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On Kinetics of Upgrading Reactions by Supercritical Water Technology of Highly Sour Qayara Crude Oil over an Activated Carbon-Based Catalyst

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Abstract

Currently clean energy and zero emission fuel is a priority as there is a growing level of pollutants in air, sea and soil. Also, the conventional Iraqi crude oil is going to deplete according to the statistical analysis. Thus, methods of upgrading should attract attention in Iraqi fuel sector. The method of supercritical fluids (SCF) is one of the advanced approaches to upgrade the unconventional crude oil and removal of high levels of sulfur compounds. The present work aims at developing a kinetic model for upgrading reactions by supercritical water technology of a sour Iraqi crude oil. This aim was achieved via conducting sets of experiments in a hydrothermal autoclave reactor over a cobalt/activated carbon catalyst. The AC was used as a support for Co as an active metal. A set of upgrading kinetics experiments were applied at different temperatures (290-350 °C) and reaction times (0-45 min). Upon evaluation of the prepared catalysts for kinetics of upgrading by supercritical water technology, it was found that the process flows pseudo first order mechanism. Also, the activation energy of the chemical reaction was found to be 204.1 kJ/mol which is much less compared to previous studies.

Keywords: Kinetics, upgrading of heavy oil, supercritical water, activated carbon.

1. Introduction:

Tremendous amounts of crude oil production were expelled due to the depositional environment of sourced by terrestrial paleodepositional environment that lead to form sulfur rich oil. As a result of this harsh handling of crude oil storage, the amount of the current crude oil of heavy molecular weight keeps increasing[1]. Furthermore, the price of high-quality crude oil has been maintained at a high level for a long time. Furthermore, refineries are confronted with additional obstacles when the sulfur content of crude oil rises. It is critical to make better use of crude oils, particularly heavy oils (bitumen, asphaltene, etc.) and residues, to fulfill the growing demand for high-quality motor fuels and petrochemical materials (coal tar, residual oil, etc.), which contain a high amount of heteroatoms, a low H/C atomic ratio, and a high viscosity (sulfur, nitrogen, nickel, etc.)[2]. Modern heavy-oil upgrading solutions are centered on increasing the hydrogen content or reducing the carbon content of the oil to improve the H/C ratio[3, 4]. Furthermore, neither the products of the distillation column nor the products of other upgrading procedures may be employed directly for commercial reasons[5, 6]. Heavy trace metals, particularly sulfur compounds, tend to concentrate in heavy bottom products, which are used as feedstock in upgrading operations. As a result, further operations such as hydrotreating are required before the fuels may be sold to fulfill environmental laws[7-9]. However, hydroconversion procedures need a lot of hydrogen, and hydrogen generating units are one of the refineries' most expensive activities[2, 9, 10]. As a result, new heavy oil upgrading procedures with minimal or no hydrogen consumption, enhanced heteroatom removal, greater conversion (i.e. higher light liquid oil output), and suppressed coke deposits are needed[11-13]. The use of supercritical water (SCW) in upgrading technologies might allow for the external addition of a large amount of hydrogen at a low cost. Supercritical water (at 375°C and 22.1MPa) is particularly successful in converting bitumen-derived asphaltenes to lighter end products in recent research[14]. The SCW has a high reaction activity and may be employed as an acid/base catalyst to regulate the pressure field and engage in chemical reactions[15]. Date stones might be regarded as one of the greatest candidates among agricultural wastes for the synthesis of activated carbon that can be used as a support of the catalyst as they are inexpensive and plentiful, especially in Mediterranean nations. The use of such a catalyst is determined by the possibility of application as a kinetic reaction[15, 16].

Galarraga et al. [17] studied the catalytic upgrading of heavy fractions at extreme conditions (400 °C and 6 MPa). They determined the kinetics of the reactions using dispersed NiWMo catalysts. They aimed to determine the kinetics rate law within the range of 320–380 °C and prolonged reaction times up to 70 h. For this study, they used a batch reactor with stirring with hydrogenation at 3.45 MPa. They found that the upgrading reactions followed first-order kinetics and the activation energy was 200 kJ mol^{-1}. Kang et al.[18] conducted a study on upgrading crude oil upgrading using supercritical methanol in a batch reactor. To understand the reaction mechanism of the technology they worked on developing a kinetic model at conditions of 653–693 K and reaction time up to

120 min. They showed that the cracking of asphaltene is the highly determined reaction among the other upgrading reaction network components.

