

# Heavy Oil Residue Upgrading With Iron Based Catalysts Under High Hydrogen Pressure

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## Research Article

**Abstract** – In this study, effective and easily accessible cheap catalysts that assist converting heavy oil residue to lighter products with high yield are investigated. Hydrocracking experiments were carried out in a 10 ml stainless steel bomb-type reactor with up and down stirrer at 200 times of reciprocation per minute. The catalyst mixture provided the minimum coke production was investigated. FeSO<sub>4</sub>.H<sub>2</sub>O, the binary mixtures of FeSO<sub>4</sub>.H<sub>2</sub>O with metal oxides (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, SiO<sub>2</sub>) and the mixtures Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with elementary sulphur were used as catalyst. Experiments were conducted at 425 °C for 90 minutes with the initial pressure 100 bar H<sub>2</sub>. The amount of coke, liquid products and C5- gas products were calculated for each experiment. Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (<sup>1</sup>H NMR) and elemental analysis were used for Iranian heavy oil residue. Differential Scanning Calorimeter (DSC) was used to analyze the catalyst. According to the results, minimum coke production is achieved by FeSO<sub>4</sub>.H<sub>2</sub>O+SiO<sub>2</sub> catalyst. Although minimum coke production achieved with FeSO<sub>4</sub>.H<sub>2</sub>O+SiO<sub>2</sub>, middle distillate containing toluene soluble fraction (TSF) was maximized with Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>+Sulphur catalyst mixture. In addition, the product selectivity in the reactions with the least coke formation showed selectivity in the direction of the formation of gas and light products, not in the direction of liquid product formation.

**Keywords** – Heavy oil, iron catalysts, residue, residue Upgrading, slurry phase hydrocracking reactions

## 1. Introduction

Iranian oil is still heavily processed in oil refineries around the globe despite recent sanctions employed by US and European Union on Iran's crude oil and petroleum products imports (Farzanegan, 2011). Iranian Heavy Oil blend in particular, demanded at cheap high sulphur crude market especially by refineries which have the capabilities to upgrade heavy oil residue.

Refinery hydrocarbon margin which is based on the difference between the cost of crude oil and product prices, varies according to the process ability of the refinery; that is its' complexity. Fluid Catalytic Cracking (FCC), Hydrocracker, Coker units are some of the conversion units that increases the complexity of the refineries. Recently global trend across crude oil refining majors is to get highest hydrocarbon margin via expanding their strategically selected refineries with residue upgrading complexes that import cheap intermediate raw materials such as atmospheric straight run fuel oil (ASRFO) or vacuum residue (VR) (JBC Energy Global Refinery Margins Weekly Report, 2013).

During last decade world has witnessed closing of significant number of refineries: these were mainly small yield hydro-skimming and FCC-centered refineries. Nowadays refineries with only Heavy Vacuum Gas Oil

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(HVGO) crackers have been reporting shrinking margins, on the other hand complex refineries, which have residue conversion units, have stated very good margins and enjoyed high profits (Torchia et al., 2012). Unconventional products such as heavy vacuum residue (VR) can be evaluated to meet the need for valuable fuels, given the significant reduction in energy resources. However, these products contain extremely high molecular weight species as well as heteroatom structures that cause pollution, poisoning of catalysts and deactivation. These reasons cause a pressure drop in hydrocracking reactions in fixed bed reactors. However, slurry-phase hydrocracking reactions allow the hydrogenation reactions to be enhanced by dispersion of the catalysts and help overcome these disadvantages (Tareq et al., 2019). Major companies in the oil and energy business focused on designing new residue upgrading technologies such as slurry hydrocracking that use catalysts. Critical point in conversion of high boiling point residue into low boiling products is to minimize the coke make thereby maximizing liquid products (Zhang et al., 2007). Catalytic hydrogenation is an effective method for the depolymerization of organic materials and to obtain liquid products with a high hydrogen-carbon (H/C) ratio (Hongwei et al., 2019).

