

# Oxidation Behavior and Kinetics of Light, Medium, and Heavy Crude Oils Characterized by Thermogravimetry Coupled with Fourier Transform Infrared Spectroscopy

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## Abstract

© 2018 American Chemical Society. The oxidation behavior of three crude oils was characterized by thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) to investigate the oxidation mechanism of crude oils. The results indicated that the entire oxidation process can be divided into three main reaction intervals: low-temperature oxidation (LTO) interval (<400 °C), coking process (400-500 °C), and high-temperature oxidation (HTO) interval (500-650 °C). For the LTO interval, oxygen addition reactions to produce hydroperoxides were believed to be dominant at the early stage, while the isomerization and decomposition reactions of hydroperoxides became more significant at the later stage. For light and medium oils, the isomerization and decomposition reactions that release H<sub>2</sub>O started at about 200 °C and the isomerization and decomposition reactions that release CO<sub>2</sub> and CO started at about 300 °C. However, no CO<sub>2</sub> and CO were detected in the LTO interval of the heavy oil, which means that the reaction pathways of the heavy oil might be a little bit different from those of the light and medium crude oils in LTO intervals. Evaporation played an important role during the entire LTO interval. In the coking process, the coke formation by the oxidative cracking of the LTO residue is believed to be the main reaction with the release of gaseous products of CO<sub>2</sub> (and CO), H<sub>2</sub>O, and hydrocarbons. In the HTO interval, the combustion of coke was considered as the only one significant reaction. For the LTO and coking process, the activation energies increased with the decrease of the American Petroleum Institute (API) gravity of crude oils. However, for the HTO stage, the activation energies were similar (100-125 kJ/mol) for different crude oils.

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## References

- [1] Li, J.; Mehta, S.; Moore, R.; Ursenbach, M.; Zalewski, E.; Ferguson, H.; Okazawa, N. Oxidation and ignition behaviour of saturated hydrocarbon samples with crude oils using TG/DTG and DTA thermal analysis techniques. *J. Can. Petrol. Technol.* 2004, 43, 45-51, 10.2118/04-07-04
- [2] Kuppe, G.; Mehta, S.; Moore, R.; Ursenbach, M.; Zalewski, E. Heats of combustion of selected crude oils and their SARA fractions. *J. Can. Petrol. Technol.* 2008, 47, 1-8, 10.2118/08-01-38
- [3] Kok, M.; Karacan, C. Behavior and effect of SARA fractions of oil during combustion. *SPE Reserv. Eval. Eng.* 2000, 3, 380-385, 10.2118/66021-PA
- [4] Kok, M. V.; Gul, K. G. Thermal characteristics and kinetics of crude oils and SARA fractions. *Thermochim. Acta* 2013, 569, 66-70, 10.1016/j.tca.2013.07.014
- [5] Li, J.; Mehta, S.; Moore, R.; Ursenbach, M. New insights into oxidation behaviours of crude oils. *J. Can. Petrol. Technol.* 2009, 48, 12-15, 10.2118/09-09-12-TN