Chang et al. [19] conducted a study on evaluating upgrading kinetics. They used lumped parameters for the evaluation and especially marcokinetics. The feedstock of the study was coal tar and the upgrading was conducted at supercritical conditions for xylene. They evaluated the different study parameters such as yield that was studied at different reaction times, the pressure of hydrogen, and the solvent (xylene)-to- feedstock ratio. They obtained that the reaction is first order and can be conducted at 380°C with high productivity.

Tan et al.[20] studied the supercritical water (SCW) in terms of upgrading reaction kinetics that occurred between the upgrading in the SCW and oil phases. They concluded that the reaction of pyrolysis can be conducted much faster at the SCW conditions based on comparison with the upgrading of the heavy oil regularly in an oil phase. Despite the faster rate of reaction, it was found that the rate of reaction was retarded as mixing was increased. To obtain the kinetic parameters, the lumping approach with four nodes was used. The decomposition of asphaltenes was found to be influenced by the mass transfer promoted by the uniform heating and pressurizing conditions provided by the SCW method. The present work aims to develop a kinetic model of a supercritical water upgrading of a highly sour Iraqi heavy oil using an AC-based catalyst under mild operating conditions.

2. Experimental work

2.1 Materials

The heavy crude oil used in the present study was a highly sour Iraqi crude oil obtained from the Qayyarah reservoir. The characteristics of the feedstock are summarized in Table (1).

Table (1) Characteristics of the Qayyarah crude oil

API at 60 F	14.1
Water, wt.%	3
Total salts, ppm	22
Total sulfur content, ppm	5435
Content of asphaltenes, wt.%	15.2
Pour point, K	263
Ash content, wt%	0.067
Initial boiling point, K	318
Specific gravity at 60F	16.8
Reid vapor pressure, bar	0.7224

For purging of the hydrothermal reactor, nitrogen gas was provided from a local supplier at 99.9999% purity. It was also used for providing an inert atmosphere for calcination of the prepared carbon from the seeds to obtain the desired porosity. This atmosphere was provided to avoid the combustion of the carbon inside the furnace. For the preparation of the AC support from the Iraqi date palm seeds, several chemicals were used. Table (2) summarises these chemicals.

Table (2) Ingredients of the AC preparation solutions

Material	Assay %
Iraqi date palm seeds	Agricultural waste
Solution of phosphoric acid	85%
Double distilled water	-

To impregnate the prepared AC with cobalt metal element, a wet impregnation method was used and there were different chemicals required for the preparation, Table (3) shows these chemicals.

Table (3) Materials used in impregnation of activated carbon with cobalt.

Chemicals	Assay%
Cobalt chloride, chemical structure: $CoCl_2.6H_2O$	98
Distilled water	Total dissolved solid=0.0, pH= 6.8

2.2 Catalyst preparation

For the preparation of the Co/AC catalyst several steps were conducted;

2.2.1 Preparation of support

The support used in the present study was a synthetic AC based on agricultural waste, Iraqi date palm seeds:

- Iraqi date palm seeds (DPS) collected from a local supermarket were cleaned by washing with tap water and deionized water. The clean DPS were dried in an oven (Gallen Kamp ((Sanyo/Weiss, UK) overnight at 120°C. The dried DPS were crushed, sieved, and stored in a desiccator for use in preparation steps. Figure (1) shows the processed seeds.