Many studies have been performed to find out better catalysts for slurry phase hydrocracking reactions of heavy oil residue. In literature, they can be grouped as heterogeneous solid dust and homogeneous water or oil soluble catalysts. Bearden et al. (1978) used metal phthalocyanine and iron based catalysts in their slurry hydrocracking experiments. They determined that 7 %  $\text{Fe}_2\text{O}_3$  and 400 ppm cobalt phthalocyanine mixture showed the best performance in reducing the amount of coke. Slurry-phase hydrocracking reactions of heavy oil occur in the form of mass transfer between hydrogen bubbles and the oil phase with a nano-sized, well-dispersed, submicron catalyst. (Álvarez et al., 2019) In the slurry phase hydrocracking process, hydrogenation reactions were carried out in a bubble column type reactor with homogeneously dispersed catalysts under high temperature (420–460 °C) and 120–200 bar pressure (Angeles et al., 2014). Kim et al., (2017) investigated at variable temperature, pressure and reaction time of slurry phase hydrocracking reactions of vacuum residue (VR) in the presence of dispersed  $\text{MoS}_2$  catalyst. Reactions of vacuum residue were carried out in a batch reactor at 400 °C and 100 bar pressure. As a result, 23% of coke was formed as well as 77% of the main products such as vacuum kerosene. The temperature and degree of the conversion of VR's hydrocracking reactions were determined as the most important factors causing the physical change in the products (Suk et al., 2021). Kadijeva et al. (2018) synthesized iron-containing catalysts for the hydroconversion of tars. Catalyst compositions were prepared based on water-soluble iron compounds ( $\text{FeSO}_4$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{COOCH}_3)_2$ ). Studies worked on a vertical flow hydroconversion reactor. Catalyst compositions containing  $\text{Fe}_{1-x}\text{S}$  nanosized and  $\text{Fe}(\text{COOCH}_3)_2$  forms of iron under hydroconversion conditions showed catalytic activity close to the studies performed with  $\text{MoS}_2$  catalyst, which was prepared as nanodispersed before. The disadvantage of catalysts containing water-soluble iron compounds such as  $\text{FeSO}_4$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{COOCH}_3)_2$  is that they form relatively high coke products in hydroconversion reactions. Belinko et al. (1990) used iron sulfate monohydrate material in their experiments ( $\text{FeS}$  is the active form) up to 5 % in weight. They report that the best performance can be achieved by catalyst mixture with max 45  $\mu$  in size and with a distribution of at least 50 % under 5  $\mu$ . Ni et al., (2019) worked magnetic molybdenum disulfide catalyst ( $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{MoS}_2$ ) and this catalyst mixture was found to reduce the viscosity of the oil sand. Catalytic reactions were carried out at 150 bar hydrogen pressure and 400 °C. As a result of the studies, it was observed that the viscosity of liquid products at the viscosity measured at 50 °C decreased from 4660 mPa·s to 76.9 mPa·s. This shows that there is a viscosity reduction of approximately 98%. Jain & Pruden (1991) carried out slurry hydrocracking experiments with petroleum coke (0.5 – 0.9  $\mu$ ) and  $\text{FeSO}_4\cdot\text{H}_2\text{O}$  at 440, 445 and 450 °C. They stated that the maximum conversion 88% achieved at 450 °C. Yang et al. (2020) prepared a well-dispersed Fe-Ni-S catalyst in their work. In this study, carboxylate ligands were attached to active metal salts and sulphation was performed. The Fe-Ni-S catalyst outperformed not only the monometallic nickel catalyst but also the commercial molybdenum. The synthesized catalyst composition gave much better results than the commercial molybdenum and monometallic commercial catalyst. In this study, it has been clearly seen that the presence of sulfur has a positive effect on heavy residue upgrading. Bhattacharyya et al. (2011) used  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  mixture with a particle size distributed between 200 - 600  $\mu$ ; they claimed heat

