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REDUCTION TOTAL ACID NUMBER (TAN) OF SOME SUDANESE CRUDE OILS BY ZEOLITE AND CLAYS

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ABSTRACT

The aim of this study was to reduce total acid number (TAN) of some Sudanese crude oils (remove of naphthenic acid) by zeolite and clays. Two sample of zeolite and two samples of clay were used in this study, samples were collected from Hamshcoreep, Glabat and Hatana in east and middle Sudan, and synthetic zeolite was brought from Khartoum refinery. Samples were characterized by X-ray Diffraction (XRD) and the results showed that they are composed of Enstatite, Feldspar, N. Zeolite and synthetic Zeolite. These four samples were used to treat four portions of crude oil (obtained from two types of Sudanese crude oil, Fula blend and Tharjath blend). Total acid number (TAN) of crude oil samples was measured using 484 potentiometric titration instrument (ASTM D644) before and after treatment. One sample of clay, Enstatite, was characterized by Infrared (IR) before and after treatment with crude to insure the presence of acidic material on it after treatment. According to the obtained results, it is evident that Enstatite clay reduced TAN from 1.44mgKOH/g to 0.05mgKOH/g, natural Zeolite reduced TAN from 7.7mgKOH/g to 5.9mgKOH/g, Feldspar reduced TAN from 1.37mgKOH/g to 0.76mgKOH/g, and ZSM-5 Zeolite reduced TAN from 1.98mgKOH/g to 1.57mgKOH/g.
In conclusion, all Zeolites and clays used in this study succeeded in decreasing (TAN) of crude oil when they were treated in high temperature (200-220 deg°C.).

Keywords: *crude oil, naphthenic acid, total acid number (TAN), Zeolite, Enstatite, feldspar, clay.*

1. INTRODUCTION

1.1 Naphthenic acids in crude oil

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, trace metals and naphthenic acids. The name naphthenic acid (NA) is derived from the first observation of the acidity in naphthenic-based crude from the Baku Region, of Russia in 1920’s [1]. The chemical composition

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of NAs is extremely complex and a great variety of structures and compositions fall within the classification of NA [2, 3]. In general, NA is characterized by a carboxylic acid functional group attached to a hydrocarbon molecule, and a

generalized chemical formula of R(CH2)nCOOH 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. The presence of NA compounds contributes to the acidity of crude oils and is one of the major sources of corrosion in oil pipelines and distillation units in oil refineries [4-6]. Consequently, crude oils with high naphthenic acid concentrations are considered to be of poor quality and marketed at a lower price.

1.2. Total acid number

Total acid number (TAN), defined as the number of milligrams of KOH required neutralizing the acidity of one gram oil, is a commonly accepted criterion for the oil acidity, although its correlation with corrosive behavior is still controversial [7]. Based on this measurement, oils with a TAN number greater than 0.5 are classified as highly acidic. High TAN crude oils are commonly encountered in California, Venezuela, the North Sea, Western Africa, India, China and Russia.

1.3. Naphthenic acid removal techniques

Removing NA compounds from crude oils is regarded as one of the most important processes in heavy oil upgrading. Current industrial practices either depend on dilution or caustic washing methods to reduce the TAN number of heavy crude oils [8]. However, neither of these approaches is entirely satisfactory. For instance, blending a high TAN crude oil with a low TAN one may reduce the naphthenic acid content to an acceptable level, but the acidic compounds remain and the value of the low TAN oil is diminished. Caustic treatment can substantially remove NAs, but the process generates significant amounts of wastewater and emulsions that are problematic to treat. In particular, once an emulsion is formed, it is very difficult to remove.

Catalytic decarboxylation is a well-established chemical reaction in organic and biochemical processes that has been widely applied in organic synthesis and even applied to the identification of coal structure through oxidative decarboxylation [9]. Cu-based catalysts, predominately employed homogeneously, are commonly used [10,11], and in some cases, the presence of organic nitrogen compounds is also necessary [12]. Additionally, there are reports that ZrO2 can promote the catalytic decarboxylation of acetic acid in supercritical water (673K, 25-40MPa) [13]. Tungsten complexes facilitate catalytic decarboxylation of cyanoacetic acid through homogeneous catalysis [14]. Zeolite has also been applied in the catalytic decarboxylation of benzoic acid but the reaction occurred at around 400°C [15]. Nevertheless, most of these studies are limited to the delicate catalyst system such as transition metal complexes, which have relatively low stabilities at the increased temperatures. The application of them to crude oil is not practical.

