



# Article Kinetics of Catalytic Decarboxylation of Naphthenic Acids over HZSM-5 Zeolite Catalyst

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Abstract: Naphthenic acids are naturally occurring carboxylic acids in crude oil with cyclic or aromatic rings in their structure. These carboxylic acids are responsible for the acidity of crude oil, leading to corrosion problems in refinery equipment and the deactivation of catalysts while creating a continuous need for maintenance. Therefore, removing naphthenic acids has become an important requirement in refining acidic crude oil. In this paper, experiments are conducted to investigate the use of HZSM-5 zeolite catalyst to reduce the total acid number (TAN) of a typical acidic crude oil obtained from Al-Fula blocks in Western Sudan. TAN is an important metric signifying the acidity of crude oil. A full factorial design of the experiment (DOE) framework enabled a better understanding of the efficacy of the catalyst at three parametric levels (reaction temperature: 250-270-300 °C, reaction time: 2-3-4 h, and oil:catalyst weight ratio: 20-22-25 g/g). The results demonstrate that the HZSM-5 zeolite catalyst provides up to 99% removal of naphthenic acids via the decarboxylation route. Additionally, the removal efficiency increases with increasing temperature and residence time. The acidity of the crude oil was shown to decrease after treatment with the catalyst for four hrs.; from 6.5 mg KOH/g crude to 1.24; 0.39 and 0.17 mg KOH/g at 250; 270 and 300 °C, respectively. A sharp decrease of TAN was observed at the oil catalyst mass ratio of 20 g/g at 250  $^{\circ}$ C, and almost complete conversion of acids was achieved after 4 hrs. Another experiment at 270 °C showed a converse relationship between the oil:catalyst ratio and acid removal; suggesting the activation of side reactions at higher temperature conditions catalyzed by excess acid. Finally; a Langmuir-Hinshelwood (LH) kinetic model has been developed to enable rapid prediction of the performance of the HZSM-5 zeolite catalyst for decarboxylation reaction. The model has also been validated and tested in ASPEN® software for future simulation and scalability studies.

Keywords: naphthenic acids; TAN; catalytic decarboxylation; zeolite catalyst; acidity; corrosion

# 1. Introduction

Crude oil is a complex mixture of hydrocarbons and inorganics, such as sulfur, chlorine, nitrogen compounds, trace metals, and naphthenic acids [1]. In terms of acidity classification, crude oil could be non-acidic (high quality) or acidic (low quality). The acidity of the crude oil is characterized by its total acid number (TAN). As per the American Standard for Testing and Materials (ASTM) D664–1989, the TAN is determined by calculating the milligrams of KOH required to neutralize the acidity of one gram oil sample [2]. Crude oils with TAN of more than 0.5 mg KOH/g are considered acidic, and above 1 mg KOH/g are classified as highly acidic [3–7]. High TAN crude oils are generally found in many places worldwide, such as the United States, Venezuela, the North Sea, Canada, West Africa, India, China, and Russia [8,9]. The acidic crude oils are less desirable and have lower prices than conventional crude oils because they cause significant corrosion



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). issues [9,10]. Therefore, they create a continuous need for maintenance and could also result in the poisoning of the catalysts in the downstream refining process [11]. However, the depletion of high-quality crude oil has shifted attention towards utilizing acidic crude oil by making it economically acceptable [12].

The presence of naphthenic acids, among many other carboxylic acids, makes the crude oil acidic [13–15]. The naphthenic acids are cyclic or aromatic compounds with a general formula  $C_nH_{2n+Z}O_2$ , where *n* is the number of carbon atoms, and Z refers to hydrogen deficiency due to the formation of rings. Z has a value of 0, or a negative even number integer, which varies between (0 and -12) [16–20]. The characterization and identification of individual naphthenic acids in crude oil is an essential subject of several research studies as they have significant structure and composition complexity [18,19].

Factors, such as temperature, concentration, and molecular weight influence the corrosion characteristics of naphthenic acids. For example, at a temperature between 200 and 400 °C, high acidity is observed, beyond which the decomposition of acid takes place [15–17]. Similarly, the higher the concentration of the carboxylic acids and the lower the molecular weight (generally between 125–425 g/mol), the higher the acidic nature, which leads to corrosion [10]. Therefore, removing naphthenic acid from the crude oil is an important step to reduce the overall acidity of the crude oil. Many studies have been published on this subject. They are broadly classified under the following categories: (a) blending and inhibition, (b) physical methods, such as adsorption and liquid-liquid extraction, and (c) chemical methods, such as esterification, neutralization, and catalytic decarboxylation [4,21].

Many refineries blend two different TAN crude oils to resolve the acidity problem; however, this method is suitable for slightly high TAN crude oil [22]. On the other hand, inhibition methods have two categories: (a) adding corrosion inhibitors or (b) upgrading equipment material to withstand corrosion. Inhibitors create problems in downstream processes, as they tend to form emulsions and poison the catalyst. Corrosion-resistant materials, such as chromium and molybdenum can be used to upgrade the equipment, but they are too expensive [2,23]. Although physical methods, such as adsorption and liquid extraction are viable options, they are not desirable because of the continuous need for new adsorbents and to meet the criteria for waste disposal [21]. Chemical conversion methods via neutralization with a base to convert the acid to salt and water has also been studied; however, since they cause emulsion challenges, an additional separation process would be required. Esterification is also a costly option, as it requires a large quantity of alcohol for the reaction [4,22].

Catalytic decarboxylation is a chemical conversion method that utilizes a catalyst to convert acids to hydrocarbons and carbon dioxide. Essentially, the C-C bond in carboxylic acid is broken down to release  $CO_2$  gas in this reaction. Another possible definition is replacing the carboxyl group (-COOH) with a hydrogen atom while releasing  $CO_2$  gas [1,23,24]. Fu et al. [25] simulated decarboxylation reaction and hypothesized that the C-C bond existing in the acid structure is the weakest and most accessible to break. Among these C-C bonds, the one attached to the carboxyl group is the easiest to break, and therefore, the carboxyl group is removed as  $CO_2$ . Catalytic decarboxylation of different types of carboxylic acids, such as benzoic acid by zeolite, acetic acid by  $ZrO_2$ , and acetic acid by tungsten-based catalysts, have been reported in the literature [1,26,27].