treatment and pre-sulfurization steps are not needed. Through X-ray diffractometers (XRD) results it has been shown that at 410 °C, Fe<sub>2</sub>O<sub>3</sub> completely turns into active form through reactions involving reaction by product H<sub>2</sub>S and sulphur in the feed. Bin et al. (2019) obtained catalyst and they conducted VR to a slurry phase hydrocracking reaction presence of presulfided oil-soluble MoS<sub>2</sub> catalyst at 100 bar H<sub>2</sub> pressure at 410 °C for 1 hour. After hydrocracking reactions, it was observed that the resin content decreased from 25.21 wt% to 3.54 wt% and the C7-asphaltene content was very close to zero from 6.82 wt%. In the reactions where the catalyst was used, the yield of the liquid product increased from 75.03% by weight to 96.43% by weight, while the coke production was 0.19% by weight and the gas yields were 3.38% by weight. These values were significantly lower than the coke and gas values of 14.05% and 10.92% by weight, which were the results of the reactions in which the catalyst was not used. Many different types of catalysts are used in slurry phase reactions. Generally, we can classify them as solid supported catalysts and homogeneously dispersed catalysts. Dispersed catalysts are classified as fine powder catalysts that dissolve in water or oil, soluble dispersed catalysts show higher catalytic activity than others. When the technologies on the petroleum upgrading of the catalysts of the mountain were examined, it was seen that studies were carried out with the combination of two-phase catalysts (Tareq et al., 2019).

In this study, elemental, molecular weight and saturates, aromatics, and resins and asphaltene (SARA) analysis performed to determine main properties of the Heavy Iranian VR. In addition, Differential Scanning Calorimetry (DSC) analysis is performed for catalyst catalysts to find out their thermal transitions and then cracking reactions of vacuum residue of Iranian crude in a laboratory scale slurry hydrocracker by using FeSO<sub>4</sub>.H<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, SiO<sub>2</sub> and S are investigated. Coke, gas and toluene soluble liquid part in reactor effluent is measured after reactions of each catalyst. Catalysts with high overall conversion and low coke production are determined.

## 2. Materials and Methods

### 2.1. Materials

For catalyst trials 99.5 % FeSO<sub>4</sub>.7H<sub>2</sub>O, 99 % Al<sub>2</sub>O<sub>3</sub> obtained from Merck; and >99 % Fe<sub>2</sub>O<sub>3</sub> purity, 98 % CaO and 99 % SiO<sub>2</sub> obtained from Sigma – Aldrich, and >99.8 % elemental sulfur obtained from Turkish Petroleum Refineries Corporation (TUPRAS) were used. For measuring amount of coke make, 99 % n-heptane, >99.5 % carbon disulfide obtained from Merck and >99.7 % toluene obtained from Sigma- Aldrich were used. For molecular weight determination 99 % tetrahydrofuran obtained from Merck was used. Soxhlet extraction was done with 28x80 mm Macherey Nagel cellulose cartridges.

### 2.2. Methods

#### 2.2.1. Resid Analysis

Iranian heavy VR was taken as the feedstock from TUPRAS for slurry phase hydrocracking reactions. VR obtained when the vacuum distillation unit was processing 100 % Iranian Heavy crude originated ASRFO and HVGO ASTM D1160 95 % cut was 550 °C. VR has specific gravity of 1045.0 Kg/m<sup>3</sup> (at 15 °C) which corresponds to 3.9 API (EN-ISO-3675).

Elemental analysis was performed by Thermo Finnigan Flash EA 1112 Series Elemental Analyzer. Helium used as a carrier gas, 2 mg of sample analyzed by burning with oxygen at 1000 °C.

Molecular weight analysis is performed by Agilent 1200 series GPC. 300 x 7.5 mm sized mixed gel Zorbax column is used, detector was refractive index. Tetrahydrofuran was used as solvent and carrier phase. 20 µ injections with 1 ml/min volumetric rate is used.

<sup>1</sup>H-NMR analysis were performed by Varian UNITY INOVA 500MHz NMR spectrometer. 0,5 ml chloroform (CDCl<sub>3</sub>) used as solvent for 5 mg IRHV sample. <sup>1</sup>H-NMR analysis is shown in Figure 1.

SARA analysis was performed by dissolving IHVR with n-heptane; asphaltene part separated out, and maltenes part was recollected by removing n-heptane from the filtrate. This portion separated into saturates, aromatics, and resins parts according to the SARA protocol.

Elemental analysis, molecular weight analysis and SARA analysis results are given in [Table 1](#).

