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Evaluation of Two Kurdistan-Iraq Crude Oil (T-21A, PF2) by Derivatographic Method

Sherwan Mohammad Simo[1*], Salah Aldin Naman[1], Kanaan Ramadan Ahmed[1] and Akhmetov Arslan Faritovich[2]

[1]*Department of Chemistry, Faculty of Science, University of Zakho, Iraq.*
[2]*Department of Oil and Gas Technology, Ufa State Petroleum Technological University, Ufa, Russia.*

Authors' contributions

This work was carried out in collaboration among all authors. Author SMS designed the study and wrote the protocol. Authors SMS, SAN, KRA and AAF preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Evaluation of crude oil and its residue using derivatography, is one of the most common physical and chemical methods analytical research. Crude oil residues 350+ obtain from two Iraq-Kurdistan crudes (Tawke T-21A well and Shekhan PF2 well) by using atmospheric distillation after removing all volatile fractions. The sample characterized by direvatographic method. The thermo analysis, reactions were carried out at temperature range 20- 700℃ for reaction time 68 min. These derivatograph curves show the weight change and heat energy (Enthalpy) change as the function of time and temperature. It shows that the crude oil residues have different composition. The curve which marks the weight changes of the sample heated is the thermogravimetric curve, TGA. Whereas the curve, which records heat energy or enthalpy changes during thermal decomposition is the DTA or differential thermoanalytic. By means of the derivatograph, it is possible to record simultaneously curve of weight change (TG), and enthalpy change (DTA) as a function of temperature. This method analysis shows good evaluation of these two crude oil well.

**Corresponding author: E-mail: sherwan.simo@uoz.edu.krd;*

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1. INTRODUCTION

The petroleum residue is black, viscous materials [1] and obtained by distillation of a crude oil after has removed all the volatile materials [2,3] under atmospheric pressure its atmospheric residuum or under reduced pressure its vacuum residuum. They may be liquid at room temperature in generally atmospheric residue or almost solid in generally vacuum residua depending on the nature and chemical constituent of the crude oil [4].

Derivatography, is one of the most common physico-chemical research methods. It allows one to study the behavior of individual substances and compositions under programmed heating conditions. In practice, the classification and quantitative assessment of various processes occurring during the heating of samples are carried out according to the curves of heat release or change in mass during the processing of thermograms [5].

In the 1950s, after some fruitful decades of work, thermo analysis reaches a new stage for evaluation of crude oil. The classical methods were not accurate enough for the new requirements and efforts to improve the methods encountered great difficulties [6]. In most cases the accuracy of the results could not be improved by technical perfection of the instruments [7].

Thermal methods are a group of methods of physical-chemical analysis, in which is measured a physical parameter of the system, depending on the temperature. Calorimetry and Thermogravimetry are thermal analysis methods. In thermogravimetry measured parameter is the mass of a substance in the calorimeter heat [8, 9]. Differential thermal analysis (DTA) is based on registration of the temperature difference between the test substance and an inert reference material at their simultaneous heating or cooling. When the temperature changes in the sample can flow processes enthalpy change such as fusion, rearrangement of the crystal structure of evaporation [10].

The aim of this research is for evaluation these crude oil and its residue by thermogravometry and which depend chemical constitute of hydrocarbons trace metals. A key to understanding crude oil samples from two Kurdistan-Iraq crude oils, behavior during refining operation is to develop an understanding of the principle precursors such as residue and the relationship between the residue and other constituents of petroleum feedstock. The limitations of processing heavy oils and residue depend to a large extent on the amount of principal precursors present in the feedstock. We believe that this method of evaluation of crude oil may be more applicable than classical distillation.

2. METHODS

2.1 Crude Oil Sampling

Two Kurdistan feedstock which is collected from the wells of Tawke and Shekhan fields.

2.2 Preparation of Residue > 350℃

Tawke T-21A residue and Shekhan PF2 residue were obtained from two Kurdistan crudes by removing distillates boiling point up to 350 ℃ using atmospheric distillation.

