Sudan University of Science & Technology
College of petroleum Engineering
Department of Transportation & Refining

Reduction of Total Acid Number (TAN) of El-Fula Crude Oil by Zeolite and Magnesium Oxide

تقليل الاحماض النفثينية من خام الفولة باستخدام الزيولايت واكسيد الماغنزيوم

A Project Submitted in Partial Fulfillment of the Requirements for the Degree of B.SC. (Honors) in Transportation & Refining Engineering

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الآية

بسم الله الرحمن الرحيم

﴿ وقل ربي زدني علما ﴾

صدق الله العظيم

Dedication

Great thanks to Allah, for giving us patience and power to finish this project

&

Sincere appreciation to our parents

Acknowledgements

We would like to acknowledge our supervisors ***Dr. Dallia Mamon Basher & Dr. Nihad Omer Hassan*** *for their help and support.*

We are deeply thankful to ***Dr. Waleed Salih Ibrahim Osman*** *for his assistance and useful suggestions in the experiments.*

We also want to thank the ***Team*** *in* ***Crude lab*** *in* ***Petroleum Laboratories, Research &Studies***

Thanks also extended for everybody who gave us some of his precious time.

Abstract

The objective of this project is to reduce the naphthenic acids from Al-Fula crude oil by using decarboxylation technology based on magnesium oxide and zeolite as catalysts. The naphthenic acid reduction operation started by experimental studies in petroleum laboratories, research and studies.

The project involves a description of the catalysts (zeolite & magnesium oxide) behaviour, and the assay of AL- Fula crude oil according to the 2015 results.

It's also includes mechanism which is used in the catalytic reactions and technology used to reduce the naphthenic acids. Finally the experimental data of AL-Fula crude analytically compared with California crudes by magnesium oxide catalyst. It was found that the total acid number (TAN) of AL-Fula crude, Moga [AL-Fula crude oil sample according to central processing facilities-using magnesium oxide] decreased from 7.56 to 6.45 and, Keye [AL-Fula crude oil sample according to central processing facilities] using zeolite decreased from 3.31 to 1.56.

التجريد

الهدف من هذا البحث هو تقليل الاحماض النفثينية الموجودة في خام الفولة باستخدام تقنية ازالة الأحماض النفثينية بأستخدام اكسيد الماغنيزيوم والزيولايت كعوامل حفازة.

بدأت عملية تقليل الاحماض النفثينية عن طريق تجارب معملية في المعامل والبحوث والدراسات النفطية.

يحتوي البحث على وصف للعوامل الحفازة المستخدمة (الزيولايت,اكسيد الماغنيزيوم) وتكوين خام الفولة لعام 2015.

يحتوى البحث أيضا على ألألية المستخدمة في التفاعل وعلى التقنية المستخدمة لتقليل الاحماض النفثينية كما يحتوي على مقارنة نتائج التجارب المعملية لخام الفولة وخام كلفورنيا بنفس الحفاز المستخدم (أكسيد الماغنيزيوم) حيث تم تقليل الرقم الحمضي لخام الفولة (للعينة موجا بأستخدام أكسيد الماغنيزيوم) من 7.56 الى 6.45 وتم تقليل الرقم الحمضي لخام الفولة (للعينة كايي بأستخدام الزيولايت) من 3.31 الى 1.56 .

Table of Contents

List of Figures

List of Tables

Chapter 1
Introduction

1.1 Introduction

Liquid petroleum, or crude oil, is a complex mixture of organic compounds predominately composed of hydrocarbons, and often contains large amounts of other compounds such as organic and inorganic sulfur species, chloride and nitrogen compounds, oxygen compounds, trace metals and naphthenic acids. Liquid petroleum is thus a mixture of cyclic, aromatic, and linear monocarboxylic acids present in the crude oil with the general formula $C_n H_{2n+z} O_2$, (where n indicates the number of carbon atoms and z indicates the deficiency of hydrogen because of the presence of cyclic or aromatic groups) (Zhang, 2006).

The chemical composition of naphthenic acids (NAs) is extremely complex and a great variety of structures and compositions fall within the classification of NA. In general, NAs is characterized by a carboxylic acid functional group attached to a hydrocarbon molecule, and a generalized chemical formula of $R(CH_2)_n COOH$ can be applied where R is a cyclopentane ring and n is typically greater than 12. However, a multitude of other acidic compounds are also present, and the chemistry of petroleum related naphthenic acids has yet been completely characterized Calcium naphthenates are particularly bad actors (Shah, 2016).

The acid number of oils is mainly caused by naphthenic acid. The term [naphthenic acids] is used to account for all carboxylic acids present in crude oil, including acyclic and aromatic acids, which are complicated mixtures. Aromatic rings or fused aromatics are usually present in high-molecular-weight acids. On the other hand, two-third of the naphthenic

acid produced is converted to metal salts for various applications as important raw material in the chemical industry, such as wood preservative, paint driers, lubricants, and fuel additives, timber antiseptic (Sun, 2012).

The problems associated with the presence of naphthenic acids in the crude oil can be avoided by a number of approaches, such as neutralization, solvent extraction, adsorption, thermal decomposition, catalytic decarboxylation, and esterification.

Pure naphthenic acids are important raw material in the chemical industry. Two-third of the naphthenic acids produced is converted to metal salts for various applications, such as wood preservatives, paint driers, lubricants, and fuel additives (Shah, 2016).

Corrosion problems in refinery equipment arise during the processing of highly acidic crude oils. Corrosion because of naphthenic acids occurs at temperatures between 200 and 400 °C and primarily affects the transfer pipes between the heating furnaces and atmospheric and vacuum distillation units.

A metal oxide catalyst, MgO has been developed and its effectiveness in catalysing decarboxylation reactions involving carboxylic acids compounds such as naphthenic acids has been determined based on the formation of CO2 and the conversion of acids.