### 2.2.2. Catalyst Analysis

In order to investigate IHVR and catalyst transformations over certain temperature ranges Mettler Toledo 822e Differential Scanning Calorimeter was used. DSC plots for VR obtained via placing sample to aluminum crucible, under N<sub>2</sub> atmosphere. Temperature was scanned between the range of -50 to +300 °C; ramp up rate was 10 °C/min. Catalyst placed into porcelain crucibles and temperature was scanned between the range of -100 to +670 °C. DSC analysis is shown in [Figure 2](#).

### 2.2.3. Pre-treatment Phase

FeSO<sub>4</sub>.7H<sub>2</sub>O was dried for an hour at 120 °C in an oven. Then, metal oxides and FeSO<sub>4</sub>.H<sub>2</sub>O were mixed with 1:1 weight ratios and put into a Retsch PM 400 ball mill. After sufficient time passed (ca. 20 minutes) mixtures sieved in an analytical sieve shaker (Retsch AS 450). After sieving 45 - 300 microns catalyst catalysts stored in closed desiccators for use in the hydrocracking reactions. Elemental sulfur also put into a Retsch PM 400 ball mill. Mixing ratios of the catalysts shown in [Table 3](#).

### 2.2.4. Reactors

All hydrocracking reactions were performed in batch tubing bomb reactors (10 ml) that comprised of two sections; upper part has a D-Pro high pressure needle valve connected with 1/4 inch stainless steel Swagelok tube fittings. A metal ball with 9.5 mm diameter is placed into the reactor for stirring reaction mixture which can provide 200 rpm stirring velocity.

### 2.2.5. Experimental Conditions

The reactors were typically loaded with 1.2 g of Iranian heavy oil resid and 0.05 grams of catalyst catalysts initially purged 5 times with nitrogen and then with hydrogen. Then reactor loaded with hydrogen up to 100 bars and the shut-off valve was closed, and the reactor was plunged into a fluidized sand bath that had been preheated to 425 °C.

After 90 minutes reaction time has elapsed, the reactor was removed from the sand bath and immediately immersed into icy cold water in order to quench the reaction for 10 minutes. The reactor assembly had cooled and equilibrated at room temperature for half an hour.

Reactor was weighted accurately, the gas yield was determined after the high pressure needle valve opened and weighted again. Soxhlet extraction was performed with 28x80 mm cellulose cartridges with toluene. Remaining solid part is regarded as coke plus catalyst and weighed. Toluene soluble part is calculated by extracting weight of gas and solid part from initial weight of reactive mixture.

## 3. Results and Discussion

### 3.1. Resid Analysis Results

Iranian heavy VR (IRHV) elemental analysis, molecular weight analysis and SARA analysis results are given in [Table 1](#).

Table 1

## IRHV Analysis

Elemental Analysis	C (%)	H (%)	S (%)	N (%)	O (%)
	84.48	9.81	4.43	0.81	0.47
GPC Analysis	Mn (g/mol)		Mw (g/mol)		
	797		1601		
SARA Analysis	Saturates (%)	Aromatic (%)	Resin (%)	Asphaltene (%)	
	25	45	17	13	

As a result of the elemental analysis, the H/C ratio was found to be 1.38. The low H/C ratio confirms the result that the percentage of aromatic structures revealed in the SARA analysis is high. A high H/C ratio indicates the presence of long aliphatic chain compounds, while a low ratio indicates the presence of multi-nucleated aromatic groups.

In this oil residue, the number average molecular weight is 767 g/mol and the weight average molecular weight is 1601 g/mol. When we compare these results with the molecular weight (580 – 1010 g/mol) of the crude oil found in the Southeastern region of Turkey, it is possible to say that this oil residue has heavier structure.

Four fractions important for petroleum chemistry were obtained. These fractions (SARA) are saturated, aromatics, resin and asphaltene. The first three fractions were obtained from maltene. In the SARA analysis, 25% saturated, 45% aromatics, 17% resin and 13% asphaltene content were found.

Iranian heavy VR  $^1\text{H-NMR}$  analysis area up to 1 ppm indicates 28,23 % methyl groups; area between 1 and 1,7 ppm % 50,80 methylene branching. This ratio is a sign of aliphatic chain branching attached to asphaltene honeycomb structure. Area between 1,7 and 1,9 ppm shows 8,95 % naphthenic rings; between 2,1 and 2,4 ppm 6,78 %  $\alpha$ -methyl branching. 2,4 and 3,5 ppm point to CH, CH<sub>2</sub> methylene structures around aromatic ring. Area between 6 and 7 ppm specifies monocyclic structures attached with bridges. Between 7 and 8 ppm 2 and 3 ringed structures can be seen.