Fig. (1): The agricultural waste (DPS) used for support preparation

- To activate the DPS and creation of pores, 200 ml of 85 wt.% H_3PO_4 solution was used for soaking 100 g of the DPS. It was previously found that the optimal ratio of impregnation of the seeds with phosphoric acid is 2: 1 (acid: seeds) to digest the cellulose in the agricultural seeds[21-23]. Soaking of the dried DPS in phosphoric acid solution occurred with agitation over a hot plate stirrer (JISICO, Korea) at 75°C for 4 h.
- The stirring was conducted inside a fuming hood to get rid of the impregnation gases that evolved during soaking.
- The soaked sample was then placed inside the oven for 24 h at 120 °C.
- The dried sample was moved to a tubular furnace (SafeTherm, China) for activation and generation of the porous texture. The activation was completed via heating from room temperature to 500 ºC with a heating ramp of 4 ºC min^{-1}. The sample was left at that temperature for 2 h with the continuous blowing of nitrogen gas to avoid combustion of the carbon. After the 2 hrs, the sample was left to return to room temperature at the same rate of 4 °C per min. It was then taken out of the furnace and rinsed with ultrapure water to neutralize the sample to a pH of 7.

2.2.2 Impregnation with cobalt

Cobalt was chosen as an active metal element for upgrading reaction in the present study. To load 6% Co over the AC, the basic Incipient Wetness Impregnation (IWI) method was utilized. The step of impregnation was as follows:

1- A salt of cobalt chloride ($CoCl_2$) was used as a precursor for the preparation of the impregnation solution. 7.5 g of the salt was completely dissolved in 50 ml of deionized water.

2- A sample of the AC obtained in section 2.2.1 was weighed (24 g) and placed in a conical flask. The impregnation solution was added to the AC sample with continuous agitation in a water bath.

3- The impregnated AC sample was sonicated in an ultrasonic homogenizer sonicator (Toption, China) at 650 W for 120 min. It was then left to set overnight.

4- The mixed sample was heated to evaporate the water over the hot plate at 65°C.

5- The evaporated sample was transferred to the oven for drying overnight at 120°C.

6- The last step is calcination of the Co/AC sample in the tubular furnace to create a solid linkage between Co and Ac, to get rid of the pore water and convert Co into Co oxide over the AC. The calcination process was conducted at 530 °C for 3 h in presence of nitrogen gas blowing at a heating ramp of 4 °C/min. The calcination was conducted in the tubular furnace. The calcinated sample was then tagged as Co/AC catalyst sample and was placed in a laboratory desiccator for dry use.

2.5. Kinetics and evaluation experiments

2.5.1 Experimental setup

A hydrothermal autoclave reactor was used in the present study to evaluate the prepared catalysts for upgrading heavy oil. The specifications of the autoclave reactor are shown in Table (4). It consists of a 316 stainless steel microreactor placed inside a heating chamber (furnace). A picture and a schematic diagram are shown in Figure (2).

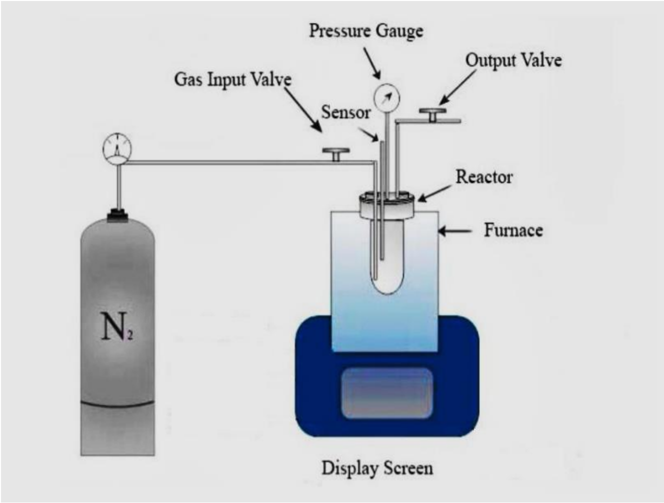


Fig. (2): Schematic diagram of the hydrothermal autoclave reactor

Table (4) Specifications of the hydrothermal autoclave reactor

Temperature	Room temp - 500°C
Heating method	Heating jacket
Temperature control mode	PID artificial intelligence instrument
Speed	0 – 2500 rpm
Volume	250 ml
Lining material	Direct stainless steel kettle liner
Kettle material	316L
Heating power	210W
Temperature control accuracy	± 1°C
Power supply	220V /110
Furnace wire	$Cr_{20}Ni_{80}$
Temperature sensor	K-type thermocouple

2.5.2 Running of experiments

The experimental runs planned in Table (5) were conducted to determine kinetic parameters of the upgrading reaction over the prepared Co/AC for upgrading of the heavy oil in the hydrothermal autoclave reactor.