As shown in Table 1, several studies published earlier focused on developing lowtemperature, high selectivity, and more stable catalysts for the catalytic decarboxylation process [3]. Alkaline earth metal oxide, zinc oxide (ZnO), zeolite, Mg-Al hydrotalcite/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, acidic solid, graphitic carbon nitride, and hybridized basic graphitic carbon nitride coated on the acidic ferrierite zeolite have been shown good performance for catalytic decarboxylation. The alkaline earth metal oxides (considered a low-temperature catalyst) demonstrated the complete removal of naphthenic acids. However, one limitation of these reactions is the co-production of metal naphthenates that tend to dissolve in the crude oil and may lead to the fouling of the transportation pipelines. Consequently, highpressure drops in the transportation network will result in maintenance challenges and high pumping costs [3,24]. Acidic solid catalysts have demonstrated effective performance for decarboxylation of naphthenic acids with conversion up to 97%. Zeolite is a well-known acidic catalyst. Zeolite catalysts have attracted substantial scientific attention due to their high surface area, adsorption capacity, non-toxic nature, non-corrosive nature, high-temperature stability, pore-structure, ease of regeneration, and ability to facilitate cations exchange. Moreover, Zeolites contain strong acid sites (bronsted acid sites) that can aid in reactions where proton transfer is required [25,28,29].

In an earlier study, Zhang et al. [1] demonstrated using ZSM-5 zeolite catalyst for the decarboxylation of model naphthenic acid. Takemura et al. [28] used zeolite for catalytic decarboxylation of benzoic acid. Zeolite catalysts find application in many processes, such as catalytic cracking, isobutane alkylation, isomerization of light gasoline and light alkenes, and conversion of methanol to gasoline or olefins is relatively more accessible and convenient for naphthenic acid removal [30].

Previous publications on catalytic decarboxylation over zeolite catalysts used model naphthenic acids dissolved in dodecane or model naphthenic acids dissolved in diesel oil [1,25]. Moreover, most of these studies were conducted on very small-scale reactors, e.g., a 9 mL batch reactor in Zhang et al.'s [1] study, and an 80 mL autoclave in Takemura et al.'s [27] study. The uniqueness of the current study is that it has been conducted in a larger reactor (500 mL volume). More importantly, this work aimed to remove naphthenic acid from a real and highly acidic heavy crude oil instead of model compounds. In addition, a wider range of operating conditions (temperature, reaction time, and oil:catalyst ratio) were tested in the current work using a systematic Design of Experiments (DOE) framework. Finally, the study also covers the development of Langmuir–Hinshelwood (LH) kinetics of catalytic decarboxylation process utilizing the HZSM-5 zeolite catalyst based on experimental results. The model has also been incorporated in ASPEN<sup>®</sup> process simulation to validate the performance and enable future scalability studies.

Model Oil	Catalyst	System	Total Acid Conversion (%)	Temperature (°C)	Reference
Benzoic acid	Zeolite	80 mL Autoclave	-	400	[27]
Model naphthenic acids dissolved in dodecane	Alkaline earth metal oxide (CaO, MgO, BaO, SrO)	3/8- inch stainless steel tube reactor	~100	200–300	[31]
Model naphthenic Acids dissolved in dodecane	ZSM5 zeolite catalyst	9 mL Sealed glass batch reactor	65%	200–300	[1]
2-naphthoic acid, cyclohexane carboxylic acid, and cyclohexane propionic acid.	Magnesium oxide (MgO)	2 mL sealed glass tube batch reactors—stainless steel reactor (0.4 cm i.d. and 29 cm in length)	92.5%	150–250	[3]
Model naphthenic acids in diesel oil	Acidic solid catalyst (activated alumina (γ-Al <sub>2</sub> 0 <sub>3</sub> )- quartz sands)	Fixed bed reaction	97%	460	[25]
Crude oil and industrial naphthenic acids	Mg–Al hydrotalcite/c-Al <sub>2</sub> O <sub>3</sub>	200 mL Autoclave	80%	330	[32]

Table 1. Selected catalysts and the targeted naphthenic acid systems for the decarboxylation reactions.

Model Oil	Catalyst	System	Total Acid Conversion (%)	Temperature (°C)	Reference
Heavy crude oil and naphthenic acids	Co-Mo/γ-Al <sub>2</sub> O <sub>3</sub> catalyst	Fixed bed reactor (1.0 cm in inner diameter and 45 cm in length)	76.6%	250	[6]
Dodecane solvent (model chemical having a similar average molecular weight with crude oil) NAs (mixtures of cyclopentyl and cyclohexyl carboxylic acids mainly)	Graphitic carbon nitride	100 mL Batch reactor	37.2%	250	[9]
A mixture of dodecane solvent and benzoic acid (BA) and a mixture of NAs	Hybridized heterogeneous basic graphitic carbon nitride coated on the acidic ferrierite zeolite	100 mL Batch reactor	54.4%	300	[33]
Bitumen derived heavy vacuum gas oil (HVGO)	Alkaline earth metal oxides and ZnO	300-mL Autoclave	8.5%	350	[24]

# Table 1. Cont.

#### 2. Results and Discussions

This section discusses the experimental results of the decarboxylation of naphthenic acid in the acidic crude oil sample. Firstly, the effect of reaction parameters, i.e., temperature, time, and oil:catalyst ratio, are presented. The evaluation is conducted in terms of reduction in TAN number. Next, a systematic DOE framework of 3<sup>3</sup> designs is implemented to identify suitable conditions for each parameter that result in the highest reduction of TAN. Finally, an LH kinetics model is developed to rapidly predict the results in future simulation and scalability assessments.

# 2.1. Naphthenic Acid Removal Assessment

## 2.1.1. Effect of Reaction Temperature

The effect of temperature on the deacidification process is studied at three levels: 250 °C, 270 °C, and 300 °C, at oil:catalyst mass ratio of 22 g/g over a time on a stream of 4 hrs. The result of TAN dependency on reaction temperature is provided in Figure 1. A significant decrease in TAN occurs at all temperature conditions during the four hours of reaction. Specifically, the crude oil original TAN of 6.5 mg KOH/g decreases to 1.24, 0.39, and 0.17 at 250 °C, 270 °C, and 300 °C, respectively, during the decarboxylation reaction using the HZSM-5 catalyst. Additionally, all three temperatures have the same effect on the removal process during the first and second hours of the operation, wherein, the TAN is approximately 4.1 mg KOH/g after two hours for all three temperatures. A noticeable effect of temperature is seen at 270 °C, and 300 °C temperatures, wherein up to 80% additional TAN removal takes place compared to 250 °C after 4 h. However, Zhang et al. [1] reported similar results for a different catalyst. Zhang et al. [1] reported that the naphthenic acid removal rate increases with increased temperature and reaches a maximum value at 300 °C. These results also corroborate with Ding et al. [24]. They reported that the naphthenic acid removal rate increased with temperature from 250 to 360 °C. It should be noted that the catalytic decarboxylation reaction is not preferable over 300 °C, as beyond this temperature, hydrocarbons present in the crude oil may decompose. Ding et al. [24] stated that catalytic

Temperature 250 °C 7 Temperature 270 °C Temperature 300 °C 6 TAN number (mgKOH/g) 5 4 3 2 1 0 2 3 0 1 4 Time(h)

decarboxylation over alkaline earth metal oxides and ZnO catalyst was not preferable under high temperatures as the initial boiling point of heavy gas oil was 261 °C.