2.3 Physical and Chemical Properties of the Two Crude Oils and Residues

The physical and chemical properties of the samples were carried out using the standard test methods, GOST 3900 Pycnometer to determine density of liquids, and GOST 1461 determine the percentage of the ash content of the samples, and GOST 1437 for measurement the sulfur content of heavy fraction. The results are shown in Table 2. Using SPECTROSCAN MAX G X-ray fluorescent WDXRF scanning spectrometer for determination of chemical elements in the samples, the result is shown in Table 3.

2.4 Device "Linsies STA PT-1000"

The instrument employed for thermal analysis in this study was a Linsies STA PT-1000 derivatograph. TGA, DTG and DTA analysis were carried out in the temperature range of 20-700℃ in oxidizing atmosphere (air). 1.6 L/min at furnace heating mode 10 deg/min and the reaction time 68 minutes. Weight of the T-21A Residue > 350℃ sample was 12.2 mg and weight of the PF2 Residue > 350℃ sample was 14.6 mg.

3. RESULTS AND DISCUSSION

The Tables 1 & 2 show the physicochemical properties of T-21A & PF2 Crude oil and Residues>350℃, Distillate volume percentage were collected at standard temperature range with the initial boiling point (IBP) and the final boiling point (FBP) for T-21A and PF2 crude oils for each of them. These results indicated that T-21A is lighter than the PF2 crude oils. Chemical compositions due to Table 2. the sulfur content of PF2 is higher than T-21A and in another reason it is ash content.

You have to compare the result of thermal analysis with conradson carbon residue, the carbon residue wt. % is higher in residue as show in Table 2. than crude oil. Since the former products are relative nonvolatile samples that don't decompose in distillation at atmospheric pressure and contain ash forming constituents, so they will have erroneously higher carbon residue than the latter ones.

The Table 3. illustrates the trace metals (lead, nickel, iron, manganese and vanadium) were analyzed by spectros can max g. However, the vanadium content in PF2 crude oil and residue is higher than T-21A crude oil and residue. PF2, crude oil contains 114 ppm, residue contains 252 ppm and T-21A, crude oil and residue contains 26 ppm and 51 ppm respectively. However, T-21A crude oil and residue contains a less amount of vanadium, which might be due to low amount of aromatic compound. PF2 crude oil and residue contains high amount of aromatic more than T-21A. Usually aromatic hydrocarbon is lead to high asphaltene in crude oil. The asphaltene and resin contain high amount of trace element. Also crude oil shows good correlation between sulfur and vanadium concentration [11]. PF2 crude oil contains high amounts of sulfur which is 5.0598, 5.15, T-21A crude oil contains less amount of sulfur than PF2 which is 2.8. The high content of sulfur in crude oil means that contains high amount of vanadium in crude oil.

Table 3. shows that the nickel content of PF2 crude oil is 43 ppm, T-21A crude oil 7 ppm. Whereas, that nickel content for PF2 residue is 86 ppm, T-21A residue is 18 ppm. The concentration of nickel depends on the amount of asphaltene and resin in crude oil. PF2 crude oil and residue contains a little high amount of nickel more than T-21A crude oil and residue. Nickel content found in asphaltene less than vanadium content [11], during the migration and maturation of crude oil.

Table 1. Results from atmospheric distillation of crude oil

Results	Crude oil	
	T-21A	**PF2**
Volume (ml)	100	100
IBP-FBP	73-350 °C	79-350 °C
Product Volume (ml) %	57	62
Residue Volume (ml) %	43	38

Table 2. Physicochemical properties of T-21A & PF2 crude oil and residues>350℃

Result	T-21A		PF2	
	Crude oil	**Residue> 350℃**	**Crude oil**	**Residue> 350℃**
Density at 20**°C**	0.8943	1.0122	0.9441	1.1055
Sulfur wt. %	2.8	4.39	5.15	6.7
Carbon Residue wt.%	5.65	8.59	9.39	17.93

Table 3. Elemental determination in crude oil and residue by spectroscan max G

Metals (ppm)	T-21A		PF2	
	Crude oil	**Residue> 350℃**	**Crude oil**	**Residue> 350℃**
Pb	5	9	7	16
Ni	7	18	43	86
Fe	1	2	6	7
Mn	1	0	1	2
V	26	51	114	252

Also the crude oil show correlation between sulfur and metal nickel content and this show an increase in metal content due to an increase in sulfur content. According to the organometallic compound of nickel, nickel can make stable organometallic complexes with sulfur [12].