The naphthenic acid, existing in complex mixture of organic compounds, can be selectively extracted and condensed through solid adsorbents. If the two processes can reach a complementary for each other, it would be an ideal concept for the process design. (16)

1.4. Zeolites

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural Zeolites have been identified during the past 200 years; the most common are Analcime, Ahabazite, Clinoptilolite, Erionite, Eerrierite, Heulandite, Laumontite, Mordenite, and Phillipsite. More than150 Zeolites have been synthesized; the most common are Zeolites A, X, Y, and ZMS-5. Natural and synthetic Zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

2. EXPERIMENTAL

2.1. Materials

Natural Zeolite and clay samples were collected from Hamshcoreep, Glabat and Hatana in east and middle Sudan), Synthetic Zeolites (ZSM-5) were brought from Khartoum Refinery Company, the two types of Sudanese crude oil used in this study (Tharjath crude oil and Fula heavy crude oil) have been provided by Central Petroleum Labs (Sudan).

2.2. Methodologies

2.2.1. XRD analysis

Zeolite and clay samples (natural and synthetic) were analyzed by XRD to estimate their composition (figure 1, 2, 3).

2.2.2. Determination of Total Acid Number

Total acid number (TAN) was measured for crude oil sample before and after treatment with Zeolites and clays using ASTM D664 test method (484 potentiometric titration instrument).

2.2.2.1. Apparatus

Meter, a voltmeter potentiometer that operates with an accuracy of 60.005 V and a sensitivity of 60.002 V over a range of at least 60.5 V when the meter is used with the electrodes specified when the resistance between the electrodes falls within the range from 0.2 to 20 MV, Sensing Electrode and Reference Electrode, Silver/Silver Chloride (Ag/ AgCl) Reference Electrode filled with 1M–3M LiCl in ethanol, Variable-Speed Mechanical,

Burette, 10-mL capacity, graduated in 0.05-mL divisions and calibrated with an accuracy of 60.02 mL. The burette shall have a tip that extends 100 to 130 mm beyond the stopcock and shall be able to deliver titrant directly into the titration vessel without exposure to the surrounding air or vapors. The burette for KOH shall have a guard tube containing soda lime or other CO_2-absorbing substance. Titration Beaker, 250 mL capacity, made of borosilicate glass or other suitable material. Titration Stand, suitable for supporting the electrodes, stirrer and burette.

2.2.2.2. Reagents

Ethanol, Hydrochloric Acid (HCl) Relative density 1.19, Lithium Chloride, LiCl. Lithium Chloride Electrolyte, Prepare a 1M–3M solution of lithium chloride (LiCl) in ethanol, Methanol ,Potassium Hydroxide, Propan-2-ol, Anhydrous, (less than 0.1 % H_2O). Toluene, Hydrochloric Acid Solution, Standard Alcoholic, (0.1 mol/L). (Mix 9 mL of hydrochloric (HCl, relative density 1.19) acid with 1 L of anhydrous propan-2-ol. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of approximately 8 mL (accurately measured) of the 0.1-mol/L alcoholic KOH solution diluted with 125 mL of CO_2-free water. Commercial Aqueous pH 4, pH 7 and pH 11 Buffer Solutions, Potassium Hydroxide Solution, Standard Alcoholic, (0.1 mol//L), Titration Solvent—(prepared by Adding 5 mL of water to 495 mL of anhydrous propan-2-ol and ,mixed well and Added to it 500 mL of toluene, Chloroform.

2.2.2.3. Procedure of TAN measurement

Around 2.1 gm. of the sample was dissolved in a 125 ml of the mixture of toluene and propan-2-ol containing 5 mL of distilled water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode. The meter readings were plotted automatically against the respective volumes of titrating solution and the end points were taken and Total Acid Number was calculated.

2.2.3. Crude oil sample treatment with zeolite and clay

(100) gram of Tharjath crude oil was treated with (50 gram) of Enstatite clay at 220 deg °C or 5 hours, (100 gram) of Tharjath crude oil was treated with (50 gram) of Feldspar clay at 220 deg °C for 5 hours, (100 gram of Tharjath crude oil was treated with (50 gram) of ZSM-5 zeolite at 220 deg °C for 5 hours and (100 grams) of Fula crude oil was treated with (50 gram) of natural zeolite at 220 deg°C for 5 hours.