Table (5) Variables of the upgrading of the heavy oil

Parameter	Level	Value
Temperature (°C)	5	290, 310, 330, 350
reaction time (min)	14	5-45 (5 min interval)

Also, these experimental runs aim to examine the lifetime of the prepared Co/AC catalysts against deactivation reaction. The experiments were conducted as follows:

1. 24 ml of the feedstock, 12 ml of distilled water, and 1.5 gm of the catalyst were poured into the reactor vessel shown in Figure (3. a). The reactor was sealed with screws and high-temperature and pressure gaskets. Then the reactor vessel was placed in the heating furnace chamber of the reactor system while maintaining all valves closed and the reactor furnace off.
2. The reactor furnace was set at the desired temperature via the temperature controller (Autonics TK4 s series, USA) for the desired time of reaction according to the matrix of the experiment shown in Table 6.

3. During the experiments, nitrogen gas was flown through the reactor vessel to aid uniform agitation of the reaction ingredients.
4. Due to the synergetic effect between temperature and pressure in the hydrothermal processes, the pressure was spontaneously raised with raising the reaction temperature and the operating pressure was observed on the pressure gauge shown in Figure (3) and recorded accordingly. The maximum operating pressure was obtained upon raising the operating temperature to 350°C as it approached 235 bar.
5. At the end of each run, the reactor furnace was set to OFF according to a controlling cycle that returns the reactor furnace temperature to room temperature at a rate of 10°C/min.
6. The reactor vessel was taken out of the furnace chamber and after approaching atmospheric pressure the vessel was unsealed with a screwdriver and the products were poured into a sample vial to prepare for analysis.
7. The reactor vessel was rinsed with ethanol solution and deionized water and left to dry to prepare for the next run.

2.5.3 Product analysis

Sulfur contents are measured by X-Ray Sulfur Analyzer (the specifications are shown in Table (6). The method of sulfur concentration determination is based on energy-dispersive X-ray fluorescence with selective filters according to the ASTM D2622 standard[24]. A polyethylene terephthalate (PET) film (3.0 µm, 75 mm, 100 mm) was used to cover the sample holder. X-ray radiation of the low-duty X-ray tube inside the analyzer converted by primary radiation PET filters excites the fluorescence radiation of atoms of the sample under examination. Radiation flows (primary radiation scattered on the sample and secondary fluorescence radiation) comes in the proportional gas meter and sulfur atom fluorescence radiation (SKa) is separated from radiation with other energies utilizing the PET selective filters.

Table (6) Specifications of the X-ray sulfur analyzer

Specification	Value
Model	ASE-2
Manufacturer	Bourevestnik, Russia
Statistic limit of detection, max, ppm	3
Range of determined sulfur concentration, ppm	5-50,000
Limits of basic relative error, %	±0.5
Power consumption,	220 V, 50 Hz
Dimensions (L×W×H), mm	470×350×215

2.5.4. Catalyst characterization

Atomic absorption spectrophotometers (Shimadzu AA6200, Japan) were used to examine the Co content in the prepared catalyst. Scanning electron microscope Electron Diffraction X-ray (EDX) (SEM) (CHL-SEM60/150, China) was used to characterize the surface morphology. The multipoint surface area was determined using the nitrogen adsorption method in Quantachrome cooperation, Autosorb, Oxford, UK).