1.2 Problem statement

The presence of NAs compounds contributes to the acidity of crude oils and is one of the major sources of corrosion in oil pipelines distillation units in oil refineries, harmful for the production equipment, storage and transport facilities, and can reduce the service performance of oil consequently. This leads to high maintenance costs, and may create environmental disposal problems. Hence, crude oils with high naphthenic

acid concentrations are considered to be of poor quality and marketed at a lower market price.

This study was executed to remove the naphthenic acid in crude oils using alkaline earth metal oxide (MgO) and zeolite (Shah, 2016).

1.3 Objectives

The objectives of this research are:

1. Measure TAN of light Fula crude.
2. Study the ability of MgO catalyst to reduce naphthenic acids.
3. Study the ability of zeolite catalyst to reduce naphthenic acids.
4. Study the effect of temperature on the acid conversion.
5. Analyse the results obtained from MgO and zeolite.

Chapter 2

Literature Review

2.1 Previous Studies of Decarboxylation Technology

In 2002-2003, Zhang et al, developed both glass and stainless steel micro batch type reactors for the fast screening of various catalysts with reaction substrates of model carboxylic acid compounds and crude oil samples (Zhang, 2005).

In 2006, Zhang et al, studies of MgO has been developed and its effectiveness in catalysing decarboxylation reactions involving carboxylic acid compounds such as naphthenic acid has been determined based on the formation of CO2 and the conversion of acid (Zhang, 2006).

In 2012, Mandal et al, work to reduce total acid number (TAN) from NA in an environmentally benign way, suppressing the solid deposition using supercritical water (SCW) (Mandal, 2012).

In 2015, Osman, W.S.I, reduced total acid number (TAN) of some Sudanese crude oils (remove of naphthenic acid) by zeolite and clays (Osman, 2015).

In 2016, Faisal Zafara et al, reduced the TAN of NAs was by using subcritical methanol and then a mixture of 1-butyl-3methylimidazolium octyl sulphate ([BMIM] [C8HSO4]) and subcritical methanol (Zafar, 2016).

2.2 The background of Decarboxylation Technology

The term "decarboxylation" literally means removal of a carboxyl group (-COOH) and its replacement with a hydrogen atom. The term relates the state of the reactant and product. Decarboxylation is one of the oldest known organic reactions, since it often entails simple pyrolysis, and volatile products distilled from the reactor. Heating is required

because the reaction is less favourable at low temperatures. Yields are highly sensitive to conditions. In retrosynthesis, decarboxylation reactions can be considered the opposite of homologation reactions, in that the chain length becomes one carbon shorter. Metals, especially copper compounds are usually required. Such reactions proceed via the intermediary of metal carboxylate complexes (Smith, n.d.).

2.3 Naphthenic acids

The term naphthenic acid has roots in the somewhat archaic term “naphthene” (cycloaliphatic but non-aromatic) used to classify hydrocarbons. It was originally used to describe the complex mixture of petroleum-based acids when the analytical methods available in the early 1900s could identify only a few naphthene type components with accuracy (Qian, 2001).

Today "naphthenic" acids is used in a more generic sense to refer to all of the carboxylic acids present in petroleum, whether cyclic, acyclic, or aromatic compounds, and carboxylic acids containing heteroatoms such as N and S. Although commercial naphthenic acids often contain a majority of cycloaliphatic acids, multiple studies (Clemente, 2005).

Naphthenic acids (NA) are a complex mixture of organic acids, they naturally occur in crude oils as a complex mixture of saturated acyclic, monocyclic and polycyclic carboxylic. The presence of acidic compounds in crude oils tends to cause aggravated equipment corrosion, especially at high temperature (230 – 400°C), and this leads to high maintenance costs, may pose environmental disposal problems and low quality of the crude oils produced. Therefore, any reduction in naphthenic acids content would alleviate corrosion related problems (SHOHAIMI, n.d.).

2.3.1 Chemical Structure

The name naphthenic acid is derived from the early discovery of monobasic carboxylic acids in petroleum, with these acids being based on a saturated single-ring structure. The low molecular weight naphthenic acids contain alkylated cyclopentane carboxylic acids, with smaller amounts of cyclohexane derivatives occurring. The carboxyl group is usually attached to a side chain rather than directly attached to the cycloalkane. The simplest naphthenic acid is cyclopentane acetic acid. Naphthenic acids are represented by a general formula CnH2n−z O2, where n indicates the carbon number and z specifies a homologous series. The z is equal to 0 for saturated, acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids. Naphthenic acids in the range of C-7 to C-12 consist mainly of monocyclic acids. The more complex acids contain larger proportions of multicyclic condensed compounds (Brient, 2000).

2.3.2 Properties

- A brown viscous liquid, MW: 180~350.
- A variable composition and ingredients at high temperature.

2.3.3 Characterization of naphthenic acids

The most abundant NA components are carboxylic acids with a COOH group attaching to an alkyl-substituted saturated ring with a chemical formula of Ring-(CH2) m-COOH. Here, the ‘Ring’ represents a combination of saturated 5-member and 6-member ring structure and the (CH)m is the carbonyl chain, the COOH group can either directly attach to the ring or to the alkyl-chain. Classifications of this group of NA based on its chemical formula and the ring structure have been made via representing their homologues by a general formula CnH2n+ZO2, where n indicates the carbon number and Z specifies a homologous series. The

relation between the Z value and number of the saturated ring N can be established:

$$N = - Z/2 \text{ (saturates)} \quad (1)$$

Although saturated carboxylic acids are the predominant compounds found in most crude oils, aromatic and even heterocyclic compounds have also been reported. For example, an early investigation by the Royal Dutch/Shell Laboratory at Amsterdam of NAs from the lubrication oil found more than 50% of saturates, but also found over 15% of monoaromatics and about 10% of diaromatics1. A more detailed analysis on the aromatic compounds separated by Elution SiO2 and Gel Permeation Chromatography (GPC) by Seifert and colleagues found more aromatic compounds, such as naphthalene, fluorine's, Pyrenees etc. A recent 13C NMR analysis also found the chemical shifts in the 120-150 ppm region, which confirms the presence of aromatic carbons. For aromatics we have:

$$N < - Z/2 \text{ (aromatics)} \quad (2)$$

Another classification method is based on double bond equivalent (DBE)

$$DBE = 1 + \Sigma \tfrac{1}{2} [Ni (Vi - 2)] \quad (3)$$

Where Ni is the number of atoms of element i, Vi is the valence of atom i. Since VC = 4, VH = 1 and VO = 2, a relation between DBE and the Z number for carboxylic acids can be established as:

$$DBE = 1 - Z/2 \text{ (carboxylic acids)} \quad (4)$$

It is worth noting that DBE represents more general compositions than that of the Z-number representation, not only for its applicability for aromatics, but also for its extension to more complex compounds containing other elements. For example for the sulfur (S) and nitrogen (N) compounds that widely exist in crude oils. However, the Z-number is more useful to distinguish more detailed isomeric structures of the

carboxylic acids. A comparison of the Z-numbers and DBE of some aromatics and their saturated carboxylic acid forms (Figure 2.1) is listed in (Table 2.1). (Zhang, 2005).

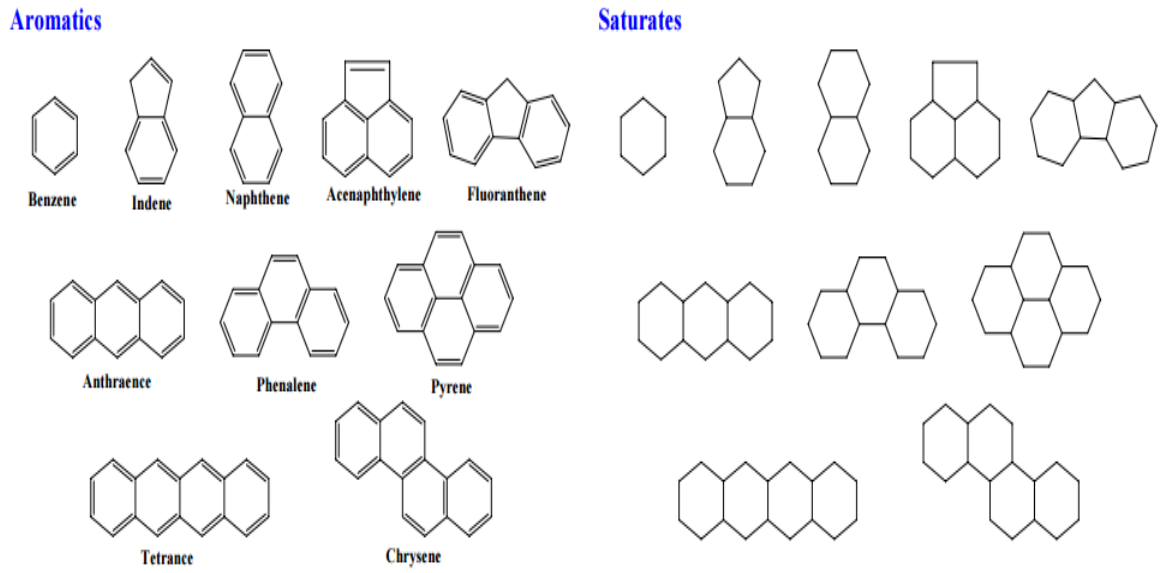


Figure (2.1): Different ring structures of the hydrocarbon backbones to be attached by the carboxylic acid to form the naphthenic acids.

Table (2.1): Calculated Z-numbers and the Double Bond Equivalent of Selected Naphthenic Acids

Ring	Saturates			Aromatics		
	Formula	Z	DBE	Formula	Z	DBE
Benzene	$C_7H_{12}O_2$	-2	2	$C_7H_6O_2$	-8	5
Indene	$C_{10}H_{16}O_2$	-4	3	$C_{10}H_8O_2$	-12	7
Naphthalene	$C_{11}H_{18}O_2$	-4	3	$C_{11}H_8O_2$	-14	8
Acenaphthylene	$C_{13}H_{20}O_2$	-6	4	$C_{13}H_8O_2$	-18	10
Fluoranthene	$C_{14}H_{22}O_2$	-6	4	$C_{14}H_{10}O_2$	-18	10
Anthraence	$C_{15}H_{24}O_2$	-6	4	$C_{15}H_{10}O_2$	-20	11
Phenalene	$C_{15}H_{24}O_2$	-6	4	$C_{15}H_{10}O_2$	-20	11
Pyrene	$C_{17}H_{26}O_2$	-8	5	$C_{17}H_{10}O_2$	-24	13
Tetracene	$C_{19}H_{30}O_2$	-8	5	$C_{19}H_{12}O_2$	-26	14
Chrysene	$C_{19}H_{30}O_2$	-8	5	$C_{19}H_{11}O_2$	-26	14

2.4 Total Acid Number (TAN)

Total acid number is defined as the amount of potassium hydroxide (KOH) (in mg) required to neutralize 1 gram of oil sample. As determined by ASTM D664, the test method for Acid Number of Petroleum Products done by semi micro colour titration, it provides an indication of the organic acid content of a crude oil. It will also indicate the presence of remnant inorganic acids such as hydrochloric and hydrofluoric acids that may have been used in production well work over operations. If TAN > 0.5 mg KOH/g, it is considered that the corrosion is high.

