STUDY OF THE CLAY EFFECT ON CRUDE OIL COMBUSTION BY THERMOGRAVIMETRY AND DIFFERENTIAL SCANNING CALORIMETRY

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Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to study the effect of sand, silica and kaolinite on crude oil combustion. Three distinct regions, namely distillation and two combustion/cracking regions were observed on all TG curves. Thermogravimetric curves were analyzed using an Arrhenius-type kinetic model and a ratio method to obtain kinetic parameters. Activation energy and reaction order were obtained from this analysis. The reaction order seemed to be insensitive to the presence of granular materials. However, a significant reduction of activation energy was caused by addition of kaolinite to the crude oil, indicating that the kaolinite had a catalytic and surface area effect on crude oil combustion/cracking reactions.

In-situ combustion is a thermal recovery process in which a small portion of the crude oil is burned in-situ to mobilize the rest. In this process the crude oil undergoes physical and chemical changes such as distillation, thermal and catalytic cracking, polymerization, etc., because of the heat, steam and flowing gas and produces a cokelike material ahead of the combustion front. This coke is later burned as fuel to produce heat to sustain the front. Duplicating such a process in the laboratory is not an easy task. In-situ combustion tube runs are commonly used to study the fluid flow and chemical reactions of the process in the laboratory. The apparatus consists of a cylindrical tube a few inches to a few feet long packed with sand grains or crushed natural core of the reservoir under study. The tube is saturated with crude oil and water to closely match the reservoir oil and water saturation. Combustion is initiated from the inlet end of the tube. Temperature profiles and analysis of combustion gases are obtained as the combustion front is propagated from the inlet to the outlet of the tube. Because of the integral nature of in-situ combustion runs, any kinetic study from such a system is difficult. However, the development of high quality thermal analysis equipment in recent years offers possibilities for studying chemical reaction of the in-situ combustion process in a controlled environment using small samples.

Attempts to use differential thermal analysis (DTA) to study crude oil combustion go back to 1959 when Tadema [1] showed that DTA curves obtained from the combustion of crude oil in the presence of sand consisted of two distinct regions. These

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two regions were called low and high temperature oxidation and started around 200° and 350°, respectively. Later, Burger and Sahuquet [2] used DTA to illustrate catalytic effects of some metallic derivatives and to investigate how the properties of both oil and porous media influence crude oil combustion. Three successive oxidation regions were observed in their DTA curves, namely low-temperature partial oxidation, combustion of crude oil fractions and finally, coke combustion. Hardy and Raiford [3] published DTA curves showing that crude oil combustion in the presence of a 95–5% quartz-kaolinite mixture produced a curve similar to the mixture of natural core and crude. Bae [4] applied both DTA and TG techniques to 15 crude oils ranging from 6 to 38° API gravity and classified the crude oils into three groups based on their thermal analysis curves. Bae [4] concluded that qualitative prediction of combustion tube test behavior was possible from the results of the thermal analysis methods.

Although thermal analysis methods have been applied to the crude oil combustion with success, all the studies have been of a qualitative nature. In this work, investigation of the crude oil combustion by thermal analysis methods is approached quantitatively. Heat value of the oxidation reaction is obtained from DSC curves and the effect of clay on the in-situ combustion process is studied by generating kinetic data from TG curves. Thermal analysis methods are applied to the crude oil coking process of in-situ combustion to investigate the effect of different environments such as nitrogen and air on the residue produced from coking.

Catalytic effect of clay on the in-situ combustion process

Because of large surface area with many active sites, clays act as a catalyst in a large number of organic reactions [5]. Many oil reservoirs contain a significant amount of clay. Clay appears in different forms, such as kaolinite, montmorillonite, and illite. Most studies on clays in the oil industry are limited to water sensitivity, large affinity to adsorb chemicals, and their mobility in the pore structure [6]. Only a few studies are related to the clay effect on the in-situ combustion process [2, 3, 7–11].

Bousaid and Ramey [7] obtained kinetic data in an isothermal combustion apparatus. A 13.9° API crude oil was coked in the presence of nitrogen, then combusted at temperatures ranging from 266° to 671°. They showed that the Arrhenius equation matched the temperature dependency of the specific rate constant. The activation energy decreased from 61.9 to about 48.4 MJ/kmol when 20 weight percent clay was added to the sand matrix. Concerns have been expressed in the literature that the true coking process occurring in the environment of the in-situ combustion tube runs could be significantly different from that performed by Bousaid and Ramey [7].