3. Kinetic upgrading reactions:

Due to the complexity of upgrading reaction, desulfurization will be considered here as the main reaction being analyzed for the kinetics parameters. Based on the power law model:

$$-r_A = k{C_A}^n \tag{1}$$

For n= 1

$$-r_A = kC_A \quad = \frac{dC_A}{dt} \tag{2}$$

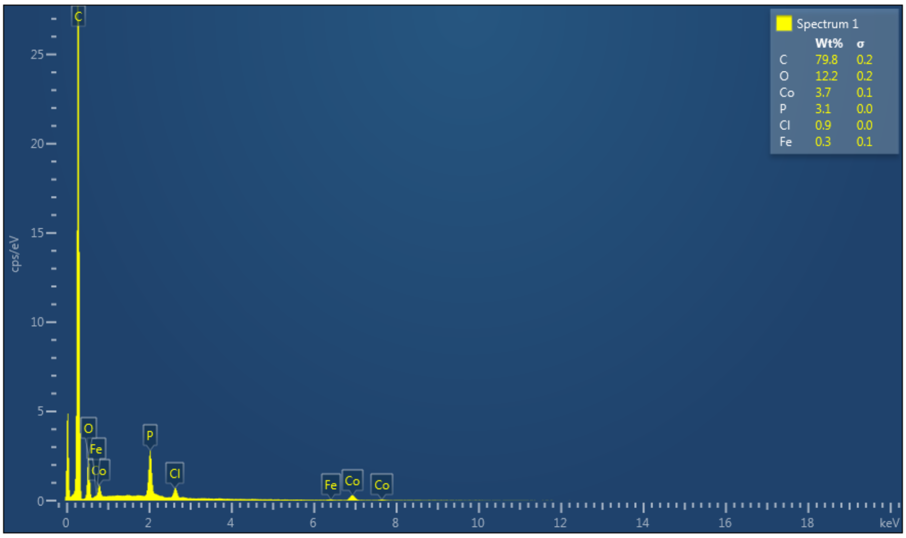
$$\ln (1-X) = -kt \text{ or } -\ln (1-X) = kt \tag{3}$$

Plotting of -ln (1-X) versus t and fitting the plot to a straight line resulted in a slope of the line that will be recorded as the value of reaction rate constant at the given reaction temperature as four temperatures were examined (290, 310, 330, and 350 °C).

4. Results and Discussion

4.1 Catalyst characterization

The characterization of the Co/AC catalyst showed that the BET surface area was 409.385 m²/g. For the pore volume, it was found that it was 0.521 cm^3/g, 0.452 cm^3/g for the microporous volume, and 0.069 cm^3/g for the mesoporous volume. Thus, it can be observed that the prepared AC is mostly microporous. Also, the pore diameter was found to be 1.685 nm that confirming the dominance of the microporous size of the pore developed[25] upon activation of the seeds and calcination of the carbon prepared. Figure (3) shows the EDX spectrum of the Co/AC catalyst. The spectrum obtained shows the surface elements of the prepared catalyst. It can be seen that Co was found at 3.7%, and the other elements such as P (3.1%), Cl (0.9%), Fe (0.3%), and O (12.2%) are present in different percentages due to the use of solvents such as H_3PO_4 and metal oxides those were used for catalyst preparation. In addition to the components of the seeds[26, 27].



	Wt%	σ
C	79.8	0.2
O	12.2	0.2
Co	3.7	0.1
P	3.1	0.0
Cl	0.9	0.0
Fe	0.3	0.1

Fig. (3): EDX spectrum of the prepared Co/AC catalyst

Figure (4) shows the SEM analysis of the Co/AC catalyst. It can be seen the Co element particles were well distributed within the microporous AC matrix. It can also be seen that the particle size has a narrow range of distribution. The porous texture of the AC prepared is well observed and marked in the Figure. Thus, it can be concluded that the simple wet impregnation method was satisfactory for the preparation of metal/AC catalyst.