**Figure 1.** Results are showcasing the reduction in TAN number of the crude sample at 250, 270, and 300 °C reaction temperatures up to 4 h on stream.

#### 2.1.2. Effect of Reaction Time

The effect of time in the range of 0 to 4 h is studied at three different temperatures, i.e., 250, 270, and 300 °C, and at a constant oil:catalyst mass ratio of 22 g/g. The results are provided in Figure 2. As time increases for all conditions, the TAN value decreases due to the long interaction between the catalyst and naphthenic acids in the sample. We hypothesize that this could be because of the increased transfer of protons (H<sup>+</sup> ions) from acid sites to naphthenic acid in the model. It was reported earlier that the almost negligible change takes place beyond 4 h in a previous study by Zhang et al. [1]. Additionally, since there is always a concern of evaporation of light hydrocarbons that have boiling points below the reaction temperature, it is not advisable to continue the reaction beyond the condition of diminishing returns. Evaporation of lights will also increase the viscosity of the left-over sample leading to operational complications, such as poor mixing, clogging in transfer lines, and catalyst deactivation due to coking.



**Figure 2.** Results showcased reaction time's impact from 0 h, 2 h, 3 h, and 4 h, on TAN numbers at 250 °C, 270 °C, and 300 °C, respectively.

## 2.1.3. Effect of Oil:Catalyst Ratio

The critical factor that influences the activity of the HZSM-5 zeolite catalyst is the amount of the Lewis and brønsted acidic sites [31]. The objective is to provide sufficient acid sites (and therefore, the quantity of catalyst) to facilitate a sustained decarboxylation reaction for up to 4 h on stream. Consequently, we have evaluated the effect of the oil:catalyst ratio to determine the minimum quantity of catalyst needed for satisfactory removal of naphthenic acid in a unit mass of the crude sample. Catalyst quantity is critical from an economics standpoint as a catalyst is a significant cost of a process plant. Moreover, excess amounts will only increase the need for separation, and therefore, the operational cost.

In this assessment, firstly, we studied the effect of the oil:catalyst mass ratio at a temperature of 250 °C for a fixed reaction time of 4 h. Figure 3a illustrates the influence of the oil:catalyst ratio on the TAN number of the sample. It can be observed that the removal rate was similar for the oil:catalyst mass ratio of 22 and 25 g/g. On the other hand, a ratio of 20 g/g (entailing a higher quantity of catalyst) resulted in almost complete conversion. In other words, 20 g/g could be considered an optimal oil:catalyst ratio for the decarboxylation reaction, as negligible naphthenic acid content will be available for a response.



Figure 3. TAN dependency on oil/catalyst ratio at temperature (a) 250 °C; (b) 270 °C.

To further study the combined effect of temperature and oil:catalyst ratio and to ensure that the percentage of 20 g/g is also applicable for higher temperatures of 270 °C, we repeated the above experiment for the reaction time of four hours. In Figure 3b, it can be observed that the TAN reduction for oil:catalyst ratio of 20, 22, and 25 g/g happens in the order: of 1.35, 0.39, and 0.05 mg KOH/g, respectively. These results are surprisingly converse to that obtained at 250 °C, where TAN decreased with a decrease in oil:catalyst ratio. It is plausible that the higher temperature might have activated side reactions of other hydrocarbon species present in the sample that were catalyzed with the excess catalyst. However, more studies are required to investigate the effect of higher catalyst loading on side reactions, which is beyond the scope of this work. However, this study exemplifies the fact that oil:catalyst ratio and temperature have a secondary interaction due to unknown factors/side reactions that become prominent at higher temperature conditions.

#### 2.1.4. Combined Effect of Temperature, Time, and Oil:Catalyst Ratio

We studied the combined effect of temperature, time, and oil:catalyst ratio parameters to understand their interaction in detail. Figure 4 illustrates the results. A DOE matrix of 33 data points was designed to systematically understand the results and reduce redundancies. Table 2 presents three of the developed DOE matrices comprising a three-factor-three-level factorial design matrix with response value. Our primary interest in this work was identifying the conditions that result in naphthenic acid removal beyond 90%. Table 3 presents only those data points and conditions that result in more than 90% conversions. Maximum removal of 99.23% was obtained at 270 °C, 4 h, and an oil/catalyst ratio of 25.



Figure 4. Acid removal percentage vs. time.

No	Temperature (°C)	Time (h)	Crude Oil/Zeolite Ratio (g/g)	TAN
1	270	2	22	4.27
2	250	4	25	1.24
3	270	4	20	1.35
4	250	3	25	2.42
5	300	4	22	0.17
6	250	4	22	1.24
7	300	2	25	2.18
8	250	3	20	0.16
9	300	3	20	-
10	250	4	20	0.14
11	270	3	20	2.55
12	270	4	25	0.05
13	270	2	25	1.4
14	300	2	20	-
15	270	3	25	1.04
16	300	4	20	-
17	250	2	22	4.1
18	250	3	22	2.23
19	270	3	22	1.20
20	300	4	25	0.35
21	270	4	22	0.39
22	270	2	20	5.01
23	300	3	25	0.85
24	250	2	25	3.36
25	300	2	22	4.10
26	250	2	20	4.97
27	300	3	22	0.90

**Table 2.** Full 3<sup>3</sup> Factorial design matrix with experimental levels of the independent variables and response values obtained.

Temperature (°C)	Time (h)	Oil/Catalyst Ratio (g/g)	Removal %
250	3	20	97.54
250	4	20	97.85
270	4	22	94.00
270	4	22	99.23
300	4	25	97.38
300	4	25	94.62

Table 3. Conditions at which naphthenic acid% removal exceeds 90%.

The reliability of the developed model is evaluated with the help of ANOVA assessment. The results of ANOVA are shown in Table 4, which lists the results of one-way interaction (or single parameter effect), two-way interaction (two-parameter effect), and three-way interaction (three-parameter effect), the residual error, and the absolute error. The relationship between the parameters is captured in the following regression equation: The coefficient of determination ( $R^2$ ) is used to measure the model's reliability. To fit a model, both  $R^2$  and  $R^2_{adj}$  values should be at least 0.80 [34]. According to Table 4, the model achieves an  $R^2$  value of 0.9164 and an  $R^2_{adj}$  value of 0.8870, which indicates that the model accurately predicts the experimental results [35]. Additionally, the model has an F-value of 31.08 and a *p*-value < 0.05, respectively, implying reliability of more than 95% in predicting the values. From Pareto Chart in Figure 5, it can be seen that Time\*ratio has the largest effect on response, followed by time.

**Table 4.** Analysis of variance (ANOVA) regression model for naphthenic acid removal using the catalytic decarboxylation process.