2.4.1 World Bank correlated discount price as a function of TAN

- Less than 0.5 TAN no discount
- Above this each point of excess TAN lowers the price of crude by $0.051 per dollar of Brent
- Excess defined as TAN of crude oil minus TAN of Brent (0.07)

- World Bank correlates discount as function of API gravity, sulfur content, and TAN.

2.4.1.1 EXAMPLE DISCOUNT CALCULATION

- Fula Crude TAN = 7.7mg KOH/g
- Brent Price – US$50 per barrel
- Discount = (7.7-0.07)*0.051*50
  = 19.46 $/bbl.

High TAN crude oils are commonly encountered in California, Venezuela, the North Sea, Western Africa, India, China and Russia. High Acid Crudes (HAC) which have a TAN > 1.0, are projected to increase from 7.5% of total supply in 2000 to 10% in 2010 (to around 9 million barrels/day). HACs are found all over the world as follow:

- Gryphon (North Sea) → 4.2 mg KOH/g
- Doba (Chad) → 4.7 mg KOH/g
- Some Syncrudes (Canada oil shale) → 2 to 3 mg KOH/g
- Light fula crude (Sudan) → 7.7 mg KOH/g

2.4.2 Current Solutions

- Blending to bring average TAN to < 1.
- Continuous injection of corrosion inhibitors – Nalco's SCORPION.
- Upgrade material of construction to a higher chrome or molybdenum in severely corroded areas of plant (Crude Oil Quality Group, 2006).

2.5 Fula Crude oil

The Fula oil is an oil field located in Muglad Basin, it was discovered in 2001 and developed by China National Petroleum Corporation, it began production in 2004. The total proven reserves of the Fula oil field are around 745 million barrels (100*10^6 tonnes) and production is cantered on 55,000 barrels per day (8,700 m^3/d).

2.5.1 Light Fula Crude Assay

Table (2.2): Feed Stock

Test	Method	Unit	Results
Density at 15 C	ASTM D5002	g/cm^2	0.8639
Specific Gravity	ASTM D5002	Degree	0.845
API Gravity	ASTM D5002		32.16
Kinematic Viscosity @ 80 C	ASTM D445	mm^2/s	9.903
Kinematic Viscosity @ 100 C	ASTM D445	mm^2/s	7.436
Pour Point	ASTM D97	C	39
Micro Carbon Residue	ASTMD4530	%Wt.	2.47
Water	ASTM D4006	%vol	0.30
Asphaltine Content	IP 143	%Wt.	0.25

Total Acid Number	**ASTM D664**	**mgKOH/g**	**7.7**
Total Sulphur	**ASTM D4294**	**%m**	**0.0713**
Compositional Analysis	**ASTM D2887**		**
As	**ICP**	**PPM**	**< 0.0281**
Fe			**5.153**
K			**1.307**
Na			**3.232**
Ni			**7.087**
V			**0.0867**
Mg			**0.9762**

Ca			**25.94**
Pb			**<0.0150**

Chapter 3
Methodology

3.1 Experimental methods for crude oil

3.1.1 Crude oil sample

All the crude oil tests were performed with a crude oil sample that was provided by Sudanese Petroleum Corporation (SPC), which is our industrial collaborator for this project. This particular crude oil is typical of many acidic, sour, and viscous oil with TAN, sulfur-content and the API gravity values of 7.7, 7.13% and 32.16 (60°F) respectively.

The structures and physical properties of the carboxylic acids used in this study were listed in Table (3.1).

3.1.2 Catalyst materials and catalyst preparation

Two types of solid catalysts, which are alkaline earth metal oxides (MgO) and zeolite were involved in this study. For MgO, it was calcined at 800°C for 10hrs prior to use for activation.

A strong acidic zeolite, ZSM-5 type zeolites were applied in this work. The materials were obtained from ZEOLYST and the products data were shown in Table (3.2). The high SiO2/Al2O3 ratios indicate their strong acidities. Before the running, all of the three zeolites were activated at 450°C overnight. With this treatment, the ammonium type zeolites (CBV 3024E and CBV 8014E) could be converted to their hydrogen type.

Table (3.1): Structures and properties for several carboxylic acids

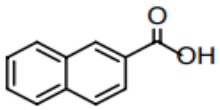
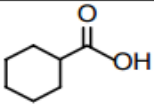
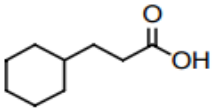
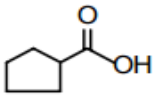
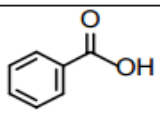
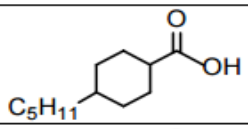
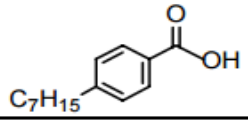
Carboxylic Acids	Structures	Molecular Weight	MP(°C)	BP(°C)
2-Naphthoic acid		172.18	185.5	>300
Cyclohexane carboxylic acid		128.17	31.5	232.5
Cyclohexanepropionic acid		156.22	16.0	276.5
Cyclopentane carboxylic acid		114.14	4.0	216.0
Benzoic acid		122.12	122.4	249.2
Trans-Pentylcyclohexanecarboxylic acid		198.31	51-53	110.0
4-Heptyl benzoic acid		220.31		

Table (3.2): Data of ZSM-5 type zeolites

Catalyst	SiO_2/Al_2O_3 Mole ratio	Nominal cation form	Na_2O Weight %	Surface Area (m^2/g)
CBV 3020E	30	Hydrogen	0.10	400
CBV 3024E	30	Ammonium	0.05	400
CBV 8014E	80	Ammonium	0.05	425

The zeolites were activated overnight at 450°C prior to use.