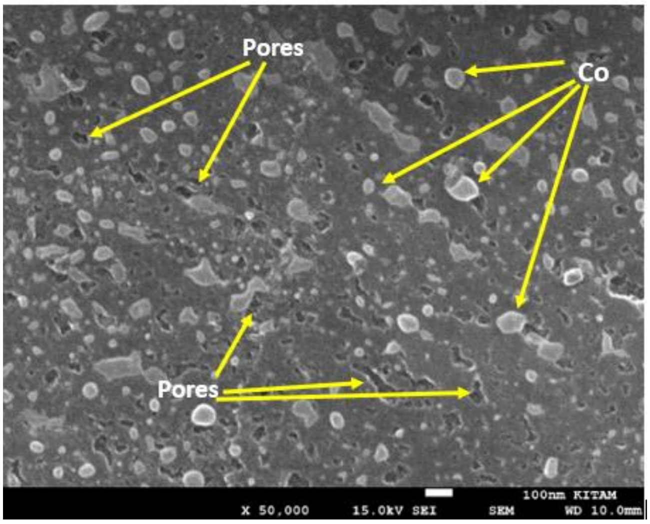


Fig. (4): SEM image of the prepared Co/AC catalyst

3.2 Kinetics of upgrading reaction

The kinetics of the upgrading reaction in terms of sulfur removal was determined using experimentation at different reaction temperatures of 290°C, 310°C, 330°C, and 350 °C and different reaction times (0-45 min, with an increment of 5 min) over the Co/AC catalyst. The feedstock: water ratio was 2:1. Figures (5) to (8) show the plots of upgrading the reaction profile against the reaction time.