In practice classification and quantitative assessment of various processes occurring during the heating of sample are carried out according to the curves of the heating release or mass change during processing of thermograms [5,13].

In our studies, we have used thermogravimetry (TGA), the dependence of the change in sample weight (mass) on the temperature during programmed temperature changes. The first derivative of the weight (mass) signal with respect to time is called derivative thermogravimetry (DTG) and is a criterion for the reaction rate. It is usual to record both the slope of the weight (mass) versus the time or temperature (TGA), and the differentiated curve versus the time or temperature (DTG). That combines the following methods of thermal: Differential thermal analysis (DTA) heat absorption or evolution (DTA) due to phase transitions (solid-solid, liquid-gas, solid-liquid, etc.), adsorption, or chemical reaction [14], thethermogravimetric (TG) method is based on periodic heating and weighing of the test material. Currently, measurements by this method are made by means of a thermobalance that measures and continuously records the sample weight change, Derivative thermogravimetry (DTG) is of independent value, and it also supplements to a considerable degree the thermogravimetric method of recording the differential curve of weight loss or gain of the test material.

To decide the change in thermal stability of samples we carried out derivatographic investigations before and after atmospheric distillation. According to the results of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) of the crude oil and residue the thermal decomposition takes place over same stages, respectively (Figs. 1 and 2 for T-21A) and (Figs. 3 and 4 for PF2) well for both crude oil and residue.

Thermal decomposition is marked on the DTG curves for (T-21A, PF2) crude oils and residues in an air atmosphere are shown in Figs. 1-4. There were two endothermic peaks for all samples, with three exothermic peaks. For all samples, the first Stage corresponded to moisture evaporation at temperatures ranging from 40 to 200°C. For T-21A crude oil and residue, first exothermic peaks consisted of the release of volatiles and combustion, and second peak was combustion of the sample. Final peaks where the combustion of fixed carbon and mineral decomposition. For the PF2 crude oil and residue, first peak consisted mainly of the burning of volatiles in the sample. Next peaks were mostly the combustion of crude oil and residue, final peaks where the fixed carbon combustion and mineral decomposition in the both samples.

The sample of thermal diagram for a representative predominating four samples is given in Figs. 1-4. On the DTA curve, for T-21A crude oil and residue, it’s similar, there are three endothermic peak at 350° , 410° and 540° and three exothermic peaks at 375°, 390° and 420°. For PF2 crude oil and residue, it’s different, there are four endothermic peak at 350°, 430°, 540° and 610° respectively, and three exothermic peaks at 390°, 460° and 590° of crude oil. For the PF2 residue there are three endothermic peaks at 340°, 420° and 520° and two exothermic peaks at 360° and 430°.

The TGA curves of the T-21A crude oil and residue are shown in Figs. 5 and 6. These curves show that four stage temperature range of T-21A crude oil and residue of the thermal effect. Corresponding mass change and the effect of endothermic and exothermic peaks in temperature range are shown in the Table 3.

The shape curves in Figs. 1 to 4 shows that different peaks with temperature which it a fuction of hydrocarbon and metal in each of the both well, and both Figs. 5 and 6 for T-21A and Figs. 7 and 8 for PF2, give different mass change with temperature. As a final curve of T-21A and PF2 in the Figs. 5 to 8 and in Table 4. different values of mass loss, these different values are due to differences in sulfur content and different chemical compositions of our residue of both samples.