3. RESULTS AND DISCUSSION

Table.1. Total acid number results before and after processing with zeolite and clays.

Crude type	T°C	Type of mineral	TAN Before (mgKOH/g)	TAN After (mgKOH/g)	reduction %
Tharjath blend	220	Enstatite	1.44	0.05	96.5
Fula blend	220	N. Zeolite	7.70	5.90	23.4
Thargath blend	220	ZSM-5 ZEOLITE	1.98	1.57	20.7
Thrgath blend	220	Feldspar	1.37	0.76	44.5

Table.2. Fula blend Oilgeneral properties(before treatment).

Test name	ASTM Method	Unit	Result
Density @15 C°	ASTM D5002	g/ml	0.9353
API	ASTM D5002	g/ml	19.66

S.G	ASTM D5002	g/ml	0.9361
Pour Point	ASTM D5853	C°	+15
TAN	ASTM D664	Mg koh/g	7.72
Kinematics Viscosity @ 50 C°	ASTM D445	Cst	593.0
MCR	ASTM D4530	Wt%	4.3

Table.3. Fulablend+Zeolite(general properties)after treatment.

Test name	**ASTM Method**	**Unit**	**Result**
Density @15 C°	ASTM D5002	g/ml	0.9444
API	ASTM D5002	g/ml	18.19
S.G	ASTM D5002	g/ml	0.9453
Pour Point	ASTM D5853	C°	+15
TAN	ASTM D664	Mg koh/g	5.93
Kinematics Viscosity @ 50 C°	ASTM D445	Cst	1012
MCR	ASTM D4530	Wt%	7.7

XRD result:

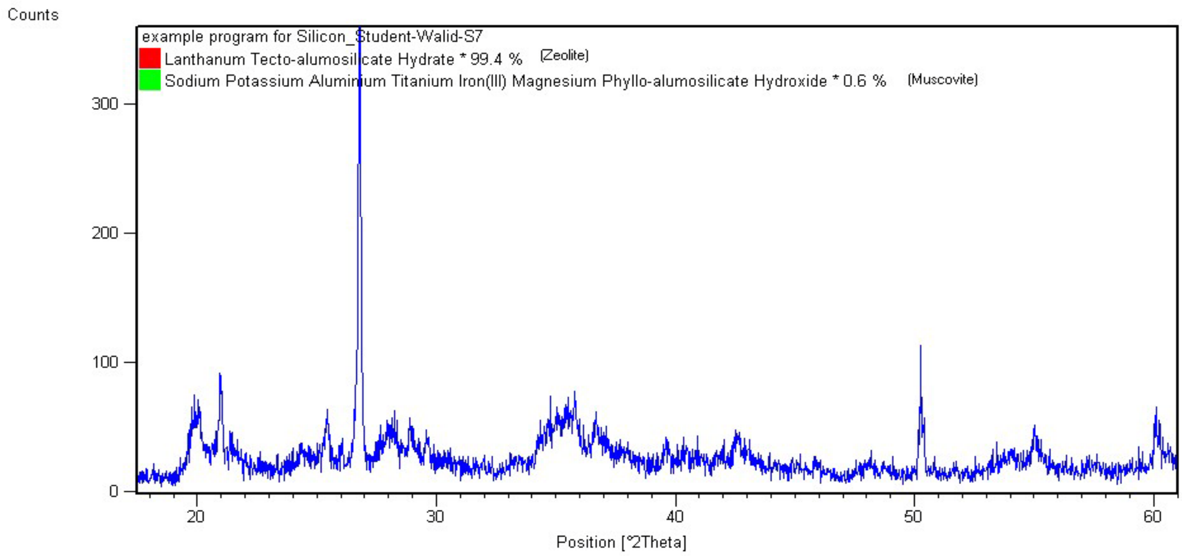

Fig.1. XRD result of natural zeolite sample.