Source	DF	Adj SS	Adj MS	F-Value	<i>p</i> -Value
Regression	6	50.4624	8.41041	31.08	0.000
Temperature	1	0.3774	0.37738	1.39	0.254
Time	1	3.8291	3.82914	14.15	0.002
Ratio	1	0.0206	0.02059	0.08	0.786
Temperature * Time	1	0.0041	0.00410	0.02	0.903
Temperature * Ratio	1	0.6309	0.63090	2.33	0.145
Time * Ratio	1	4.6237	4.62373	17.08	0.001
Error	17	4.6008	0.27063	-	-
Total	23	55.0632	-	-	-

S = 0.520223,  $R^2 = 91.64\%$ ,  $R^2_{adj} = 88.7\%$ . \* two-way interaction (two-parameter effect).



Figure 5. Pareto Chart of the standardized effects.

The kinetic parameters of three derived models (refer to Section 3.4.2 for more details) have been estimated by non-linear regression in Polymath<sup>®</sup>. Table 5 shows the coefficient of determination ( $\mathbb{R}^2$ ), the root means square deviation ( $\mathbb{R}_{MSD}$ ), the adjusted  $\mathbb{R}^2$ , and variance values. Since the adjusted  $\mathbb{R}^2$  and variance values are the same for all the models, we based our model selection criterion on the coefficient of determination ( $\mathbb{R}^2$ ), and the root means square deviation ( $\mathbb{R}_{MSD}$ ). The results show that both surface reaction and desorption rate equations perform poorly compared to adsorption rate equations.

Туре	Equations	Temperature (°C)	Pr	ecision
		250	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$\begin{array}{c} 0.7865 \\ 0 \\ 2.429 \times 10^{-5} \\ 1.0 \times 10^{99} \end{array}$
Adsorption	$r_{ADS} = \frac{k_A \left[C_A - \frac{C_B C_C}{K}\right]}{(1 + K_R C_B C_C + K_B C_B)}$	270	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$\begin{array}{c} 0.91799 \\ 0 \\ 3.379 \times 10^{-5} \\ 1.0 \times 10^{99} \end{array}$
		300	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$\begin{array}{c} 0.9877 \\ 0 \\ 1.078 \times 10^{-5} \\ 1.0 \times 10^{99} \end{array}$
		250	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	0.44439 0 $3.92 \times 10^{-5}$ $1.0 \times 10^{99}$
Surface Reaction	$r_{S} = \frac{k\left[C_{A} - \frac{C_{B}C_{C}}{K}\right]}{(1 + K_{A}C_{A} + K_{B}C_{B})}$	270	$\begin{array}{c c} & & 1.0 \times 10^{59} \\ \hline R^2 & & 0.9136 \\ R^2_{adj} & & 0 \\ R_{msd} & & 3.47 \times 10^{-5} \\ Variance & & 1.0 \times 10^{99} \end{array}$	
		300	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$0.9865 \ 0 \ 1.13  imes 10^{-5} \ 1.0  imes 10^{99}$
		250	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$0.4499 \\ 0 \\ 7.21 \times 10^{-5} \\ 1.0 \times 10^{99}$
Desorption	$r_{D} = \frac{k \left[\frac{C_{A}}{C_{C}} - \frac{C_{B}}{K_{P}}\right]}{\left(1 + K_{A}C_{A} + \frac{K_{R}C_{A}}{C_{C}}\right)}$	270	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$0.4399 \\ 0 \\ 8.82 \times 10^{-5} \\ 1.0 \times 10^{99}$
		300	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$0.4499 \\ 0 \\ 7.21 \times 10^{-5} \\ 1.0 \times 10^{99}$

Table 5. Experiment regression results.

The parameter estimation is conducted at three temperatures, 250, 270, and 300  $^{\circ}$ C, at a fixed pressure of -0.2 bar, stirring rate of 425 rpm, and an oil:catalyst ratio of 25 g/g. The pre-exponential factor and activation energy for each kinetic parameter and the estimated parameters' temperature sensitivity is obtained from the Arrhenius relationship. The kinetic parameter values are listed in Table 6. The linear regression of activation energy and

constant are listed in Table 7. Also the linear regression of adsorption constants are listed in Table 8. Since the constants in Equations (2)–(6) change with temperature, the model parameters are sensitive to temperature. The final rate equation of catalytic decarboxylation of naphthenic acid on HZSM-5 zeolite catalyst is shown in Equations (1)–(5):

$$r_{ADS}\left(\frac{mol}{gcat \cdot min}\right) = \frac{k_A \left\lfloor C_A - \frac{C_B C_C}{K} \right\rfloor}{\left(1 + K_R C_B C_C + K_B C_B\right)}$$
(1)

$$k_{\rm A} \left(\frac{{\rm mol/gcat}}{({\rm mol/L})\cdot{\rm min}}\right) = -2.1 - \frac{1475.292}{{\rm T}}$$
 (2)

$$K (mol/L) = -28.81 + \frac{10980}{T}$$
(3)

$$K_{\rm R} \left(1/({\rm mol}/{\rm L})^2\right) = -9.265 + \frac{6522.173}{{
m T}}$$
 (4)

$$K_{B}\left(\frac{1}{\frac{mol}{L}}\right) = -0.572 - \frac{1253.258}{T}$$
(5)

Table 6. Kinetic and adsorption constants values.

Constant (Units)	Initial Guess	Value
	Experiment 1	
$\mathbf{k}_{\mathbf{A}}\left(\frac{\mathrm{mol/gcat}}{(\mathrm{mol/L})\cdot\mathrm{min}}\right)$	0.001	0.0069972
K (mol/L)	0.1	11.0996
$K_R (1/(mol/L)^2)$	10	25.10734
K <sub>B</sub> (1/(mol/L))	1	8.707089
	Experiment 2	
$\mathbf{k}_{\mathbf{A}}\left(\frac{\mathrm{mol/gcat}}{(\mathrm{mol/L})\cdot\mathrm{min}}\right)$	0.2	0.0095885
K (mol/L)	1	101.9947
$K_{\rm R}  (1/({\rm mol}/{\rm L})^2)$	1	15.16707
$K_B (1/(mol/L))$	15	3.155769
	Experiment 3	
$\mathbf{k}_{\mathbf{A}}\left(\frac{\mathrm{mol/gcat}}{(\mathrm{mol/L})\cdot\mathrm{min}}\right)$	1	0.0088041
K (mol/L)	1	101.9955
$K_{\rm R}  (1/({\rm mol}/{\rm L})^2)$	1	8.407307
K <sub>B</sub> (1/(mol/L))	15	6.423856

Table 7. Linear regression of activation energy and constant.