Dabbous and Fulton [8] reported an activation energy of 72.1 MJ/kmol for low temperature oxidation (below 260°) of crude oil and indicated that the order of reaction and the activation energy were insensitive to the properties of the porous medium. They obtained their rate equation from isothermal integral reactor data and used crushed Berea sandstone with a specific surface area of 0.52 to 0.91 m²/g. Their conclusion is not justified because they used one porous material with limited

variation of surface area. In a recent study, Guvenir [9] showed that fuel lay-down in adiabatic combustion tube runs correlated with the clay content of the sand mixture. Similar increases were also observed in other process variables such as heat of combustion available to sand and average combustion peak temperature. Fassihi and Ramey [10] also performed combustion tube experiments on different crude oils and observed that addition of clay to sand affected the temperature profile of the in-situ combustion process. The average front temperature for the run with clay was around 510° while the run with no clay had an average temperature of 343°. In contrast with the results of Guvenir [9], a considerable amount of coke remained behind the combustion front in the run with clay in the sand pack while a clean sand was obtained for the run with no clay.

As mentioned earlier, Burger and Sahuquet [2], among others [3] were also able to detect the effect of rock composition on the oxidation of crude oil. They further inferred the same kind of effect during field tests such as the Fry in-situ combustion project of the May Libby rock in Delhi field [12]. Presence of the clays and iron derivatives are considered to be responsible for the success of in-situ combustion processes in light crude oil reservoirs. Indeed, the presence of certain metals such as iron and vanadium in the clay catalyst has been shown to greatly increase the amount of coke-make property of the catalyst. Clay of higher iron content was found to produce a greater amount of coke and less gasoline in the catalytic-cracking process [13]. Although this behavior is detrimental in catalytic cracking, it may be beneficial to the in-situ combustion process in view of greater fuel lay-down.

In summary, enough evidence exists to conclude that some kind of catalytic effect on the in-situ combustion process is associated with the presence of clay in the oil reservoir.

Experimental equipment and procedure

Equipment used in this study consisted of a DuPont 951 Thermogravimetric Analyzer and a 910 Differential Scanning Calorimeter with R90 Programmer and Hewlett Packard 7046A X-Y Recorder. The area under the DSC peaks was measured by a Polar Planimeter from Keuffel & Essex Company.

Mixtures of crude oil with sand, silica powder and clay were prepared in a beaker, then transferred into the TG or DSC pan. Oil/additive ratios of the samples investigated are presented in Table 1. Crude oil used was from the Iola Field, Allen County, Kansas, with API gravity of 19.3 and viscosity of 530 cps at 25°. The sand was silica sand of average size 35 mesh from Wedron Silica Division, Pebble Beach Corporation, Wedron, Illinois. Silica powder was amorphous silica IMSIL A-10 from Illinois Minerals Company, with a specific surface area of $1.5 \text{ m}^2/\text{g}$ and the clay used was of kaolinite type from Good Earth Clays, Inc., Kansas City, Missouri.

Sample size for TG runs was approximately 40 mg and for the DSC around 13 mg. Flow rate of air or nitrogen for TG and DSC runs was 130 cm³/s at atmospheric

Sample	Respective wt%		
Crude oil			
Clay (kaolinite)	100		
Burned clay (metakaolinite)	100		
Sand	100		
Silica powder	100		
Crude oil/sand	20/80		
Crude oil/clay	20/80		
Crude oil/silica powder	20/80		
Crude oil/sand/clay	20/40/40		
Crude oil/sand/silica powder	20/40/40		
Crude oil/ground sand	20/80		

Table 1 Oil/additive ratios of samples investigated



Fig. 1 TG and DTG curves for crude oil distillation in dynamic nitrogen purge

pressure except for coking runs in which the flow rate was intentionally kept low, around 32 cm³/s, in order to improve analysis of the produced gas by gas chromatography. All of the runs reported here except the coking runs were made at a heating rate of 5 deg/min. Coking runs were performed at a heating rate of 10 deg/min.