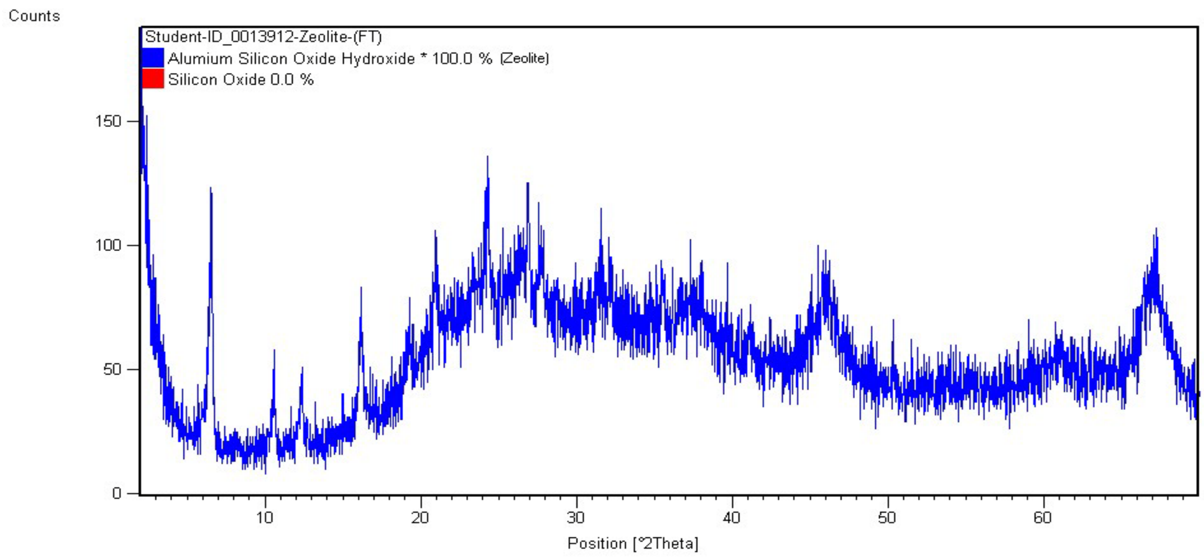

Fig .2. XRD Synthetic zeolite clay sample.

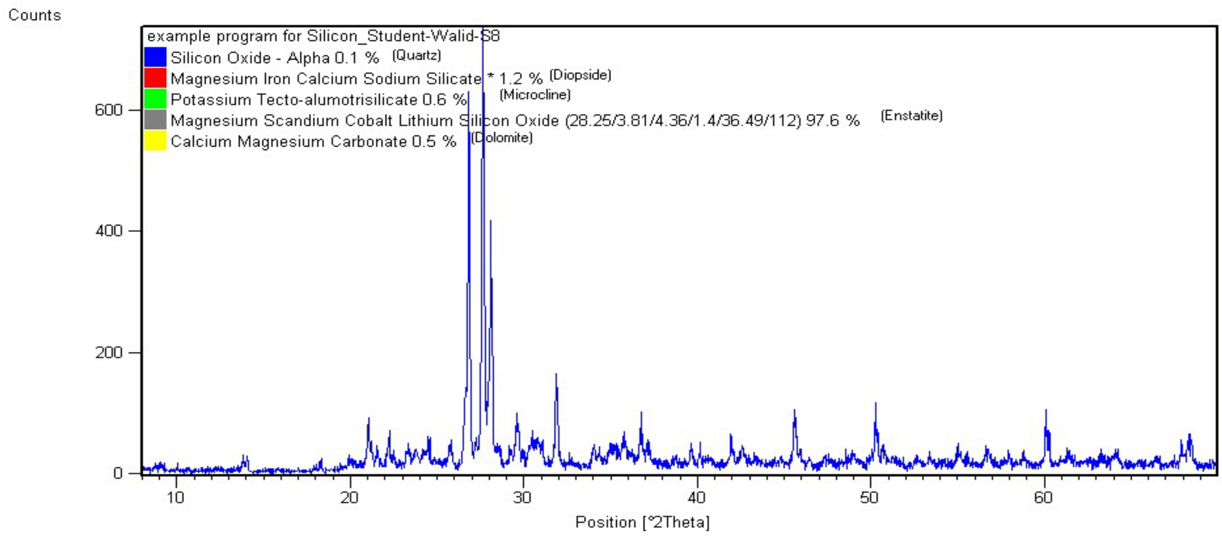

Fig.3. XRD result for Enstatite clay sample.