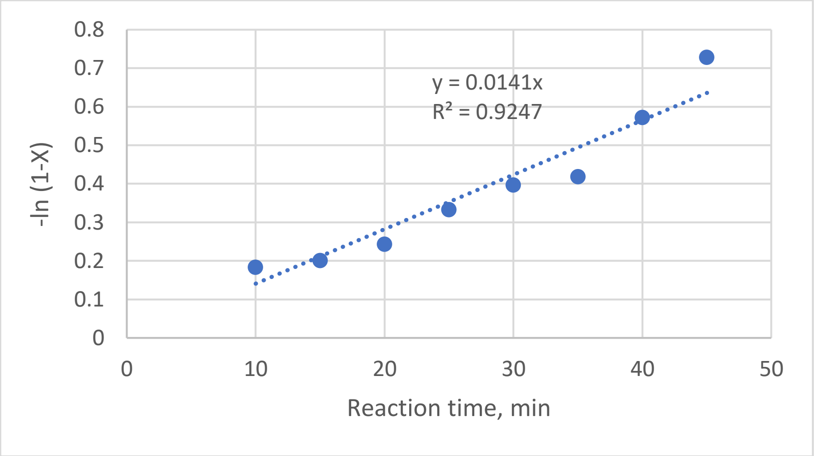


Fig. (5): Kinetic profile of the upgrading reaction at 290°C

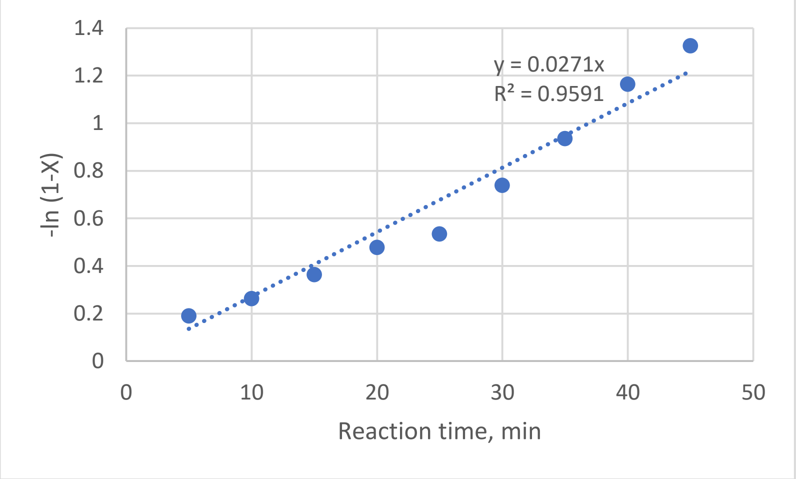


Fig. (6): Kinetic profile of the upgrading reaction at 310°C

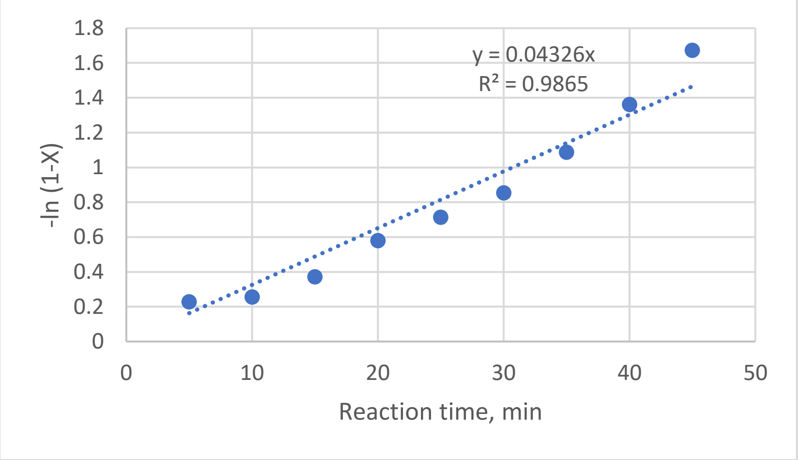


Fig. (7): Kinetic profile of the upgrading reaction at 330°C

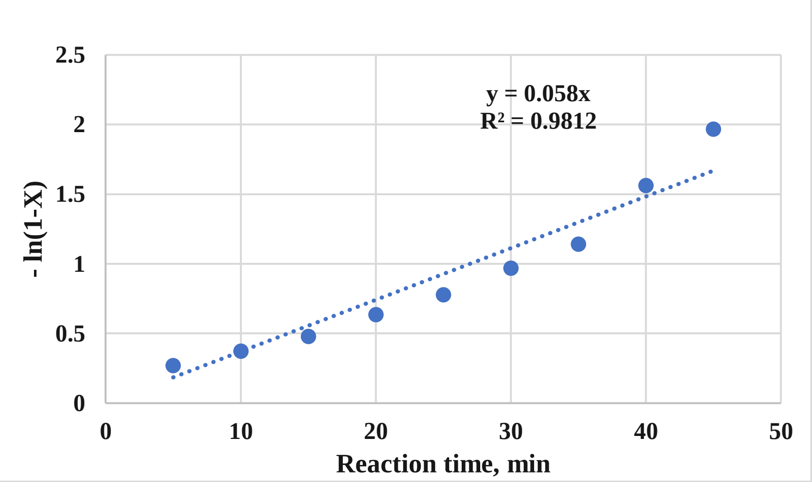


Fig. (8): Kinetic profile of the upgrading reaction at 350°C

It is seen that the upgrading reactions in terms of desulfurization of the heavy oil obey first-order kinetics and the reaction rate constants are 0.014, 0.0271, 0.0432, and 0.058 min^{-1} at 290, 310, 330, and 350°C respectively. It was previously found for the decomposition of heavy oil into the upgraded fuel that most of the transformation reactions between lumps at the time of upgrading by supercritical methanol obey first-order kinetics[15, 20, 28]. Thus, kinetics parameters for the upgrading reaction can be found from the Arrhenius plot as shown in Figure (9). ln k (measured at different temperatures) was plotted against the reciprocal of upgrading temperature. It was found the activation energy of the reaction is 238.75 kJ/mol and the frequency factor (pre-exponential kinetic parameter) is 30,333 $molecule.min^{-1}$. This is in line with the relevant study conducted by Kang et al.[18] as they found that the activation energy of the upgrading reactions is 204.1 kJ/mol and Tirado et al.[29] as they used aquathermolysis for upgrading heavy oil and concluded that a simple sulfur removal reaction is an alternative for finding upgrading kinetics as sulfur removal is the dominant reaction among the upgrading reactions. Analysis and discussion of the kinetic models focused on the aquathermolysis reaction reported up to date is performed.