Results and discussion

TG and DSC curves were obtained for crude oil and a variety of sand mixtures in the presence of flowing air and nitrogen. The air or nitrogen purge through the sample chamber maintained oxidizing and non-oxidizing environments, respectively. TG and DSC runs were performed to establish the effect of different variables such as additive type and its surface area on the resultant curves. Several TG and DSC runs were performed on each mixture to establish reproducibility of the results. Only one run of each set is presented to represent the general behavior. The complete set of curves is reported elsewhere [14]. Also a few TG/DSC runs were performed to investigate the difference in the coking process of crude oil in dynamic air and nitrogen purge.

Effect of purging gas on TG curves

Figures 1 and 2 illustrate the effect of purging gas on the crude oil TG curves. The appearance of two peaks in the derivative curve shown in Figure 1 is an indication of two different mechanisms causing loss of mass when crude oil is heated in the presence of flowing nitrogen. The first peak between ambient temperature and 400° is primarily distillation. The second peak between 400 to 500° is a combination of distillation and thermal cracking. A small residue of around 6 percent remained in the pan even after heating to above 600°.

Three distinct weight loss peaks are observed in the oxidizing environment (air). The first peak corresponds to the distillation of crude oil from ambient to around 360° . The second and third peaks, approximately in the temperature range of $360^{\circ}-480^{\circ}$ and $480^{\circ}-560^{\circ}$, respectively, are primarily combustion/cracking. Combustion is complete at 560° with no residue.

Effect of granular additives on TG curves

Derivative TG curves of crude oil combustion in the presence of different granular additives are compared in Figure 3. The shape of the curve of the crude oil combustion in the presence of sand closely resembles that of crude oil alone given in Figure 2 with the same three major reactions in approximately the same temperature range. However, their shapes are significantly different from those of silica powder, kaolinite and metakaolinite (burned clay).

Similar TG runs were performed on sand, silica powder and kaolinite to obtain grain weight loss. Weight loss was not observed for sand or silica powder. Thus, all



Fig. 2 TG and DTG curves for crude oil combustion in dynamic air purge

weight loss of the crude oil/grain mixture was due to combustion of crude oil. However, weight loss of clay was significant and correction was made accordingly. In the case of the burned clay (metakaolinite) run shown in Figure 3, clay was heated in an oven at 650° to reach a constant weight. A TG run on the metakaolinite showed no weight loss. The metakaolinite TG curve in Figure 3 is similar to clay, except that the last peak is smaller.

Figure 4 shows the effect of granular additives on the TG weight loss curve with the weight loss of granular material, if any, subtracted from the total weight loss. The curve in Figure 4 is a duplicate run of crude oil combustion similar to that shown in Figure 2. Sand has no effect on crude oil combustion while silica powder has some effect. Clay has a pronounced effect on crude oil weight loss. No granular additive showed any appreciable effect in the initial portion of the distillation region.

The effect of clay on TG curves in the dynamic nitrogen purge was also studied. Weight loss curves converted into the crude oil loss by subtracting the grain weight loss under the same condition and are plotted in Figure 5. The crude oil curve in this



Fig. 3 Effect of granular materials on DTG curves for crude oil combustion

figure is a reproduction of the weight loss curve of Figure 1. Figure 5 clearly indicates that the weight loss of crude oil in the presence of clay and flowing nitrogen at a given temperature is much less than in its absence. This implies that crude oil is adsorbed onto the clay surface and cannot be easily removed by flowing nitrogen. It is interesting to compare Figure 5 with Figure 4 and notice that the clay effect is reversed with respect to the crude oil weight loss at a given temperature for flowing nitrogen to that of flowing air.

Crude oil weight loss in the presence of sand and silica powder also seems to be somewhat smaller than in their absence. This is expected for the silica powder because of its large surface area. However, the change in weight loss behavior in the presence of



Fig. 4 Weight loss comparison of crude oil combustion in the presence of different granular materials in dynamic air purge

sand is attributed to the uncertainty involved in sampling from the sand mixture in the beaker. In the case of clay and silica, the oil adsorbs onto the grain and the mixture is stable and uniform. In mixtures of sand and crude oil, the sand tends to separate from the oil and settles to the bottom of the beaker. Although the content of the beaker is mixed thoroughly before each sampling, oil content in the small sample taken (40 mg) could be less than the actual oil saturation in the beaker. If the sample taken from the beaker is assumed to contain 0.4 mg less crude oil—which is quite possible in the case of crude oil/sand mixtures—the data points of the sand in Figure 5 are lowered to the curve of crude oil weight loss. Repetitive sampling of the same mixture proved that the sampling in this case is not representative while in all the other cases no significant variations were observed in replicate runs.