Supposing this treatment can convert ammonium type zeolite to hydrogen type zeolite.

3.1.3 Total acid number measurement

Determination of the Total Acid Number is a key technology for this project. Following the procedure of ASTM standard method D664, we developed the in-lab TAN measurement method. Briefly, this measurement involves a non-aqueous acid-base potentiometric titration using a specific solvent mixture including toluene 50.0%, iso-propanol 49.5% and water 0.5% (v/v) with which to dissolve the oil samples. An mV/pH meter (Oakton PH510 Series) was used to record the potential change. The major operation steps consist of the followings.

- Preparation of potassium acid phthalate (KHC8H4O4 or KHP) standard solution – heat KHP in oven at 80°C for about 10hrs to remove moisture. Accurately weigh the heated KHP and dissolve it into CO2-free pure water in a flask. Add water to the graduation of the flask and then calculate the mole concentration of the prepared solution.
- Preparation of alcoholic potassium hydroxide solution – Add 6g of KOH to approximately 1L of anhydrous iso-propanol. Boil gently for 30min to increase the solubility of KOH in the solution. Store the solution overnight and then standardize the solution with the prepared KHP solution.
- Standardization of alcoholic KOH solution – Standardize the solution with potentiometric titration of weighed quantities of KHP dissolved in CO2-free water.
- Preparation of oil sample – Dissolve 1-5g oil sample in 125ml titration solvent (500ml toluene/495ml anhydrous iso-propanol/5ml water), filter the sample and transfer the prepared solution to a 250ml beaker, which is used as the titration vessel.

- Titration of KOH to oil sample – Add suitable amount of KOH alcoholic solution and wait until a constant potential has been observed, then record the solution used and meter readings. When the sample was titrated close to the inflection point, add less drops of KOH and record the meter carefully. For each set of samples, make a blank titration of the titration solvent.
- Calculation – Plot the volumes of KOH solution added versus the corresponding electrode potential (mv). Mark the inflection points A and B for oil sample and solvent 17 only, which should reflect the largest potential changes for a unit KOH. Calculate the TAN as the equation

Acid number, mg KOH/g = (**A**-**B**) ×**M**×56.1/**W** (5)

M: Concentration of alcoholic KOH solution, mole/L.

W: Sample mass, g.

A: volume, in millilitres, of titrant required for the determination.

B: volume, in millilitres, of titrant required for the blank test.

	In our experiment	Oil Analysis Lab
TAN	7.71 mgKOH/g	7.7 mgKOH/g

3.2 Batch reaction – reactor, operation and analysis

Batch reactors were used for crude oil tests. The geometries and reactor volumes were different depending on the purposes of the experiments. For most oil tests, bottle shaped autoclaves were used which have reaction volume of about and 250 ml.

A highly acidic, sour, and viscous crude oil produced in Muglad Basin, SD provided by Sudanese Petroleum Corporation (SPC) was used in our studies.

About 250ml batch reactors (bottle shape) were used for crude oil reaction. Approximately 75 grams of acidic crude and 25 grams' catalyst were mixed in a batch reactor for three sample of acidic crude individually (Keye, Moga heavy and Hadida). The bottles were agitated by a reciprocal shaker in order to maintain a well-mixed system. At last, the bottles were placed in oven and the reaction can be started under controlled reaction condition. The reactions were typically carried out in the temperature range of 140 to 160°C for 5 hours.

After the reactions, the reactors were taken out from the oven and the caps should be opened carefully because of the possible gas pressure. For the oil samples collected after the reaction, measurements for TAN were conducted and the results will be discussed in the next sector.

3.2.1 Zeolite based catalyst

As C-C cleavage is involved in decarboxylation reaction (R-COOH → RH+CO2), acidic catalyst becomes one of our choices. On the other hand, the application of acidic zeolite in oil refinery has well been established, typically being represented by the famous FCC process.

As for the application of zeolite in catalytic decarboxylation, there was only one report that discussed the involvement of zeolite in the reaction of benzoic acid. However, the operation condition was relatively too harsh to be realized in practical process. The major reactions happened in these different catalyst systems are listed in Table (3.3). To explore their application in organic chemistry as well as in practical processes becomes a new challenge (Zhang, 2005).

Table (3.3) major reactions happened in these different catalyst systems

Catalyst Type	Representative Catalyst	Major Reactions and Products
Alkaline earth metal oxide	MgO	$RCOOH \rightarrow RCOR + CO_2$
Oxidative metal oxides	Ag_2O, Cu_2O	$RCOOH \rightarrow RH + CO_2 + R\text{-}R$
Acidic zeolite	HZSM-5	$RCOOH \rightarrow RH + CO_2$
Supported precious metal	Pt/Al_2O_3	$RCOOH \rightarrow RH + CO_2$

Chapter 4

Results and Discussion

4.1 Results from batch reaction on MgO

As alkaline earth metal oxides were recognized to be effective to the acid removal and in particular, MgO shows decarboxylation activity for carboxylic acids, their effectiveness for naphthenic acid removal of crude oil needs to be identified as also. Table (4.1) shows that the TAN decreased from 7.59 to 6.46, corresponding to 15% acid removal rate. Figure (4.1) represents that the acid conversion increase with reaction time in the presence of MgO.