Based on the experimental observations and the fitted kinetic data it was found the desulfurization reaction by upgrading of naphtha via supercritical water process can be categorized as a pseudo-first order reaction as the water (solvent) present in significant excess (2:1). The present investigation the mixed hydrocarbons in the sour feedstock and the organosulfur compounds concentrations were selected to follow this pseudo reaction kinetics. A homogeneous phase for the system hydrocarbons/H_2O exists at the pressure and temperature conditions of our experiments. Unfortunately, there are no solubility data available for Qayara feedstock. However, it has been reported that the solubility of heavy cut hydrocarbon in H_2O in mol fraction is fairly moderate[30]. Since the high concentration of water in our experiments, it is assumed that the hydrocarbons completely dissolve in water. Furthermore, the mixed hydrocarbons with their impurities in the reactor did not crystallize or precipitate. Thus, based on the proposed and fitted kinetic data it can be found that the correlation of the upgrading of Qayara crude oil at supercritical conditions follows the following expression:

$$R_{upgrdaing} = k' \, C_S \qquad (4)$$

$$k' = A\exp(-E/RT) \, C_S \qquad (5)$$

$$k' = 30{,}333 \exp(-238.75/RT) \, C_S \qquad (6)$$

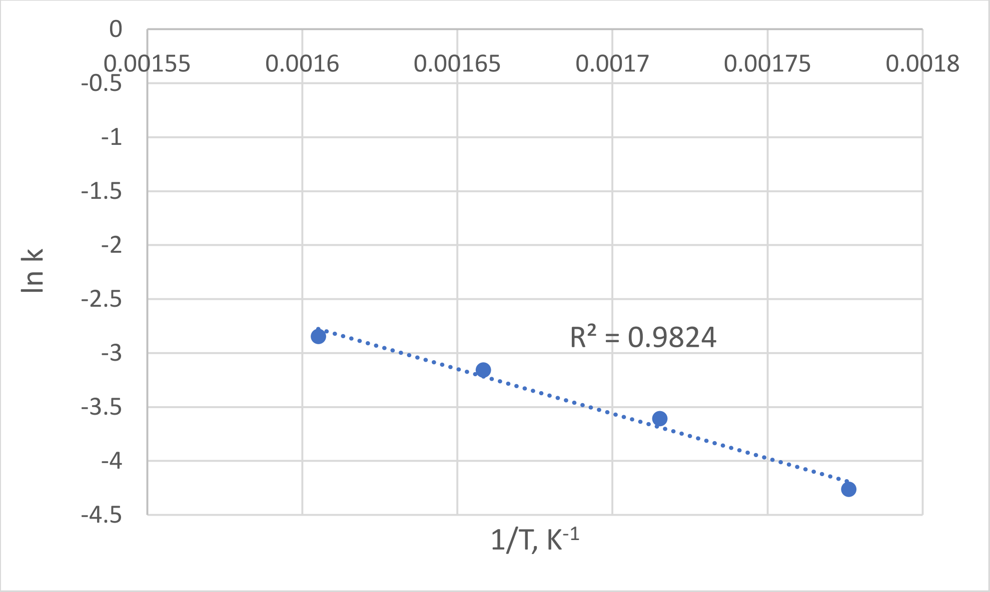


Fig. (9): Arrhenius plot of the upgrading reactions

5. Conclusions

An unconventional crude oil, highly sour crude oil, was upgraded using an agricultural waste-based catalyst in the present study. The prepared catalyst was cobalt supported on activated carbon which showed a high surface area, microporous texture, and uniform distribution of the metal element within the activated carbon matrix. Also, it was found that the particle size distribution of the prepared catalyst was narrow as most of the particles possess almost the same size. The crude oil was upgraded in a supercritical water environment at various temperatures (290-350) °C and times of reaction (0-45) min. In the present study, the kinetic of the upgrading reactions in terms of sulfur removal was investigated. The results obtained showed that the upgrading reactions conducted by supercritical water over the prepared AC catalyst were first order which is in line with relevant studies. However, compared to the other relevant upgrading methods the activation energy is less than their activation energies obtained under the same conditions. The present study paved the way for the use of Iraqi agriculture as a cost-effective catalyst for upgrading highly sour crude oil on a commercial base.

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