Variable	Constant	E <sub>a</sub> (j/mole)	Stati	stic
$k_A \ (\frac{\text{mol/gcat}}{(\text{mol/L}) \cdot \text{min}})$	2.0889	1475.29	R <sup>2</sup> R <sup>2</sup> <sub>adj</sub> R <sub>msd</sub> Variance	$\begin{array}{c} 0.425 \\ -0.151 \\ 0.068 \\ 0.041 \end{array}$

Variable	Constant	ΔH (j/mole)	Stati	istic
			R <sup>2</sup>	0.7045
$K \pmod{I}$	28 808	_10.980	R <sup>2</sup> <sub>adj</sub>	0.409
$\mathbf{K}$ (mor/ L)	-20.000	-10,700	R <sub>msd</sub>	0.281
			Variance	0.712
$K_{\rm R}  (1/({\rm mol}/{\rm L})^2)$			R <sup>2</sup>	0.443
	0.265	(500	R <sup>2</sup> <sub>adi</sub>	$\begin{array}{c} 0.7045\\ 0.409\\ 0.281\\ 0.712\\ \hline \\ 0.443\\ -0.113\\ 0.222\\ 0.442\\ \hline \\ 0.041\\ -0.918\\ 0.240\\ 0.520\\ \hline \end{array}$
	-9.203	-6322	R <sub>msd</sub>	0.222
			Variance	0.442
			R <sup>2</sup>	0.041
K <sub>B</sub> (1/(mol/L))	0.55	1052 059	R <sup>2</sup> <sub>adi</sub>	-0.918
	-0.57	1253.258	R <sub>msd</sub>	0.240
			Variance	0.520

Table 8. Linear regression of adsorption constants.

# 3. Materials and Methods

This section explains the approach, characterization tools, and analytical methods for conducting the experiments, analyzing the results, and developing the kinetics model. Figure 6 illustrates a systematic overview of the various aspects of this study and the tools and approaches used to investigate the use of the HZSM-5 catalyst for decarboxylation of Al-Fula crude oil. Specifically, there are three main parts of this study: (a) Characterization of the catalyst material to identify intrinsic attributes that will be used to determine the catalyst material. (b) Experimental testing with the help of a systematic design of experiments matrix to study system performance under a wide range of operating conditions. (c) Kinetics studies comprise mechanism evaluation, model validation, and regression for parameter estimation.



**Figure 6.** Flowchart diagram showcasing the methodology used in this research to investigate the ability of HZSM-5 catalyst to remove naphthenic acid from acidic crude oil.

# 12 of 23

# 3.1. Materials

Al-Fula crude oil, representing the acidic crude oil used in this study, was obtained from the Central Petroleum Laboratories (CPL) of the Sudan Ministry of Energy and Oil. The physicochemical properties of this crude oil are listed in Table 9. HZSM-5 Zeolite catalyst was procured from a proprietary source, while chemicals, such as toluene, isopropanol, and potassium acid phthalate were obtained from the Shifak Company in Sudan.

Table 9. The physiochemical properties and the corresponding ASTM standard are used for quantification.

Properties	Result	Method
Density @ 15 °C, kg/m <sup>3</sup>	927.5	ASTM D4052
Specific Gravity	0.9283	ASTM D4052
API°	20.93	ASTM D4052
Viscosity @100 °C, mm <sup>2</sup> /s	38.07	ASTM D7024
Pour point, °C	-1	ASTM D5853
Carbon residue, m%	4.41	SH/T 0170-92
Water Content, m%	0.50	ASTM D4006
Salt Content As Nacl mg/L	3.6	ASTM D6470
Acid number, mg KOH/g	6.5	ASTM D664
Sulfur, m%	0.127	ASTM D4294

#### 3.2. Catalyst Characterization

We have conducted X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM), and physisorption analysis to fingerprint the various aspects of the catalyst that entail its functionality. The XRD analysis was conducted to study the chemical composition and the crystal structure of the catalyst. The catalyst sample was recorded by a Rigaku Ultima IV diffractometer using Cu (K $\alpha$ ) radiation (40 kV/40 mA). Scans of 50 mg samples were recorded in the 2 $\theta$  range of 5–80° using a step of 0.02° and a step time of 2s. The pattern of X-ray diffraction analysis was compared with JCPDS (Joint Committee on Powder Diffraction Standards) reference data to identify the catalyst. Figure 7 shows the XRD pattern of the catalyst. The pattern exhibits sharp peaks located between  $2\theta = 7-9^{\circ}$  and  $2\theta = 23-25^{\circ}$ , which are the characteristic peaks of Mobil type five (MFI) structure of HZSM-5 zeolite catalyst with (Si/Al = 70, JCPDS: 89-1421) [36,37]. The catalyst is characterized as crystalline material due to the straightforward, sharp peaks present in the XRD pattern [30,38–40].



Figure 7. XRD pattern for HZSM-5 zeolite catalyst.

The SEM analysis is performed to determine the morphology and particle size of the catalyst sample. The equipment used for the SEM imaging was EFI Quanta 400 microscope operated at 200 kV. The images are displayed in Figure 8. The hexagonal-like particles,

which are the characteristic morphologies of MFI zeolite crystals (HZSM-5 type), are observed [41]. The mean particle diameter is observed to be around 383 nm as seen in Figure 9.



**Figure 8.** Scanning Electron Microscopy (SEM) surface images of HZSM-5 zeolite Catalyst with different magnifications.



Figure 9. Particle size distribution from SEM.

The Brunauer–Emmett–Teller (BET) method is used to calculate the surface area of the catalyst. The test is carried out at 77 K with liquid  $N_2$  (Micromeritics Tri-Star II 3020). Before the analysis, samples of about 100 mg are degassed at 473 K for 2 h in helium gas flow. The surface area is calculated using the BET equation (Equation (6)), whereas the total

pore volume and average pore radius are obtained from the Barrett–Joyner–Halenda (BJH) method. BET equation [42]:

$$\frac{1}{[n((P_0/P) - 1)]} = \frac{1}{n_m C} + \left[\frac{C - 1}{n_m C}\right] \times \frac{P}{P_0}$$
(6)

where n,  $n_m$ , and C are the adsorbed amount, the monolayer capacity, and a constant, respectively.

Nitrogen adsorption isotherm for the catalyst at 77 K and the Barrett–Joyner–Halenda (BJH) pore size distribution curve are displayed in Figure 10. The BET pore size, pore volume, and the surface area identified using this approach are listed in Table 10. The adsorption isotherm of the catalyst is classified as Type 1 (Adsorption on micropores) [43]. The Barrett–Joyner–Halenda (BJH) pore size distribution curve exhibits a maximum value at around 12 nm and drops to near zero above 50 nm. The catalyst has a surface area of  $300 \text{ m}^2/\text{g}$  with a pore volume of 0.18 cm<sup>3</sup>/g and a pore size of 25 Å. As shown in Figure 10 and Table 10, the HZSM-5 zeolite catalyst has a wide pore radius distribution and a high surface area that facilitates the penetration of naphthenic acids to the pores of the catalyst while providing sufficient area for decarboxylation reaction.



