical properties and hydrocarbon composition of Tsagaan-Els oil of Mongolia and its atmospheric residue (>350°C). According to the research, Mongolian crude oil has high paraffinic, has a high viscosity, and has a lower yield of the light fraction. The oil fraction (hydrocarbons) in the atmospheric residue is substantial, with 92.12 wt.% alkanes and a low concentration of asphaltene-resin. Thermal and catalytic cracking of paraffinic atmospheric residues were carried out at 450°C for 1-3 h under 5 MPa hydrogen pressure with catalyst (NiMo/Al₂O₃) and non-catalyst.

It was established that cracking the atmospheric residual of the oil with a 1% NiMo/Al₂O₃ catalyst for a 2 h catalytic cracking process at 450°C generated the highest yield of liquid product (80.72%) and the lowest gas production (6.78 %). According to the research, atmospheric residue in high paraffin

Tsagaan-Els oil can be liquefied using a cracking method, improving gasoline yield by 18.77 wt.% and diesel yield by up to 20.67 wt.%. The research is critical to the development of new liquefied technology and the improvement of petroleum product yields from Mongolian crude oil.

REFERENCES

- [1] Refining of Petroleum (01.09.2017) <https://www.aip.com.au/resources/refining-petroleum>
- [2] Myagmargerel B., Khulan B., Gantsetseg B., Khongorzul B., Tuya M., (2021) Synthetic fatty acid from crude oil of Tamsagbulag petroleum deposit (Mongolia) Mongolian Journal of Chemistry. Vol. 22 (48), DOI: 10.5564/mjc.v22i48.1645
- [3] Ochirbat P., (2013) Mongolyn gazryn tosny sudalgaanii shine ue. Ulaanbaatar, admn print, 480, (In Mongolian).
- [4] Sugimoto Y., Horie Y., Saotome Y., Tserendorj T., Byambajav E., (2012) Properties, Chemical Compositions and Hydrotreatment Reactivities of Mongolian Crude Oils. Journal of the Japan Petroleum Institute, Vol. 55(6), 363-370. DOI: 10.1627/jpi.55.363
- [5] Shirchin B., Nordob E., Monkhoobor D., Tuya M., Sainbayar A., *et.al.*, (2003) A study on Main Physical and chemical Characteristics of East Mongolian Petroleum Journal of the Korean Industrial and Engineering Chemistry, Vol. 14(4), 423-425.
- [6] Khongorzul B., Golovko A.K., Gorbunova L.V., Kamyayov V.F., Purevsuren B., (2007) Mongolian crude oil. Rational refining directions. Chemistry and Technology of Fuels and Oils, Vol. 43(6), 495-502. DOI: 10.1007/s10553-007-0086-7
- [7] Almutaser A., Varfolomeev M., Suwaid M., Djimasbe R., Garayeva D., Ulbaev A., (2019) Thermal Conversation of Heavy Crude oil in the Presence of Formic Acid as a Hydrogen-Donor Solvent. IOP Conference Series: Earth and Environmental Science. Vol.282(1), 012043. DOI:10.1088/1755-1315/282/1/012043

- [8] Usachev V.V., (1967) Karbamidnaya deparafinizatsiya. M.: Khimiya. 236 (in Russia).
- [9] Bogdanov M.F., Pereverzev A.N., (1961) Deparafinizatsiya neftiyanih productov. M.: Gostoptehizdat, 247 (in Russia)
- [10] Santos J.M., Alessandro Vetere A., Wisniewski A., Eberlin M.N., Schrader W., (2020) Modified SARA Method to Unravel the Complexity of Resin Fraction(s) in Crude Oil. *Energy & Fuels*, Vol. 34(12) 16006-16013. DOI: 10.1021/acs.energyfuels.0c02833
- [11] Monkhoobor D., (2003) Neft ba neftiin buteegdekhunii shinjilgeenii arga. NUM press, 112, Ulaanbaatar (In Mongolian).
- [12] Odebumi E.O., Ogunsakin E.A., Ilukhor P.E.P., (2002) Characterization of crude oils and petroleum products: (I) Elution liquid chromatographic separation and gas chromatographic analysis of crude oils and petroleum products. *Bulletin of the Chemical Society of Ethiopia*, Vol. 16 (2), 115-132.
- [13] Blomberg J., Schoenmakers P.J., Brinkman U.A.T., (2002) Gas chromatographic methods for oil analysis. *Journal of Chromatography A*. Vol. 972(2), 137-173. DOI: 10.1016/S0021-9673(02)00995-0.
- [14] Coronel-García M.A., de la Torre A.R., Domínguez-Esquivel, J.M., Melo-Banda, J.A., Martínez-Salazar, A.L., (2021) Heavy oil hydrocracking kinetics with nano-nickel dispersed in PEG300 as slurry phase catalyst using batch reactor. *Fuel* 283. 118930 DOI: 10.1016/j.fuel.2020.118930
- [15] Leonenko S. V., Kudryavtsev S. A., Glikina, I. M., (2017). Study of catalytic cracking process of fuel oil to obtain components of motor fuels using aerosol nanocatalysis technology. *Adsorption Science & Technology*, Vol. 35(9-10), 878-883. DOI: 10.1177/0263617417722253
- [16] Tugsuu T., Yoshikazu S., Enkhsaruul B., Monkhoobor D., (2012) A Comparative Study on the Hydrocracking for Atmospheric Residue of Mongolian Tamsagbulag Crude Oil and Other Crude Oils. *Advances in Chemical Engineering and Science*, Vol. 2(3), 402-407 DOI: 10.4236/aces.2012.23049
- [17] Hart A., Leeke G., Greaves M., Wood J., (2014) Down-hole heavy crude oil upgrading by CAPRI: Effect of hydrogen and methane gases upon upgrading and coke formation. *Fuel*, Vol.119, 226-235. DOI: [10.1016/j.fuel.2013.11.048](https://doi.org/10.1016/j.fuel.2013.11.048)
- [18] EN 228:2004. Automotive fuels – Unleaded petrol – Requirements and test methods.
- [19] EN 590:2004. Automotive fuels – Diesel - Requirements and test methods.