Table (4.1): TAN a analyses for the oil treated with MgO through a batch reactor

	Catalyst		Reaction			
Oil (g)	Composition	Weight (g)	Temp (°C)	Time (hr)	TAN	Conv (%)
75	-	-	70	-	7.59	-
75	MgO	25	140	2	6.55	13
75	MgO	25	140	5	6.46	15

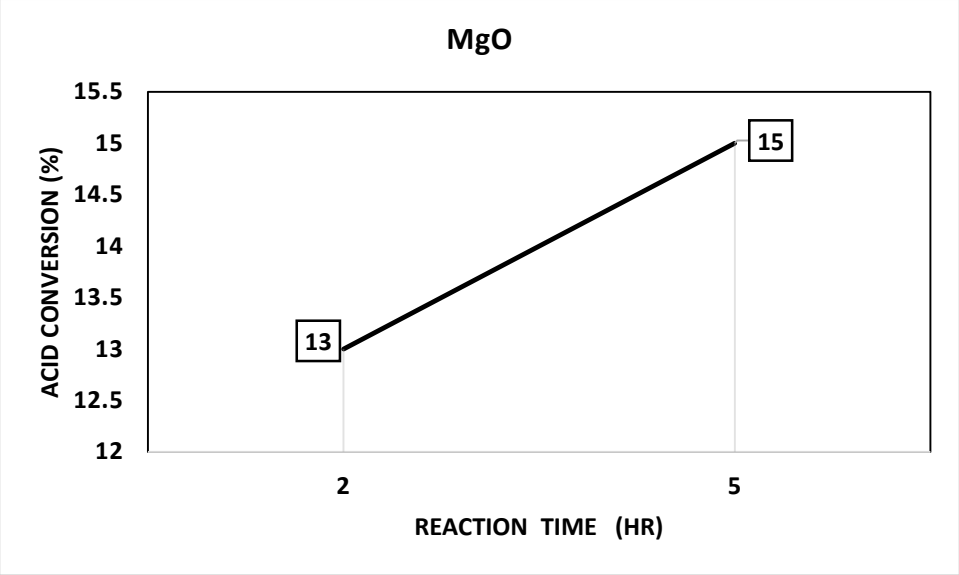


Figure (4.1): Increase of acid conversion with reaction time (MgO)

4.1.1 Behavior of the MgO catalyst

TAN reduction phenomenon can be explained by the presence of basic oxides such as MgO in the catalyst chemical composition. In Eq. (6) MgO reacts with the carboxylic acid groups of naphthenic compounds, via acid-base reaction, producing magnesium naphthenates, Mg (RCOO) 2, and water? Also, it can react with CO2 produced from thermal decarboxylation process, Eq. (7), leading MgCO3 and thus shifting the equilibrium of Eq. (8) for the decarboxylation reaction that produces CO2 (Dias, 2015).

$$2RCOOH \xrightarrow{MgO} Mg(RCOO)_2 + H_2O \quad (6)$$

$$RCOOH \xrightarrow{MgO} RH + CO_2 \quad (7)$$

$$MgO + CO2 \rightarrow MgCO_3 \quad (8)$$

Intrigued by the unique results from the MgO experiments, we have investigated its catalytic behavior in more detail. The temperature dependence of CO2 yield and acid conversion are shown in Figure (4.2). Over a temperature range from 100 to 300°C, a sharp increase in both the CO2 yield and the acid conversion was observed in the range of 150°C-

250°C, suggesting that the main reactions occur at this temperatures range. This temperature is within the acceptable range to meet our objective of identifying a low temperature decarboxylation catalyst. Figure (4.3) depicts the dependency of CO2 yield and acid conversion on the MgO loading. It can be seen that for loads of MgO up to 20 wt. %, CO2 yield and acid conversion increased almost linearly with the MgO loading. Further increases in the MgO loading gave little enhancement to CO2 yield and acid conversion, indicating the latter reaction is reaching saturation (Zhang, 2005).

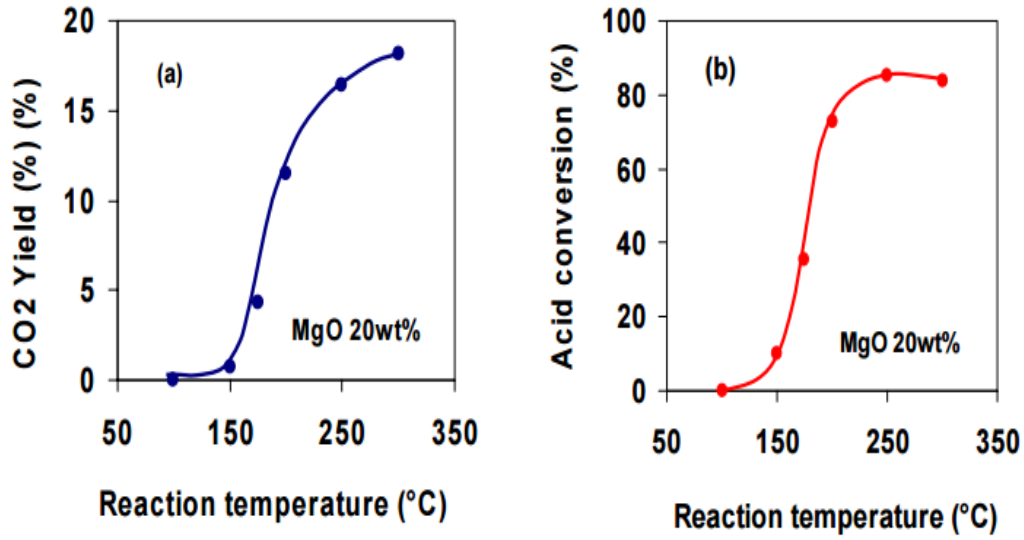


Figure (4.2): Effects of reaction temperature on naphthoic acid conversion and CO2 formation in the presence of MgO.