- [6] Murugan, P.; Mani, T.; Mahinpey, N.; Asghari, K. The low temperature oxidation of Fosterton asphaltenes and its combustion kinetics. *Fuel Process. Technol.* 2011, 92, 1056-1061, 10.1016/j.fuproc.2010.12.032
- [7] Pu, W.-F.; Yuan, C.-D.; Jin, F.-Y.; Wang, L.; Qian, Z.; Li, Y.-B.; Li, D.; Chen, Y.-F. Low-temperature oxidation and characterization of heavy oil via thermal analysis. *Energy Fuels* 2015, 29 (2), 1151-1159, 10.1021/ef502135e
- [8] Varfolomeev, M. A.; Galukhin, A.; Nurgaliev, D. K.; Kok, M. V. Thermal decomposition of Tatarstan Ashal'cha heavy crude oil and its SARA fractions. *Fuel* 2016, 186, 122-127, 10.1016/j.fuel.2016.08.042
- [9] Varfolomeev, M. A.; Nagrimanov, R. N.; Samatov, A. A.; Rakipov, I. T.; Nikanshin, A. D.; Vakhin, A. V.; Nurgaliev, D. K.; Kok, M. V. Chemical evaluation and kinetics of Siberian, north regions of Russia and Republic of Tatarstan crude oils. *Energy Sources, Part A* 2016, 38, 1031-1038, 10.1080/15567036.2015.1107866
- [10] Varfolomeev, M. A.; Nurgaliev, D. K.; Kok, M. V. Thermal, kinetics, and oxidation mechanism studies of light crude oils in limestone and sandstone matrix using TG-DTG-DTA: Effect of heating rate and mesh size. *Pet. Sci. Technol.* 2016, 34, 1647-1653, 10.1080/10916466.2016.1217234
- [11] Yuan, C. D.; Pu, W. F.; Jin, F. Y.; Zhang, J. J.; Zhao, Q. N.; Li, D.; Li, Y. B.; Chen, Y. F. Characterizing the fuel deposition process of crude oil oxidation in air injection. *Energy Fuels* 2015, 29, 7622-7629, 10.1021/acs.energyfuels.5b01493
- [12] Niu, B.; Ren, S.; Liu, Y.; Wang, D.; Tang, L.; Chen, B. Low-temperature oxidation of oil components in an air injection process for improved oil recovery. *Energy Fuels* 2011, 25, 4299-4304, 10.1021/ef200891u
- [13] Cinar, M.; Castanier, L. M.; Kavscek, A. R. Combustion kinetics of heavy oils in porous media. *Energy Fuels* 2011, 25, 4438-4451, 10.1021/ef200680t
- [14] Hascakir, B.; Ross, C.; Castanier, L. M.; Kavscek, A. Fuel formation and conversion during in-situ combustion of crude oil. *SPE J.* 2013, 18, 1217-1228, 10.2118/146867-PA
- [15] Hao, J.; Che, Y.; Tian, Y.; Li, D.; Zhang, J.; Qiao, Y. Thermal cracking characteristics and kinetics of oil sand bitumen and its SARA fractions by TG-FTIR. *Energy Fuels* 2017, 31, 1295-1309, 10.1021/acs.energyfuels.6b02598
- [16] Dejong, W.; Dinola, G.; Venneker, B.; Spliethoff, H.; Wojtowicz, M. TG-FTIR pyrolysis of coal and secondary biomass fuels: Determination of pyrolysis kinetic parameters for main species and NO<sub>x</sub> precursors. *Fuel* 2007, 86, 2367-2376, 10.1016/j.fuel.2007.01.032
- [17] Fang, M. X.; Shen, D. K.; Li, Y. X.; Yu, C. J.; Luo, Z. Y.; Cen, K. F. Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG-FTIR analysis. *J. Anal. Appl. Pyrolysis* 2006, 77, 22-27, 10.1016/j.jaap.2005.12.010
- [18] Wang, C.; Wu, Y.; Liu, Q.; Yang, H.; Wang, F. Analysis of the behaviour of pollutant gas emissions during wheat straw/coal cofiring by TG-FTIR. *Fuel Process. Technol.* 2011, 92, 1037-1041, 10.1016/j.fuproc.2010.12.029
- [19] Jiang, X.; Li, C.; Chi, Y.; Yan, J. TG-FTIR study on urea-formaldehyde resin residue during pyrolysis and combustion. *J. Hazard. Mater.* 2010, 173, 205-210, 10.1016/j.jhazmat.2009.08.070
- [20] Kök, M. V.; Varfolomeev, M. A.; Nurgaliev, D. K. Crude oil characterization using TGA-DTA, TGA-FTIR and TGA-MS techniques. *J. Pet. Sci. Eng.* 2017, 154, 537-542, 10.1016/j.petrol.2016.12.018
- [21] Kök, M. V.; Varfolomeev, M. A.; Nurgaliev, D. K. Thermal characterization of crude oils in the presence of limestone matrix by TGA-DTG-FTIR. *J. Pet. Sci. Eng.* 2017, 154, 495-501, 10.1016/j.petrol.2017.02.001
- [22] Yuan, C. D.; Varfolomeev, M. A.; Emelianov, D. A.; Eskin, A. A.; Nagrimanov, R. N.; Kok, M. V.; Afanasiev, I. S.; Fedorchenko, G. D.; Kopylova, E. V. Oxidation behavior of light crude oil and its sara fractions characterized by tg and dsc techniques: Differences and connections. *Energy Fuels* 2018, 32 (1), 801-808, 10.1021/acs.energyfuels.7b02377
- [23] Mothé, C.; de Miranda, I. Study of kinetic parameters of thermal decomposition of bagasse and sugarcane straw using Friedman and Ozawa-Flynn-Wall isoconversional methods. *J. Therm. Anal. Calorim.* 2013, 113, 497-505, 10.1007/s10973-013-3163-7
- [24] Opfermann, J.; Kaisersberger, E.; Flammersheim, H. Model-free analysis of thermoanalytical data-advantages and limitations. *Thermochim. Acta* 2002, 391, 119-127, 10.1016/S0040-6031(02)00169-7
- [25] Kök, M.; Acar, C. Kinetics of crude oil combustion. *J. Therm. Anal. Calorim.* 2006, 83, 445-449, 10.1007/s10973-005-7152-3
- [26] Liu, Q.; Wang, S.; Zheng, Y.; Luo, Z.; Cen, K. Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis. *J. Anal. Appl. Pyrolysis* 2008, 82, 170-177, 10.1016/j.jaap.2008.03.007
- [27] Freitag, N. P. Chemical-reaction mechanisms that govern oxidation rates during in-situ combustion and high-pressure air injection. *SPE Reserv. Eval. Eng.* 2016, 19, 645-654, 10.2118/170162-PA
- [28] Chawla, B. Oxidation of heavy petroleum streams at ambient temperature: Stability and compatibility of heavy oils and residua. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* 2003, 48, 6-9
- [29] Faure, P.; Schlepp, L.; Burkle-Vitzthum, V.; Elie, M. Low temperature air oxidation of n -alkanes in the presence of Na-smectite. *Fuel* 2003, 82, 1751-1762, 10.1016/S0016-2361(03)00133-9
- [30] Lee, D. G.; Noureldin, N. A. Effect of water on the low-temperature oxidation of heavy oil. *Energy Fuels* 1989, 3, 713-715, 10.1021/ef00018a009