Iranian heavy VR  $^1\text{H-NMR}$  analysis is shown in [Figure 1](#).

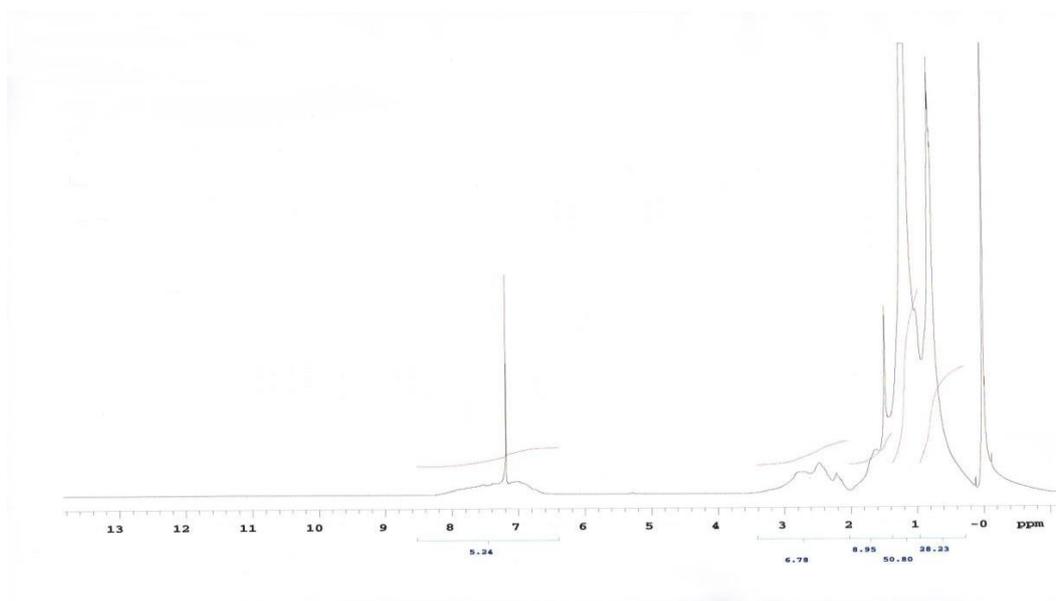


Figure 1.  $^1\text{H-NMR}$  Analysis of IHVR

### 3.2. Catalyst Analysis Results

Catalyst transformations on DSC analysis is shown in Figure 2.