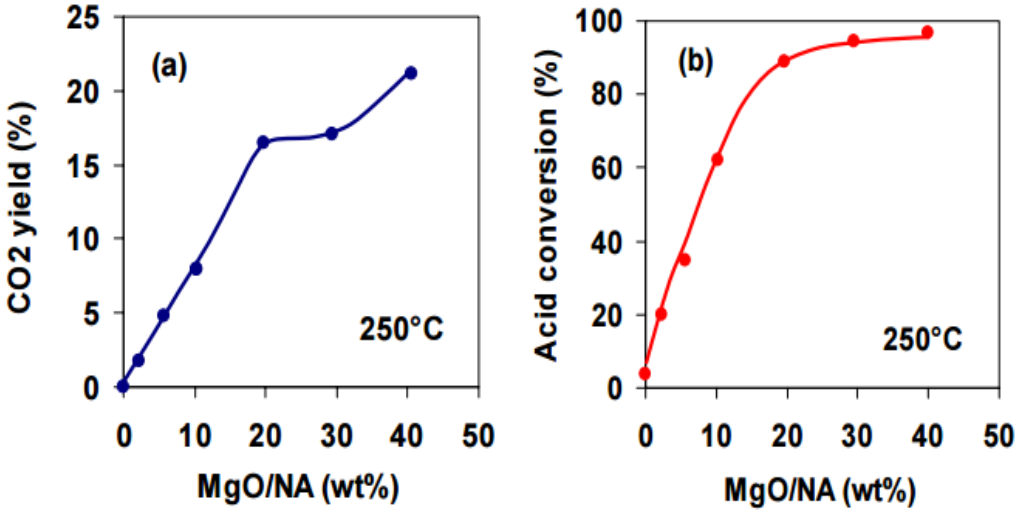


Figure (4.3): Effects of MgO loading on naphthoic acid conversion and CO2 formation in the presence of MgO.

4.2 Results from batch reaction on zeolite

Due to the large surface areas, unique pore structures, adjustable acid-base features for these special group materials, zeolites have extensive applications in petrochemical industry.

The data in Table (4.2) shows the TAN decreased from 3.31 to 1.56, corresponding to 52% acid removal rate. Figure (4.4) represents that the acid conversion increase with reaction time in the presence of zeolite.

Table (4.2): TAN analyses for the oil treated with zeolites through a batch reactor

	Catalyst		**Reaction**			
Oil (g)	Composition	Weight (g)	Temp (°C)	time (hr)	TAN	Conv (%)
75	-	-	70	-	3.31	-
75	zeolites	25	140	3	1.76	46
75	zeolites	25	140	5	1.56	52

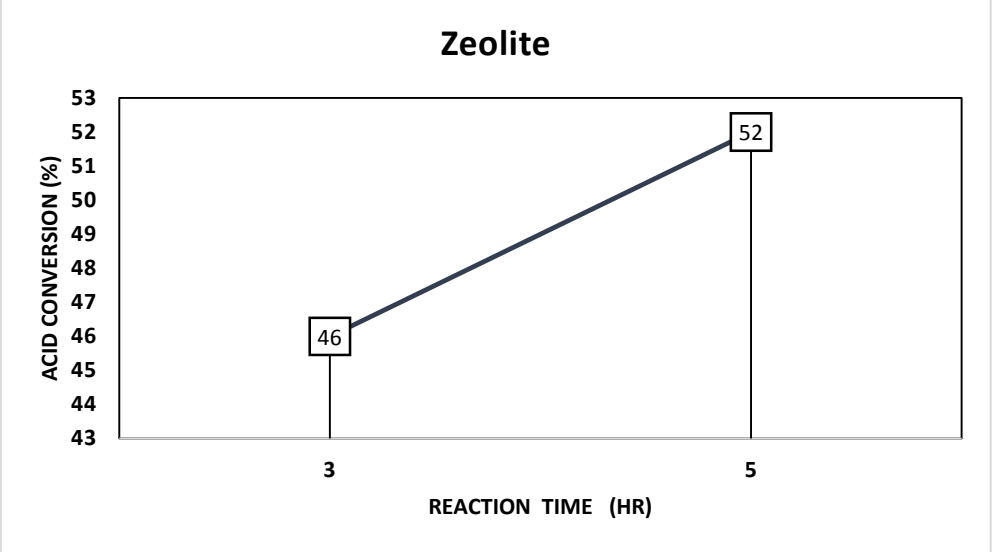


Figure (4.4): Increase of acid conversion with reaction time (Zeolite)

4.3 Results from batch reaction on pure sample

It is known that thermal treatment results in partial cracking for the oil components, accompanied by the formation of gases, lighter oils and coke. Major traditional and newly developed heavy oil upgrading processes such as visbreaking are based on this thermal cracking principle. As thermal treatment will also causes the decomposition for some naphthenic acid. Figure (4.5) shows the TAN concentration changes with the thermal treatment temperatures. It was shown that TAN decrease slowly with the temperature increase

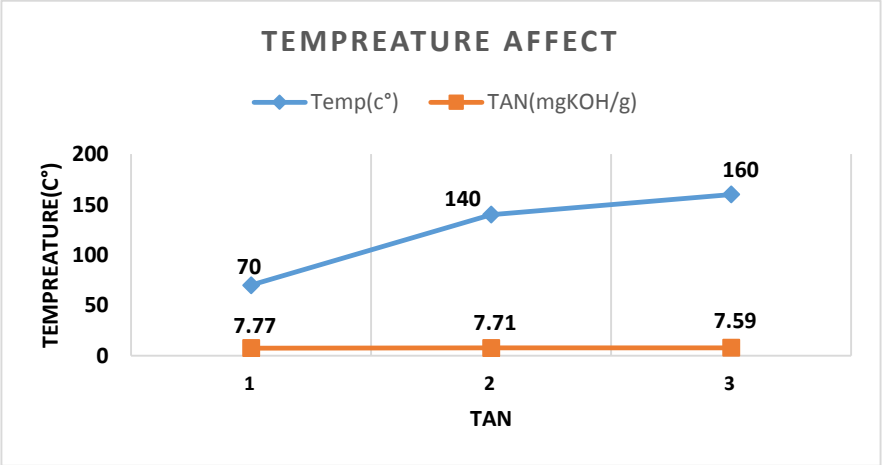


Figure (4.5): Represent that TAN decreasing slowly while temp increase (Al-Fula crude oil)

In addition to that, based on experimental data on California crude, in the temperature range from 250 to 400°C. TAN concentration changes with the thermal treatment temperatures. Figure (4.6) shown that TAN decrease slowly with the temperature increase until 350°C (Zhang, 2005).