The TGA curves of the T-21A crude oil and residue are shown in Figs 5 and 6. These curves demonstrate the four stages of thermal effects. Corresponding mass losses and the effect of endothermic and exothermic peaks for these four temperature ranges are listed in Table 4. On the first stage, the mass loss of free moisture and

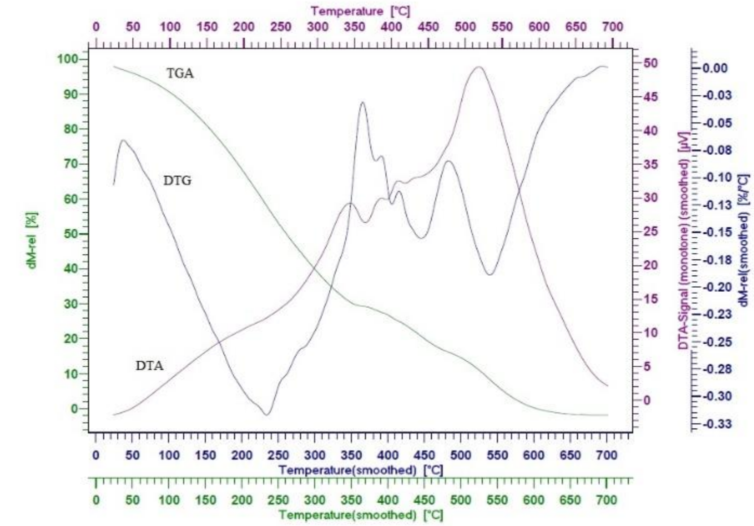

Fig. 1. Derivatogram of T-21A crude oil (air medium; Tmax = 700℃; t = 68 min; heating mode 10 deg/min)

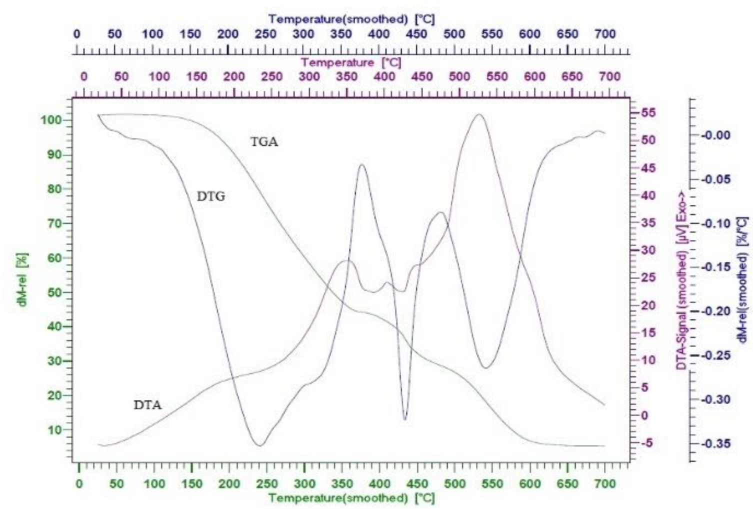

Fig. 2. Derivatogram of T-21A residue >350 ℃ (air medium; Tmax = 700℃; t = 68 min; heating mode 10 deg/min)

volatile hydrocarbons takes place in an exothermic reaction, since it is by evaporation. In the other three stages, the mass loss is accompanied by corresponding exothermic peaks. This effect is due to the oxidative degradation of different chemical composition of crude oil and residue.

Thermogravometric of the PF2 crude oil (Fig. 7) takes place over three stages. The first stage, when the mass changes the range of 20–396.1°C. This stage is accompanied by the appearance of intense exothermal effect on the TGA curve with the mass loses (48.93%) and corresponds to a thermooxidative destruction of hydrocarbons and their partial combustion. The second stage is within the range of 396.1–500.1°C. It is accompanied by the appearance of the next exothermal effect on TGA curve and corresponds to the combustion of thermal decomposition residue with mass loses (25.7%). At the third stage of thermolysis within 500.1-700.3°C the combustion of carbonized residue takes place. This process is accompanied by a slight mass loss (20.12%) and appearance of the third exothermal effect on TGA curve.

Thermolysis of the PF2 residue (Fig. 8) takes place over three exothermic effects. The first exothermic effect on the TGA curve, corresponds to the thermooxidative destruction of the residue and partial combustion of destruction products (mass loses= 42.87%, temperature range 35.1-365°C). The second exothermic effect within 365-475.6°C with mass loses (27.61%).At the third exothermic effect on the TGA curve within 475.6-700.1°C the complete combustion of pyrolysis residue takes place mass loses (29.59%).