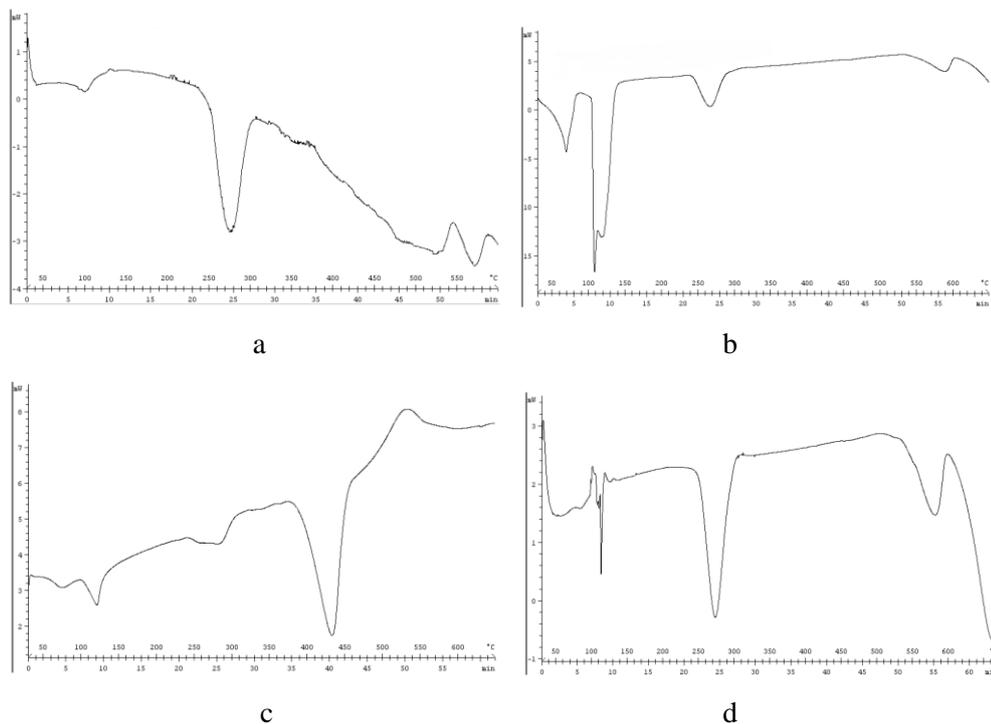


Figure 2. DSC Scans of  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Fe}_2\text{O}_3$  mixture (a),  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$  mixture (b),  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{CaO}$  mixture (c) and  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$  Mixture (d)

When the DSC results of the catalyst mixtures are examined, it is seen that  $\text{Fe}_2\text{O}_3$  has a strong energy oscillation between 300 °C-500 °C,  $\text{Al}_2\text{O}_3$  around 100 °C, CaO between 400-450 °C and  $\text{SiO}_2$  between 600-700 °C.

### 3.3. Catalyst Performance Results

In Table 2, reactants mass and product percentages stated: initial mass of resid and catalyst mixture,  $\text{H}_2$  used, and weight percent of coke, gas and toluene soluble fraction (TSF) products.

Table 2  
Products from VR slurry hydrocracking

Sample number	Catalyst Used	Resid + Catalyst Mass (g)	$\text{H}_2$ mass (g)	Coke (%)	Gas (%)	TSF (%)
1	Without catalyst	1.17	0.14	35	38	27
2	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	1.22	0.12	25	49	26
3	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	1.33	0.13	20	56	24
4	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$	1.14	0.13	12	64	24
5	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{CaO}$	1.15	0.14	23	51	26
6	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$	1.15	0.13	10	65	25
7	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.24	0.14	23	57	20
8	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.17	0.13	20	61	19
9	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{S}$	1.14	0.14	11	64	25
10	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.15	0.13	26	46	28
11	Maltene + $\text{Fe}_2\text{O}_3 + \text{S}$	2.46	0.11	22	58	20

The minimum coke production is achieved when  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$  mixture is used as catalyst with 10 % coke production. Product yields of slurry hydrocracking reactions are shown at Figure 3.

Table 3  
Mixing ratios of the catalysts

Sample number	Catalyst Used	Resid (g)	Catalyst (g)
1	Without Catalyst	1.17	-
2	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	1.10	$\text{FeSO}_4 \cdot \text{H}_2\text{O} : 0.055$
3	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	1.20	$\text{FeSO}_4 \cdot \text{H}_2\text{O} : 0.030 \text{ Fe}_2\text{O}_3 : 0.030$
4	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$	1.01	$\text{FeSO}_4 \cdot \text{H}_2\text{O} : 0.025 \text{ Al}_2\text{O}_3 : 0.025$
5	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{CaO}$	1.01	$\text{FeSO}_4 \cdot \text{H}_2\text{O} : 0.025 \text{ CaO} : 0.025$
6	$\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$	1.02	$\text{FeSO}_4 \cdot \text{H}_2\text{O} : 0.025 \text{ SiO}_2 : 0.025$
7	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.10	$\text{Fe}_2\text{O}_3 : 0.011 ; \text{Al}_2\text{O}_3 : 0.011 ; \text{S} : 0.0605$
8	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.04	$\text{Fe}_2\text{O}_3 : 0.0104 ; \text{Al}_2\text{O}_3 : 0.0104 ; \text{S} : 0.0624$
9	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{S}$	1.00	$\text{Fe}_2\text{O}_3 : 0.025 ; \text{Al}_2\text{O}_3 : 0.025 ; \text{SiO}_2 : 0.025 ; \text{S} : 0.025$
10	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$	1.02	$\text{Fe}_2\text{O}_3 : 0.0255 ; \text{Al}_2\text{O}_3 : 0.0255 ; \text{S} : 0.0255$
11	Maltene + $\text{Fe}_2\text{O}_3 + \text{S}$	1.20	Maltene : 1.035 ; $\text{Fe}_2\text{O}_3 : 0.2875 \text{ S} : 0.08625$