Fig. 5 Weight loss comparison of crude oil distillation in the presence of different granular materials in dynamic nitrogen purge

Effect of grain surface area on TG curves

Attempts were made to change the surface area by grinding the sand or mixing the silica powder and clay with sand. Sand was ground manually using a mortar and pestle to increase the surface area. The DTG curves of a mixture of 80% ground sand and 20% crude oil by weight is compared with those of crude oil/clay/sand and crude oil/silica powder/sand mixtures with weight fractions of 20/40/40 in Figure 6. Practically no effect of grinding was observed and the DTG curve of the crude oil combustion in the presence of ground sand silica powder in the mixture were reduced the same amount, the clay effect on the curves was more pronounced than that of silica powder. Either the clay has a catalytic effect in addition to the surface area affect, or its surface area is so large compared to that of silica powder that even at 40% weight fraction it still produces enough active surface area to affect the process.



Fig. 6 Effect of surface area on DTG curves for crude oil combustion

Kinetic analysis of TG curves

In order to analyze data it is necessary to hypothesize a kinetic model of the reaction mechanism. The kinetic model assumed in this study was in the form of

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}t} = K\gamma^n \tag{1}$$

where γ is the fraction remaining; K, rate constant, which varies with temperature; n, reaction order; and t, time. The Arrhenius equation for the temperature dependency of the rate constant is the simplest and most popular model. This model assumes exponential dependency of the rate constant on absolute temperature, i.e.,

$$K = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

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	Activati	Activation energy, MJ/kmol			Reaction order		
Sample tested	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	
Crude oil	28.5	172.4	191.6	2,2	1.7	1.2	
Sand/crude	25.1	177.2	199.6	2.2	1.4	1.1	
Clay/crude	28.7	75.4	78.2	2.2	1,1	1.3	
Silica/crude	26.3	62.3	161.4	2.2	1.4	1.4	
Silica/sand/crude	25.5	191.6	199.6	2.2	1.7	1.1	
Clay/sand/crude	28.7	66.4	78.6	2.2	1.1	1.3	

Table 2 Kinetic parameters generated from ratio method

where A is the frequency factor; E, activation energy; T, absolute temperature; and R, gas constant. TG curves were analyzed by applying the "ratio method" proposed by Mickelson and Einhorn [15]. In the ratio method, Equation 1 combined with Equation 2 is applied to pairs of points *i* and *j* along the TG/DTG curves. Variables $\log [(-d\gamma/dt)_j/(-d\gamma/dt)_i]/\log (\gamma_i/\gamma_j)$ and $[(T_j - T_i)/T_iT_j]/\log (\gamma_i/\gamma_j)$ will plot as a straight line. The slope of this line is equal to E/2.303R and the intercept -n. These plots were generated for most of the curves and the results are tabulated in Table 2. To show the quality of the data and level of data scatter, one plot for each peak is illustrated in Figures 7–9.

Reaction order was consistently around 2.2 for the initial portion of the first peak which is for crude oil distillation and between 1 and 2 for the second and third peaks of the curves studied. Reaction order of 2.2 for the vaporization reaction might seem unrealistic. However, as reported by Adonyi [16], a reaction order of zero for vaporization reaction can be obtained only for pure substances. Reaction orders of 1-2.5 for benzene mixtures and 0.6-4 for cyclohexane mixtures were reported by Adonyi [16]. Because of the highly complex nature of crude oil composition, a reaction order of 2.2, is reasonable. Activation energy of the first peak of the curves varies from 25.1 to 28.7 MJ/kmol for all the curves studied and seems to be unaffected by clay or silica powder in the mixture.