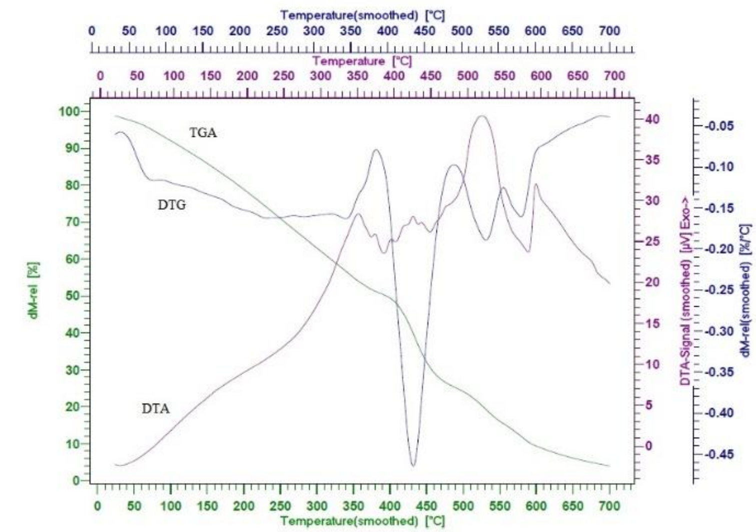

Fig. 3. Derivatogram of PF2 crude oil (air medium; Tmax = 700℃; t = 68 min; heating mode 10 deg/min)

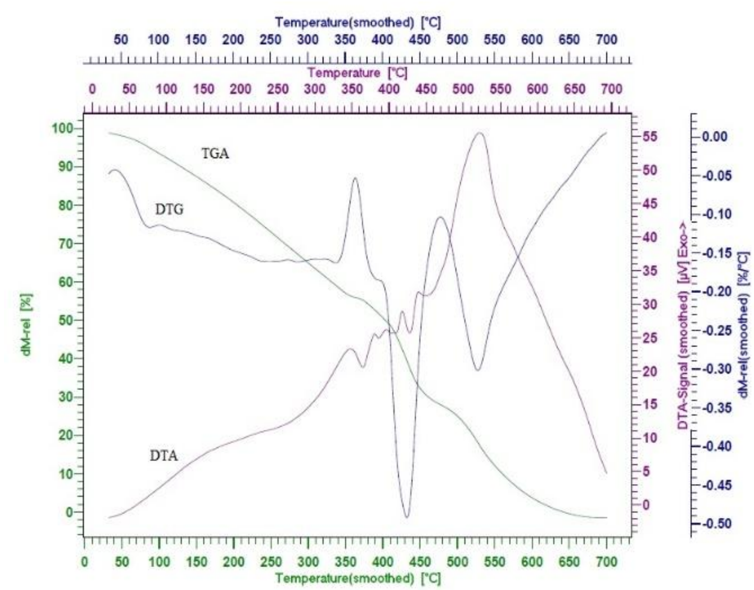

Fig. 4. Derivatogram of PF2 residue >350 ℃ (air medium; Tmax = 700℃; t = 68 min; heating mode 10 deg/min)