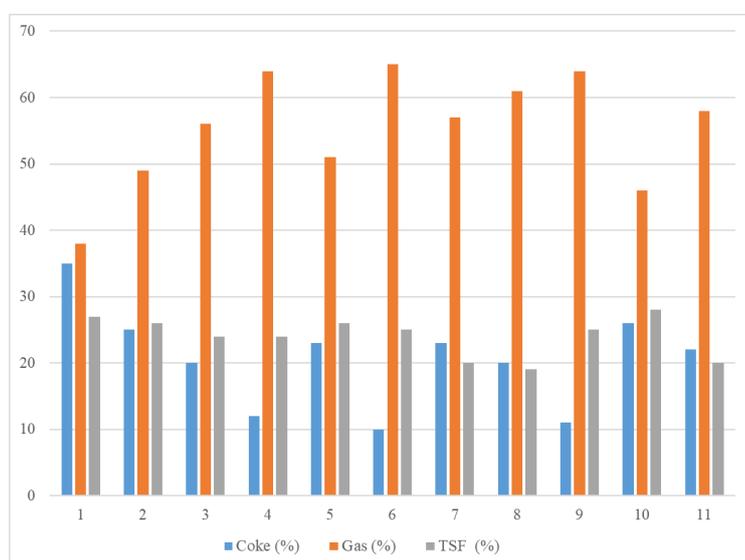


Figure 3. Product yields of slurry hydrocracking reactions

When the hydrocracking results of the catalyst mixtures are examined, it is seen that the  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$  mixture minimizes the coke ratio by 10%, followed by the  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{S}$  and  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$  mixtures with 11% and 12% respectively. These results, in addition to the emphasis on iron-based catalyst; It reveals the reducing effect of  $\text{SiO}_2$  on the formation of coke. Although minimum coke production achieved with  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$ , middle distillate containing TSF was maximized with  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$  and only 1 % higher comparing to conventional thermolysis.

Considering the fraction ratios soluble in toluene,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$  mixture had the highest percentage with 28%, while the work without catalyst took the second place. Experiments revealed that at 100 bars initial  $\text{H}_2$  pressure TSF containing middle distillate part can be increased to maximum 28%. Catalyst that give the minimum coke also make the gas products maximum in expense of TSF.

When the gas+light products ratios are examined, it is seen that the catalyst mixtures  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{S}$  and  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$ , which are catalyst mixtures that minimize the coke ratio, are 65%, 64% and 64% respectively.

These results reveal that at the point where the coke formation is minimized, the selectivity shifts to the gas+light products formation direction, not the liquid product formation.

#### 4. Conclusion

In this study, vacuum residue of crude oil was processed in a laboratory scale batch slurry reactor with the aim of determining the most effective, easily prepared and cheap catalyst.  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ , the binary mixtures of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  with metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ ) and the  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  with elementary sulfur are tried as catalysts. Gases, liquid and solid part of product mixture were separated each time and amounts of all products are calculated separately. According to the results, minimum coke production is achieved by  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$  catalyst. Although minimum coke production achieved with  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{SiO}_2$ , middle distillate containing TSF was maximized with  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{S}$ . Coke is one of the cheapest products in petroleum industry. In this study, the second aim was to identify the mixture which maximizes middle distillate fraction but it has been revealed that these cheap catalysts affect mostly the coke and gas yields. However, these results showed that  $\text{SiO}_2$  also have a strong coke reducing effect.

#### Author Contributions

Savaş Gürdal: Performed statistical analysis, collect the data and wrote the paper.

Kadir Yılmaz: Performed statistical analysis, collect the data and wrote the paper.

Solmaz Akmaz: Conceived and designed the analysis.

Muzaffer Yaşar: Conceived and designed the analysis.

#### Conflicts of Interest

No conflict of interest.

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