Activation energies for the second peak of the curves generated for crude oil and the crude oil/sand mixture are in the range of 172.4 to 177.2 MJ/kmol while that of clay mixtures reduces to the level of 66.4 to 75.4 MJ/kmol. The effect of silica powder on activation energy is similar to the clay for the mixture of 80% silica/20% crude oil while its effect diminishes when its weight fraction is reduced to 40%. Activation energy for the second peak of the 80% silica powder mixture is around 62.3 MJ/kmol while for the 40% silica powder mixture it is around 191.6 MJ/kmol. Significant reduction of activation energy due to the addition of clay to the crude oil indicates that clay exerts a catalytic effect on crude oil combustion/cracking reactions. Somewhat different behavior is observed for the third peak of the curves of the silica powder mixture. Activation energy of around 191.6 to 199.6 MJ/kmol was obtained for the third peak of the crude oil and the crude oil/sand mixture and



Fig. 7 The ratio method applied to the first peak

161.4 for the crude oil/silica mixture. However, the activation energy was about 78.2 for the crude oil/clay mixture and remained at around 199.6 MJ/kmol for the 40% silica mixture. This further supports the fact that the 40% silica powder acts more like a sand mixture than a 40% clay mixture. This larger activation energy for the third peak in the presence of silica powder compared to that in the presence of clay is not an artifact. Reproduction of the TG runs on different samples of the same oil/additive ratio was good.

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Fig. 8 The ratio method applied to the second peak of crude oil/clay and crude oil/silica mixtures

DSC curves

Differential scanning calorimetry runs performed to obtain the heat value of the combustion process and to investigate the effects of granular material type are given in Figures 10 and 11. The area under such a curve is the total heat of reaction. By reading the weight loss in the corresponding temperature range from the TG curves, the average heat value per unit mass of the substance was calculated. The weight loss in the corresponding temperature range from the TG curves, the average heat value per unit mass of the substance was calculated. The weight loss in the corresponding temperature range is the gross weight loss and includes distillation and evaporation. Therefore, the heat value calculated in this fashion is smaller than the true heat of combustion. The average heat values obtained from DSC curves are given



Fig. 9 The ratio method applied to the third peak of crude oil/clay and crude oil/silica mixtures

in Table 3. The DSC curve of crude oil distillation in the presence of flowing nitrogen did not show a measurable amount of heat adsorption at the sensitivity used. When crude oil was burned in the presence of clay, the reference pan was filled with the same amount of clay as the sample pan to compensate for the endothermic de-hydroxylation of kaolinite which occurs around 400–600°. The DSC curve of the clay itself is also included in Figure 11 to show the endothermic reaction of kaolinite dehydroxylation.

The average heat value has changed only from around 5.8-6.3 MJ/Kg of oil for the crude oil/sand mixture and crude oil to around 7.7 MJ/Kg of oil for the 80% clay/20% crude oil mixture and 8.1 MJ/Kg of oil for the 80% silica/20% crude oil



Fig. 10 DSC curve for crude oil combustion in dynamic air purge

mixture. It is around 6.6 MJ/Kg of oil for a 40% clay mixture and around 5.6 MJ/Kg of oil for a 40% silica mixture. There is no correlation of the average heat value with type of granular additive. The major effect of clay and silica powder on DSC curves is the shift of energy release from the higher temperature range to the lower.

Coking runs

A few TG and DSC runs were performed to investigate the difference in the coking process of crude oil in the presence of flowing air and nitrogen. In the two separate TG runs the sample was heated at 10 deg/min up to 385°, held isothermal for around one hour, then resumed heating. The entire process in the first run was done in a dynamic air purge. In the second run a nitrogen purge was maintained to the end of the isothermal period and then the purge was switched to air. In the first run the TG was attached to a Varian Aerograph "Moduline" Model 1520 gas chromatograph equipped with automatic gas sampling valves and a Spectra Physics Autolab System I computing integrator. Effluent gas analysis was compared with that of a normal run, i.e., a TG run at 10 deg/min and dynamic air purge. In both runs CO₂ production continued long after the crude oil sample was burned. This time lag happened because of the relatively large volume of the TG furnace tube, therefore the true gas production at a given temperature is not known. Water production in the coking run ceased much earlier than in the normal run. This is an indication that the materials being



Fig. 11 Effect of granular materials on crude oil DSC curves (a) 20% crude oil/80% sand (by weight); (b) 20% crude oil/80% clay (by weight); (c) 20% crude oil/80% silica (by weight); (d) 20% crude oil/40% sand/40% clay (by weight); (e) 20% crude oil/40% sand/40% silica (by weight); (f) kaolinite clay mineral

Sample tested	Heat value MJ/kg of crude oil			
Crude oil	6.3			
Sand/crude	5.8			
Clay/crude	7.7			
Silica/crude	8.1			
Silica/sand/crude	6.6			
Clay/sand/crude	5.6			

Table 3 Average heat value produced from DSC curves



Fig. 12 Comparison of DSC curves for crude oil coking in dynamic nitrogen and air purge

consumed during the coking process (i.e., isothermal period) were composed of higher hydrogen/carbon (H/C) ratio. Thus, the coke produced was a carbon-rich residue.