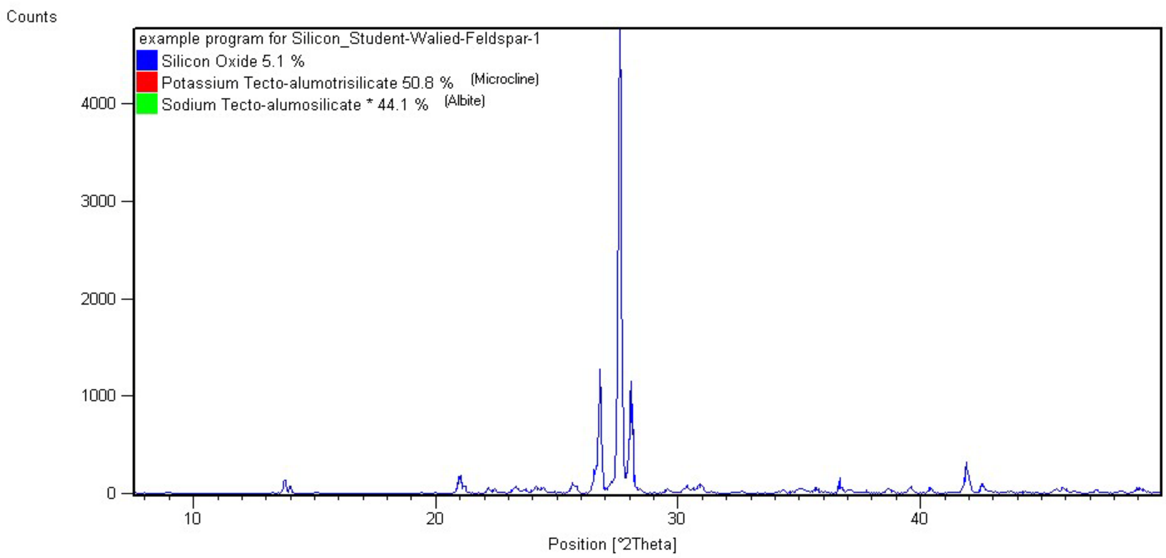

Fig.4.XRD result for Feldspar clay.

3.3 Infrared results:

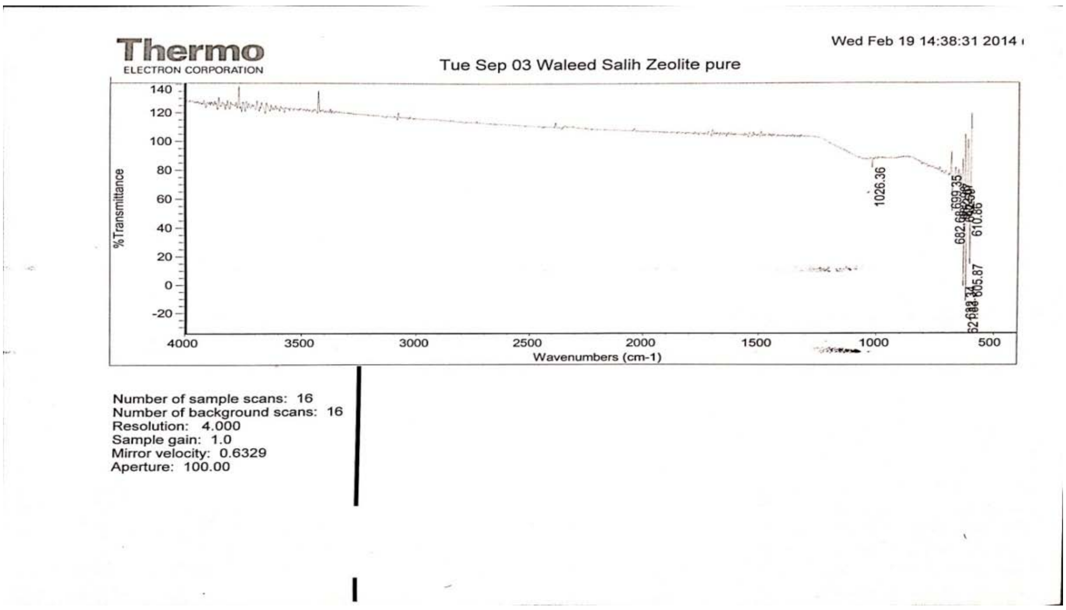

Fig.5. IR Spectrum for Enstatite clay before processing with Tharjath crude oil.