**Figure 10.** (**a**) BET nitrogen adsorption isotherm; (**b**) Barrett-Joyner-Halenda (BJH) pore size distribution curve.

Table 10. BET analysis Results.

Sample	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Size (Å)
HZSM-5 zeolite catalyst	300	0.18	25

#### 3.3. Analytical Method for TAN Number Determination

The ASTM D664 standard potentiometric titration apparatus or ASTM D974 colorimetric apparatus is generally used to measure TAN. The former is utilized in this work because it is more accurate for dark and colored samples which is the case in this study. The ASTM D664 potentiometric titration apparatus consists of an electrode, voltmeter/PH meter, stirrer, and a burette to add the titrant. Table 11 below provides the correct sample sizes of crude oil that should be weighed to measure TAN. The steps to evaluate the TAN number are provided in Figure 11 [44]. The reagents needed for the test are potassium hydrogen phthalate (KHP), isopropyl alcohol, toluene, and CO<sub>2</sub>-free water. The electrode was washed well with the titration solvent before using it to avoid errors in measurements. The titration solvent used in this work was 0.1 N potassium hydroxide [45].

TAN [mg KOH/g Sample]	Sample Weight [g]	Weighing Accuracy [30]
0.05–0.9	$10\pm 2$	100
1–4.9	$5\pm0.5$	20
5–19	$1\pm0.1$	5
20–99	$0.25\pm0.02$	1
100–250	$0.1\pm0.01$	0.5

Table 11. Indication for a correct sample size of the potentiometric titration method.



Figure 11. Block diagram of ASTM D664 potentiometric titration test steps.

The TAN calculation equation is as follows [44]:

$$\Gamma AN = \frac{(V_E - V) \times M \times 56.1}{W}$$
(7)

where,

 $V_E$  = Volume of potassium hydroxide titrated until equilibrium (mL)

V = Volume of potassium hydroxide from titration of blank (mL)

M = Potassium hydroxide concentration (mol/mL)

W = Mass of the sample (g)

#### 3.4. Experimental Section

This section presents the details on the configuration of the experimental setup, the approach used to sequence the experiments using full factorial design, and finally the various steps required to develop reaction kinetics. The experimental apparatus consisted of a 500 mL glass batch reactor and was fabricated at the University of Khartoum glassware shop. The reactor has a maximum temperature rating of 1000 °C. The reactor is heated with a heating mantle and subjected to uniform stirring. The vacuum pump, valve, and temperature controlling system (thermocouple and controller) are connected to the reactor. The experiment is conducted by following a sequence of steps that comprise weighing the catalyst and crude oil, loading the chemicals in the reactor, and adjusting the desired temperature and pressure.

#### 3.4.1. Naphthenic Acid Removal Assessment

A DOE matrix is developed to study the effect of temperature, time, and oil:catalyst ratio on naphthenic acid removal via catalytic decarboxylation over HZSM-5 zeolite. Factorial design is a powerful tool to study the effects and interactions between the various parameters. This approach helps in the identification of the various factors involved in the process that have a profound impact on the targeted response. Moreover, it reduces the number of experiments required to study the effect of different factors by eliminating redundancies [46–49].

A three-factorial design (i.e., three factors with three levels each) is employed as shown in Table 12. The levels are selected according to the optimized results reported by Zhang et al. [1]. Based on Zhang et al.'s [1] recommendations, the low, medium, and high levels of temperature are set at 250 °C, 270 °C, and 300 °C, respectively. The low, medium

and high levels of time are set at 2, 3 and 4 h, respectively. The low, medium, and high levels of oil:catalyst ratio are set at 25, 22, and 20 g/g, respectively. On the other hand, TAN is selected as a response variable. The experimental design matrix is generated by MINITAB<sup>®</sup> software, and the results are analyzed by analysis of variance (ANOVA) and coefficient of determination ( $R^2$ ).

**Table 12.** DOE matrix of the low, medium, and high levels of temperature, time, and oil:catalyst ratio using 3<sup>3</sup> Factorial frameworks.

Factors	Low Level (–)	Medium Level (0)	High Level (+)
Temperature (T in °C)	250	270	300
Time (t in h)	2	3	4
Crude Oil/Zeolite ratio (R in g/g)	25	22	20

The primary purpose of ANOVA is to identify which design parameters affect the quality characteristic. This method identifies whether the results of the experiment are significant. ANOVA table consists of a sum of squares, a corresponding degree of freedom, the F value, and the *p*-value [34].

The Pareto chart lists the effect of each variable from largest to smallest effect. The reference line in the chart depends on the value of alpha which equals 1 minus the confidence level for the analysis. When the bar in the Pareto chart crosses the reference line, the effect will be considered significant [50].

The percentage of acid removed is evaluated using the initial and the final TAN values as per the following equation [20]:

Acid removal% = 
$$\frac{\text{Initial TAN} - \text{Final TAN}}{\text{Initial TAN}} \times 100$$
 (8)

## 3.4.2. Kinetic Modeling and Regression Analysis

The kinetics model is developed based on experimental data generated from a batch differential reactor described in Figure 12. The following are the experimental conditions that are used to create the kinetic model: temperature 250, 270, and 300°, pressure: -0.2 bar, stirring rate: 425 rpm, and oil:catalyst ratio: 25 g/g. A flowchart (Figure 13) illustrates a systematic approach to kinetic assessment.



**Figure 12.** An illustration of the experimental setup. (1) Batch reactor; (2) Heating mantle; (3) Feed; (4) Condenser; (5) Mechanical agitator; (6) Vacuum pump; (7) Thermocouple and (8) Temperature controller.



Figure 13. A flow chart describing a systematic procedure to conduct the kinetic assessment.

Laboratory experiment data in the batch differential reactor

The data used to develop the kinetics model development and regression are obtained for the HZSM-5 zeolite catalyst under various conditions as provided in Table 13. Equations (9)–(11) are used to calculate the rate of reaction based on the finite differential method [51].

Initial point : 
$$\left(\frac{dC_{A}}{dt}\right)_{t0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$
 (9)

Intermediate point : 
$$\left(\frac{dC_A}{dt}\right)_{ti} = \frac{1}{2\Delta t} \left[ \left( C_{A(i+1)} - C_{A(i-1)} \right) \right]$$
 (10)

Endpoint : 
$$\left(\frac{dC_A}{dt}\right)_{t5} = \frac{1}{2\Delta t}[(C_{A3} - 4C_{A4} + 3C_{A5})]$$
 (11)

**Table 13.** Laboratory Experiment at Temperature: 250, 270, and 300 °C, pressure: -0.2 bar, stirring rate = 425 rpm, and oil:catalyst ratio: 25 g/g.