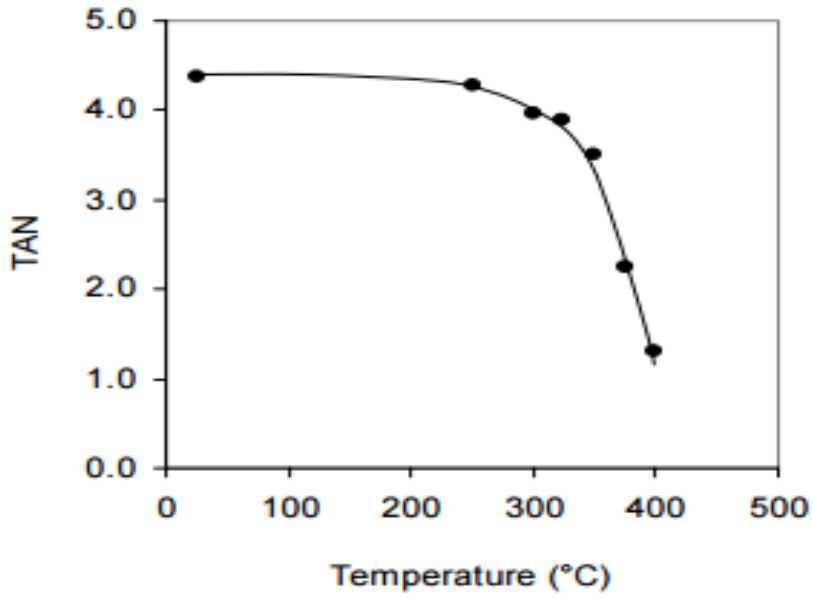


Figure **(**4.6) shown that TAN decrease slowly with the temperature increase (California crude).

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion:

From the above discussion in chapter 4 it is concluded that the reduction of light fula crude TAN was achieved.

1. Based on our experimental investigation with acidic crude, it was found that a strong acidic zeolite and MgO catalysts show excellent catalytic decarboxylation activities at relative low temperature 140-1600°C. The efficiency of NAs removal was characterized by TAN measurement. The results of batch reaction catalytic tests exposed the effectiveness of MgO catalyst that can reduce TAN from 7.59 (moga heavy sample) to 6.46, and the effectiveness of zeolite catalyst that can reduce TAN from 3.31 (keye sample) to 1.56. The temperature and catalyst load on acid conversion was analysed. The catalytic decarboxylation reactions must be carried out in temperature range between 200 to 400 C°.

In summary, due to our experiment the NA in crude oil can be effectively removed and the quality of the oil can be upgraded.

5.2 Recommendations:

From the previous results it is strongly recommended that:

1. More studies must be done in this field to reach optimum TAN content.

2. Applying the study of removal naphthenic acid petroleum industry as a unit in refineries to reduce equipment's corrosion.
3. There are three methods to do oil-catalyst separation. Three methods, thermal filtration, solvent dissolving followed by filtration and centrifuge separation were commonly used for the separation purpose. Dichloromethane, which was an excellent solvent for crude oil, was commonly used. But in this work we could not use any one of them for many limitations.

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Appendices

SAMPLE TYPE : Crude Oil

SAMPLE ID : Keye heavy

CUSTOMWER REFERENCE :

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0044	
-Vol of titration	ml	1.5056	
-Vol of blank	ml	0.1529	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	3.31	

SAMPLE TYPE : Crude Oil

SAMPLE ID : Keye heavy zeolite

CUSTOMWER REFERENCE : AFTER 3hr

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0098	
-Vol of titration	ml	0.8725	
-Vol of blank	ml	0.1529	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	1.76	

SAMPLE TYPE : Crude Oil

SAMPLE ID : Keye heavy zeolite

CUSTOMWER REFERENCE : AFTER 5hr

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0096	
-Vol of titration	ml	0.7941	
-Vol of blank	ml	0.1529	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	1.56	

SAMPLE TYPE : Crude Oil

SAMPLE ID : moga heavy

CUSTOMWER REFERENCE :

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0037	
-Vol of titration	ml	3.2136	
-Vol of blank	ml	0.1143	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	7.59	

SAMPLE TYPE : Crude Oil

SAMPLE ID : moga heavy MgO

CUSTER REFERENCE : AFTER 2hr

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0066	
-Vol of titration	ml	2.7516	
-Vol of blank	ml	0.1143	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	6.46	

SAMPLE TYPE : Crude Oil

SAMPLE ID : Moga heavy (MgO)

CUSTOMER REFERENCE : After 5hr

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0078	
-Vol of titration	ml	2.7949	
-Vol of blank	ml	0.1143	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	6.55	

SAMPLE TYPE : Crude Oil

SAMPLE ID : moga heavy pure

CUSTOMWER REFERENCE : AFTER 5hr

SAMPLE CODE : Cr-2097

DATE / TIME : 10-SEP-18

Properties	Unit	Method/Result	Done by
-TAN		ASTM D664	Malaz
-Equipment		848 Titrino plus	
-Weight of sample	g	2.0020	
-Vol of titration	ml	3.2862	
-Vol of blank	ml	0.1143	
-Normality of titration	n	0.08750	
-Total Acid Number	mgKOH/g	7.77	