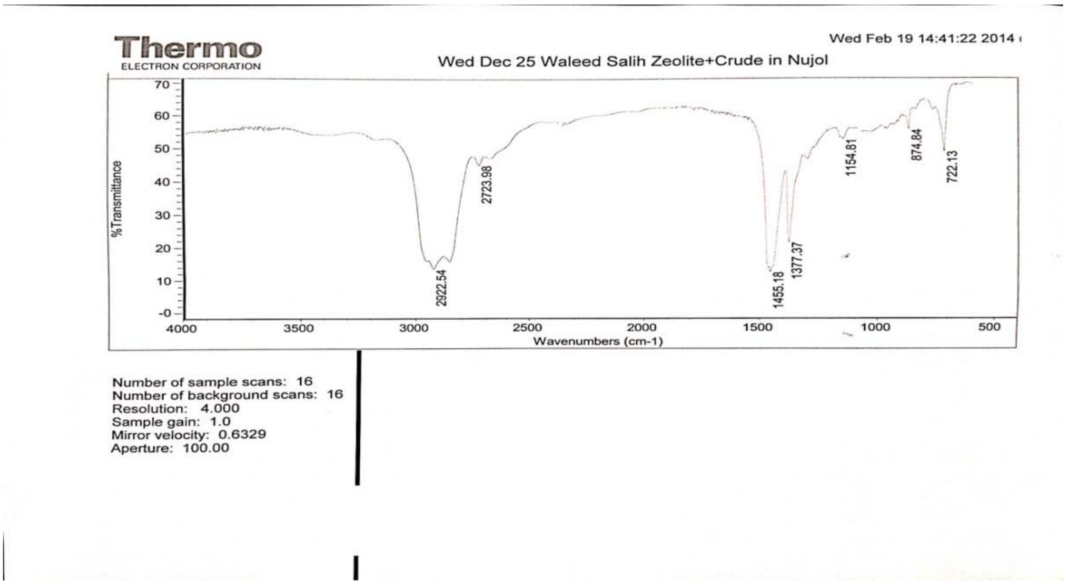

Fig .6. IR Spectrum for Enstatite clay after processing with Tharjath crude oil.

3.4 Discussion

In this study, four samples of crude oil were treated with four types of Zeolites and clay (catalysis). It was noticed that the four types of Zeolite and clays succeeded in decreasing TAN of crude oil at high temperatures (200-220 deg °C). The expected mechanism is the reaction of metal oxides exists in these four catalysts (for instance, around 97% of the Enstatite clay) with naphthenic acids according to coming equation:-

$$2RCOOH + MeO \rightarrow (RCOO)_2 Me + H_2O$$

Where

Me (Mg, Ca, Co, Li, .etc.)

Another mechanism also occur, an adsorption process happened for naphthenic acids on zeolites and clay surface.to investigate this probability, Enstatite clay was tested by IR before treatment with crude oil and no hydrocarbon compounds detected, whereas in the IR spectrum of the Enstatite clay after treatment with crude, numbers of weak peaks were noticed between 874.84 cm-1 and 722.1 cm-1 which usually indicate the presence of ester inter-linkage bonds ,these compounds indicates to presence of asphaltenese hydrocarbon adsorbed on the clay after treatment with crude oil, the bulk of naphthenic acids is usually concentrated in asphaltenes cuts, depending on this, we can say that catalytic adsorption played important role in (TAN) reduction when we use Enstatite clay.

About the chosen temperature, we have processed clay and zeolite sample with crude oil in various temperatures from 60C up to 220C,and no considerable decrease in (TAN) below 200C this may refer to the activation temperature of these catalysts (zeolite&clays).Fortunately no negative considerable changes on the general properties(table 2-3) of crude due to the TAN reduction process.

4. CONCLUSION

As we have seen in this study we succeeded in reduce (TAN) of the four samples of crude oil by using these cheap and available catalysis, we also did these tests in a mild condition (atmospheric pressure and 200 C).

We think that our ideas presented in this paper can be developed to a certain, serious pilot plane.

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