Temperature (°C)	Time (min)	TAN (mg KOH/g)	C <sub>A</sub> (mol/L)	dC <sub>A</sub> /dt (mol/L∙min)
250	0	6.5	0.10655	0.00039
	120	3.36	0.05508	0.00019
	180	2.42	0.03967	0.00014
	240	1.24	0.02032	0.00012
270	0	6.5	0.10655	0.00068
	120	1.4	0.02295	0.00025
	180	1.04	0.01705	0.00009
	240	0.05	0.00082	0.00012
300	0	6.5	0.00053	0.10655
	120	2.18	0.00026	0.03574
	180	0.85	0.00013	0.01393
	240	0.35	0.0000074	0.00574

Reaction Mechanism: The naphthenic acids are cyclic or aromatic carboxylic acids (containing cyclopentane and cyclohexane rings) with a general formula RCOOH; Catalytic decarboxylation is a chemical conversion method that utilizes a catalyst to convert acids to hydrocarbons and carbon dioxide. Essentially, the C-C bond in the carboxylic acid is broken down to release  $CO_2$  gas in this reaction. Another possible definition is the replacement of the carboxyl group (-COOH) with a hydrogen atom while releasing  $CO_2$  gas [1,23,24].

$$R-COOH \rightarrow R-H + CO_2 \qquad [Overall Reaction] \qquad (R1)$$

where R is a side group made of carbon, hydrogen, and other atoms. Therefore, the products of the decarboxylation reaction of naphthenic acids correspond to alkane (R-H) and carbon dioxide (CO<sub>2</sub>) [25,52].

Since the HZSM-5 zeolite catalyst is an acidic solid catalyst, the mechanism of decarboxylation over the acid catalyst is dependent on acid centers. Fu (2008) found that there are two types of acid centers on the acidic solids, the Brønsted acidic center, and the Lewis Center. According to the mechanism, naphthenic acids contain negative charges that are concentrated on oxygen atoms of the carbonyl section. Through the catalytic decarboxylation process brønsted acids centers give protons that are combined with oxygen atoms. Additionally, Lewis acidic centers have many low energy empty orbits that tend to combine with naphthenic acid present in crude oil. The two methods eventually result in the decomposition of the acid functional group while releasing CO<sub>2</sub> [25]. The mechanism of catalytic decarboxylation reaction over HZSM-5 zeolite catalyst is described by reactions 2 to 4 [25,52,53].

 $RCOOH + s \Leftrightarrow RCOOH.s \qquad [Adsorption of Reactant] \qquad (R2)$ 

 $RCOOH.s \Leftrightarrow RH.s + CO_2 \qquad [Surface Reaction] \qquad (R3)$ 

$$RH.s \Leftrightarrow RH + s \qquad [Desorption of Products] \qquad (R4)$$

# Development of kinetic rate equation:

ii.

The assumptions made to develop the kinetics model in the current study are as follows:

- i. The reactor was assumed to be operated under isothermal conditions.
  - The external diffusion is assumed to be negligible due to the high stirring rate, which avoids the formation of films around the catalyst. Moreover, the internal diffusion was negligible as a powder catalyst with particle size <1  $\mu$ m was used (Refer to Figure 9 for particle size distribution). Therefore, the time to diffuse into and out of the pellet is almost instantaneous.

The kinetics for catalytic decarboxylation of naphthenic acid using the LH mechanism have not been reported earlier. Since this reaction is significant in the crude oil refining industry, the kinetics model developed in this work will be necessary for designing new plants. It should be noted that the kinetics of ketonization and esterification of acetic acid on iron oxide [54] and kinetics of ketonization of carboxylic acids over  $Ru/TiO_2$  catalyst using the LH mechanism have been reported earlier [55]. However, these topics are different from the decarboxylation of naphthenic acid using zeolite catalyst, which is the subject of the present study.

The LH kinetics model approach is one of the most popular methods to develop heterogeneous reaction kinetics. For the proposed decarboxylation of naphthenic acid reaction, the LH model development comprises the following three steps [56]: (i) Adsorption of naphthenic acids on the surface. (ii) Surface reaction to form intermediate (alkane in the current case) while releasing  $CO_2$  gas. (iii) Desorption of alkane intermediate from the surface [51]. Three separate derivations were performed, assuming one of the steps above as the slowest, and therefore, signifying the rate-determining step. Below is one set of derivations for the adsorption-limited reaction, while the other two are provided in the Supplementary Materials.

For adsorption-limited reactions, the surface and desorption specific reaction rate constants ( $k_S$  and  $k_D$ ) are enormous by comparison, therefore,

$$\frac{r_{\rm S}}{k_{\rm s}} \sim \frac{r_{\rm D}}{k_{\rm D}} \sim 0 \tag{12}$$

Adsorption Rate Equation:

$$\mathbf{r}_{\mathrm{ADS}} = \mathbf{k}_{\mathrm{A}} \left[ \mathbf{C}_{\mathrm{A}} \mathbf{C}_{\mathrm{S}} - \frac{\mathbf{C}_{\mathrm{A} \cdot \mathrm{S}}}{\mathbf{K}_{\mathrm{A}}} \right]$$
(13)

19 of 23

Surface Reaction Rate Equation

$$r_{\rm S} = k_{\rm s} \left[ C_{\rm A\cdot S} - \frac{C_{\rm B\cdot S} C_{\rm C}}{K_{\rm S}} \right] \tag{14}$$

**Desorption Rate Equation:** 

$$\mathbf{r}_{\mathrm{D}} = \mathbf{k}_{\mathrm{d}} \left[ C_{\mathrm{B}\cdot\mathrm{S}} - \frac{C_{\mathrm{B}}C_{\mathrm{S}}}{K_{\mathrm{D}}} \right] \tag{15}$$

$$C_{A\cdot S} = \frac{C_{B\cdot S}C_C}{K_S} \tag{16}$$

$$C_{B \cdot S} = K_B C_B C_S \tag{17}$$

Substitution of Equations (16) and (17) into Equation (13) gives

$$\mathbf{r}_{ADS} = \mathbf{k}_{A} \left[ \mathbf{C}_{A} \mathbf{C}_{S} - \frac{\mathbf{K}_{B} \mathbf{C}_{B} \mathbf{C}_{S} \mathbf{C}_{C}}{\mathbf{K}_{A} \mathbf{K}_{S}} \right]$$
(18)

$$r_{ADS} = k_A \left[ C_A - \frac{K_B C_B C_C}{K_A K_S} \right] C_S$$
(19)

 $Total \ sites = Vacant \ sites + Occupied \ sites$ (20)

$$C_{\rm T} = C_{\rm S} + C_{\rm A\cdot S} + C_{\rm B\cdot S} \tag{21}$$

Substituting Equations (16) and (17) in Equation (21)

$$C_{\rm T} = C_{\rm S} + \frac{K_{\rm B}C_{\rm B}C_{\rm S}C_{\rm C}}{K_{\rm S}} + K_{\rm B}C_{\rm B}C_{\rm S} \tag{22}$$

$$C_{\rm T} = C_{\rm S} \left( 1 + \frac{K_{\rm B} C_{\rm B} C_{\rm C}}{K_{\rm S}} + K_{\rm B} C_{\rm B} \right) \tag{23}$$

$$C_{\rm S} = \frac{C_{\rm T}}{\left(1 + \frac{K_{\rm B}C_{\rm B}C_{\rm C}}{K_{\rm S}} + K_{\rm B}C_{\rm B}\right)} \tag{24}$$