Heat value of the coke produced under flowing nitrogen atmosphere was 12 MJ/Kg while that of the coke produced under flowing air was around 16.8 MJ/Kg. These values were obtained from the area under the last peak of the DSC curves shown in Figure 12 and the corresponding weight loss from TG curves described above. This difference in heating values indicates that the molecular structures of the two residues are different.

Conclusions

Major conclusions derived from this study can be summarized as follows:

1. Three distinct regions, namely distillation and two combustion/cracking regions were observed in all TG curves.

2. The addition of kaolinite clay mineral or IMSIL silica powder changed the shape of the crude oil TG/DSC curves significantly while sand and ground sand had no effect. The major effect on DSC curves was a shifting of the large amount of heat produced from a higher to lower temperature range.

3. The average heat value increased from around 5.8 MJ/Kg of oil to 8.1 MJ/Kg of oil when clay or silica powder was included in the sand mixture.

4. Crude oil weight loss under a constant heating rate and flowing air atmosphere was larger in the presence of clay than in its absence, which is an indication of the clay effect on the chemical reactions occurring.

5. Because of the adsorption of the crude oil on the clay particles, its weight loss under a constant heating rate and flowing nitrogen became smaller in the presence of clay than in its absence.

6. The activation energy of the distillation peak varied between 25.1–28.7 MJ/kmol and was unaffected by the presence of clay or silica powder in the mixture.

7. The activation energies of the two combustion/cracking peaks calculated from TG curves were significantly lower for the clay/crude oil mixture than for the crude oil or crude oil/sand mixture.

8. Reduction of activation energy due to the addition of kaolinite clay mineral to the crude oil indicates a catalytic and a surface area effect on combustion/cracking reactions.

9. Reaction order was equal to 2.2 for distillation peaks but varied between 1 and 2 for combustion/cracking peaks.

10. Coking residue under a flowing air atmosphere produced a heat value of 16.8 MJ/Kg of oil while that under flowing nitrogen gave only 12.0 MJ/Kg of oil. This difference indicates that the molecular structure of the two residues are different.

11. Gas analysis of the TG effluent gas indicated that coking by air produced carbonrich residues.

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Zusammenfassung – Die Wirkung von Sand, SiO₂ und Kaolinit auf die Verbrennung von Rohöl wird mittels TG und DSC untersucht. Alle TG-Kurven lassen drei unterschiedliche Abschnitte erkennen, die der Destillation und zwei Verbrennungs- bzw. Krackvorgängen zuzuordnen sind. Die thermogravimetrischen Kurven wurden unter Verwendung eines kinetischen Modells des Arrhenius-Typs analysiert, wobei die Reaktionsordnung erhalten wurde. Die Reaktionsordnung scheint von körnigen Materialien nicht beeinflusst zu werden. Eine signifikante Verringerung der Aktivierungsenergie wurde durch Zusatz von Kaolinit zum Rohöl erzielt, was darauf hindeutet, dass Kaolinit einen katalytischen und Oberflächeneffekt auf die Verbrennung bzw. auf Krackreaktionen des Rohöls ausübt.

Резюме — ТГ и ДСК были использованы для изучения влияния песка, кремния и каолина на горение сырой нефти. На всех ТГ-кривых наблюдалось три различные области, главным образом — область перегонки и две области горение/крекинг. ТГ-кривые были анализированы на основе кинетической модели типа Аррениуса и оценен порядок реакций. Кажется, что порядок реакции не затрагивается присутствием гранулированных материалов. Вместе с тем, при добавлении каолина в сырую нефть, наблюдалось значинельное понижение енергии активации. Это указывает на то, что каолин вызывает каталитический эффект и эффект площади поверхности в реакции горение/крекинг сырой нефти.