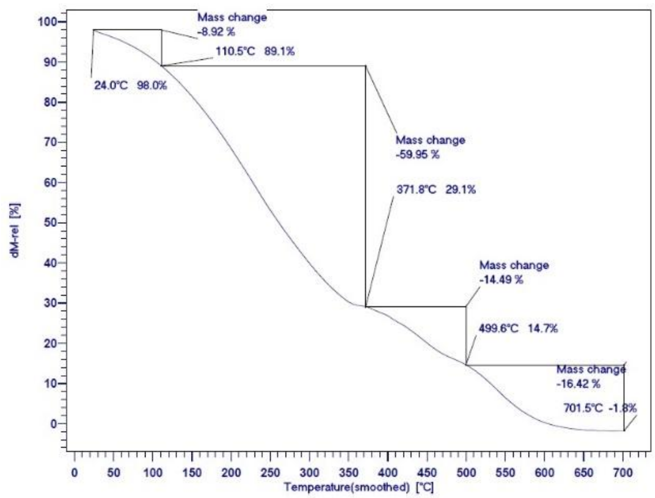

Fig. 5. Mass change with temperature of T-21A crude oil

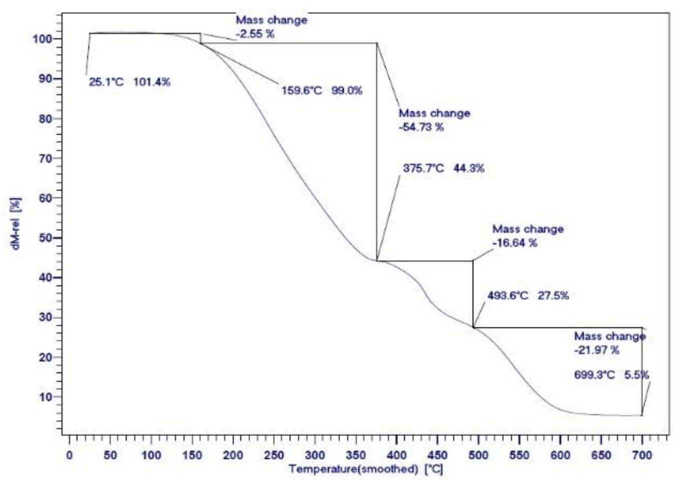

Fig. 6. Mass change with temperature of T-21A residue > 350℃

Table 4. TGA mass losses for T-21A and PF2 crude oil and residue in different temperature range

Samples		Temperature range ℃	Mass change %	T Thermal Effect ℃
T-21A	Crude Oil	24.0-110.5	8.92	Exothermic
		110.5-371.8	59.95	Exothermic
		371.8-499.6	14.49	Exothermic
		499.6-701.5	16.42	Exothermic
	Residue > 350°C	25.1-159.6	2.55	Exothermic
		159.6-375.7	54.73	Exothermic
		375.7-493.6	16.64	Exothermic
		493.6-699.3	21.97	Exothermic
PF2	Crude Oil	24.1-396.1	48.93	Exothermic
		369.1-500.1	25.7	Exothermic
		500.1-700.3	20.12	Exothermic
	Residue > 350°C	35.1-365	42.87	Exothermic
		365-475.6	27.61	Exothermic
		475.6-700.1	29.59	Exothermic