After combining Equations (19) and (24), we obtain:

$$r_{ADS} = \frac{k_A C_T \left[ C_A - \frac{K_B C_B C_C}{K_A K_S} \right]}{\left( 1 + \frac{K_B C_B C_C}{K_S} + K_B C_B \right)}$$
(25)

$$K = \frac{K_A K_S}{K_B}$$
(26)

$$K_{\rm R} = \frac{K_{\rm B}}{K_{\rm S}} \tag{27}$$

Finally, after substituting Equations (26) and (27) into Equation (25), we obtain the rate of decarboxylation reaction with the adsorption rate-limiting step:

$$r_{ADS} = \frac{k_A \left[ C_A - \frac{C_B C_C}{K} \right]}{\left( 1 + K_R C_B C_C + K_B C_B \right)}$$
(28)

Similarly, we derived the rate laws for the other two possible rate-limiting steps. All rate laws were listed in Table 14.

Rate Limiting Step	Rate Equation
Adsorption	$r_{\text{ADS}} = \frac{k_{\text{A}} \left[ C_{\text{A}} - \frac{C_{\text{B}} C_{\text{C}}}{K} \right]}{(1 + K_{\text{R}} C_{\text{B}} C_{\text{C}} + K_{\text{B}} C_{\text{B}})}$
Surface reaction	$r_S = \frac{k \left[C_A - \frac{C_B C_C}{K}\right]}{(1 + K_A C_A + K_B C_B)}$
Desorption	$r_{\rm D} = \frac{k \left[\frac{C_{\rm A}}{C_{\rm C}} - \frac{C_{\rm B}}{K_{\rm P}}\right]}{\left(1 + K_{\rm A}C_{\rm A} + \frac{K_{\rm B}C_{\rm A}}{C_{\rm C}}\right)}$

Table 14. Rate laws for each rate-limiting step.

# *Parameter Estimation:*

The non-linear rate equations are fitted to the experimental data using Polymath<sup>®</sup> software. The Arrhenius law is incorporated to evaluate the temperature dependency for pre-exponential factors and activation energy. Additionally, Arrhenius and Van 't Hoff's equation is used to investigate the relationship between the kinetic parameter, adsorption constant, and temperature as illustrated by Equations (29) and (30). The investigation is conducted at temperatures of 250, 270 and 300 °C.

$$\mathbf{k} = \mathbf{k}_0 \mathrm{e}^{-\mathrm{E}_\mathrm{A}/\mathrm{RT}} \tag{29}$$

$$K = K_0 e^{-\Delta H_{ads}/RT}$$
(30)

# ASPEN<sup>®</sup> Plus Simulation:

To study the performance of the kinetics model and the parameters, an ASPEN<sup>®</sup> Plus simulation has been developed. In particular, the Rbatch kinetics reactSectionor has been used, which is analogous to the experimental setup. The reactor was initialized at experimental conditions of 270 °C temperature, 0.8 bar pressure, and catalyst loading of 8 g. Vapor-liquid was selected as a valid reaction phase.

$$r = \frac{(\text{kinetic factor})(\text{driving force expression})}{(\text{adsorption term})}$$
(31)

where

$$\begin{split} & \text{Kinetic factor: } k'' \left( \frac{T}{T_0} \right)^n e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)} \text{ or } k'' e^{-\frac{E}{R} \left( \frac{1}{T} \right)} \\ & \text{Driving force expression: } k_1 \prod_{i=1}^N C_i^{a_i} - k_2 \prod_{j=1}^N C_j^{b_i} \\ & \text{Adsorption term: } \left( \sum_{i=1}^M K_i \left( \prod_{J=1}^N C_j^{v_i} \right) \right)^m \end{split}$$

# 4. Conclusions

This work demonstrates catalytic decarboxylation of naphthenic acid using a HZSM-5 zeolite catalyst for TAN reduction of highly acidic crude oil. In particular, the influence of reaction temperature (250 °C, 260 °C, and 270 °C), oil:catalyst ratio (20, 22, and 25 g/g), and reaction time (0 h to 4 h) was studied in detail. The assessment showed that the removal of naphthenic acid increases with an increase in temperature and reaction time. However, the oil:catalyst ratio has a different effect at a low-temperature condition of 250 °C than at a high temperature of 270 °C. Specifically, a higher oil:catalyst ratio of 20 g/g is necessary for a low temperature of 250 °C, instead of a lower ratio of 25 g/g for a higher temperature of 270 °C. This behavior could be attributed to the activation of side reactions by the excess catalyst at a higher temperature of 270 °C. However, dedicated future studies will be required to ascertain this understanding. A two-way and three-way interaction between the three parameters using the DOE matrix enabled a better understanding of the effect of the parameters on naphthenic acid removal. The maximum removal percentage obtained from this assessment was 99.23% at 270 °C, 4 h, and 25 g/g oil/catalyst ratio.

The kinetics model developed in this work utilized the LH approach to derive rate expression while assuming adsorption rate, desorption rate, and surface reactions as ratelimiting steps. The rate expression based on the adsorption rate-limiting step provided the best regression results and validation using ANOVA and Pareto charts. The rate expression developed in this work will aid future simulation studies and scalability assessments, especially for designing new refineries based on acidic crude oil.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12050495/s1.

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#### Nomenclature

А	RCOOH
Adj SS	Adjusted sums of squares
Adj MS	Adjusted mean squares
ANOVA	Analysis of variance
В	RH
С	CO <sub>2</sub>
C <sub>A·S</sub>	The concentration of component A adsorb on site
C <sub>B·S</sub>	The concentration of component B adsorb on site
CO <sub>2</sub>	Carbon dioxide
Cs	Vacant sites
CT	Total sites available
DF	Degree of Freedom
E	Activation Energy
F-Value	Test statistics use in the analysis of variance
$\Delta H_{ads}$	heat of adsorption
k	Kinetic constant
Κ	Equilibrium constant
KHP	Potassium Hydrogen Phthalate
Р	Pressure
<i>p</i> -Value	Analysis of variance test gives the significance of each factor
R	Gas constant
R <sup>2</sup>	Coefficient of determination
R <sup>2</sup> <sub>adj</sub>	Adjusted Coefficient of determination
r <sub>ADS</sub>	Rate of adsorption
r <sub>D</sub>	Rate of desorption
R <sub>msd</sub>	root-mean-square deviation
r <sub>S</sub>	Rate of surface reaction
Т	Temperature
TAN	Total acid number

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