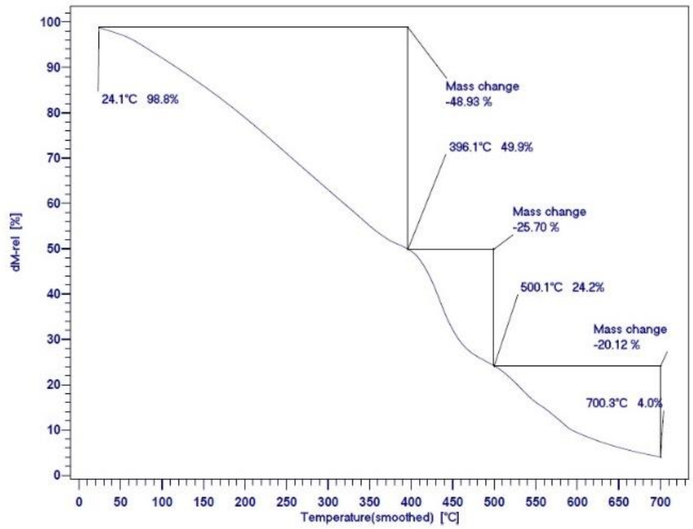

Fig. 7. Mass change with temperature of PF2 crude oil

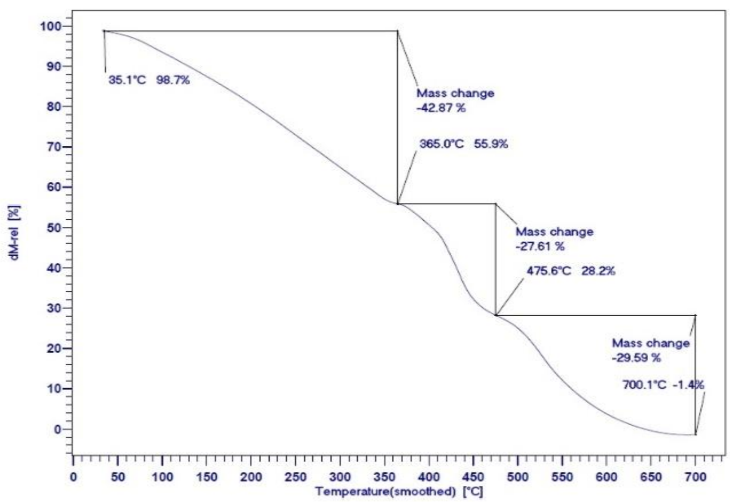

Fig. 8. Mass change with temperature of PF2 residue > 350℃

It should be noted that the residue has a lower thermal stability compared with that of the crude oil. The reason is the different amount of sulfur and chemical composition. While heating the residue loses its mass more intensive than the crude oil shows in the TGA curve and maxima of its exothermal effects is shifted to the area of lower temperatures. The combustion of thermal decomposition of residue takes place over one stage for the residue and is accompanied by the appearance of only one exothermal effect. Table 4 shows the change of mass for well T-21A and PF2 for both crude oil and residue and we can compare the results and correlate with chemical constituent of both hydrocarbon and metal.

4. CONCLUSION

The data in this research that is compressive results between the two wells. It has been studied the thermal decomposition of crude oil and residue of samples, with the help of derivatographic research, it has been established that T-21A differs in lower thermal resistance in comparison to the PF2. The crude oil is characterized by lower thermal stability in comparison to the residue, the different in DTA, DTG then TGA is due to a different trace element in the residue analysis with its sulfur content and different chemical compositions of samples. The derivatograph shows that the mass loss is accompanied by corresponding exothermic peaks. This effect is due to the oxidative of crude residue. Here the process of mass losses in TGA curve was accompanied at first by energy consumption. The change of enthalpy substance when the temperature changes recorded by measuring the temperature difference in the sample. Derivatograms give the starting data that are needed to solve problems related to the removal of contaminant residue from crude oil. This evaluation method crude oil and residues may be useable than classical distillation method.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Vargas FM, Tavakkoli M. Asphaltene deposition: Fundamentals, Prediction, Prevention, and Remediation. CRC Press; 2018.
2. Speight JG, The chemistry and technology of petroleum, fifth edition. Taylor & Francis; 2014.
3. Ali MA, Siddiqui MAB, Zaidi SMJ. Thermal analysis of crude oils and comparison with SIMDIST and TBP distillation data. Journal of Thermal Analysis and Calorimetry. 1998; 51(1):307-319.
4. Speight JG, The chemistry and technology of petroleum; 2006. CRC Press.
5. Paulik F, Paulik J. Simultaneous thermogravimetric and thermo-gastitrimetric investigations under quasi-isothermal andquasi-isobaric conditions. Analytica Chimica Acta. 1973;67(2):437-443.
6. Paulik F, Paulik J, Erdey L, Derivatography: A complex method in thermal analysis. Talanta. 1966;13(10):1405-1430.
7. Hemminger B, Hen G. Calorimetrytheory and practice. / trans. from english. OB Salamatina. - M.: Chemistry. 1989;175.
8. Strates B, Georgacopoulou C. Derivatographic thermal analysis of renal tract calculi. Clinical Chemistry. 1969;15(4): 307-311.
9. Piloyan G, Введение в теорию термического анализа (Introduction in theory of thermal analysis).Izd. Moskva: Nauka;1964.
10. Ermolaev MI, Batishchev VV, Goryachev KV. Derivatographic method of thermal analysis of lubricating oils. Chemistry and Technology of Fuels and Oils. 1972;8(6): 455-458.
11. Frankenberger A. Trace elements in New Zealand oils, their significance for analytical chemistry, geochemistry and oil classification: A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Massey University. Massey University; 1994.
12. Vicic DA, Jones WD. Modeling the hydrodesulfurization reaction at nickel. Unusual reactivity of dibenzothiophenes relative to thiophene and benzothiophene. Journal of the American Chemical Society. 1999;121(33):7606-7617.
13. Shishkin YL. An automatic apparatus for the rapid differential thermal analysis of medicinal substances with variable pressures of the gas phase. Pharmaceutical Chemistry Journal. 1972;6(1):64-66.
14. Stock SR, Microcomputed tomography: methodology and applications.CRC press; 2019.

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