

Sparing Crude Oil Rejection: Technical and Economic Feasibility Evaluation



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1. Introduction

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3. Results & Discussion

A rise in the heavy crude oil supply is becoming a known fact. This lead to an increase in the distillate residues as well as in the amount of their sulfur content. Despite effort in upgrading these residuals, final heavier bottom of the barrel such as tar, coke and asphalt is eminent. Refineries will be faced with the challenge of management of their hazardous and rising waste, unless high temperature thermochemical processes is integrated to current mid-size to large refineries. Gasification answers this challenge as the process converts these remaining residual to added values, i.e. hydrogen, Ammonia, other chemicals, steam or electricity. Gasification integration to the refinery is multifold solution to accommodate their existing residue, convert their rising residual, and gaining refinery economic. This profitable approach is facilitated by the availability and required gasification process infrastructure in the refinery except the gasifier, including air separation unit, the power island, gas separation and emission control units. Gasification is a stronger alternative compared to the upgrading or selling blended residual with gas oil Tamburrano [1]. He and Furimsky [2] highlighted such risk amidst the increase in the inorganics hazardous catalysts and sulfur contents in these residuals and the growing tighter legislations. This is also to avoid similar and past US crises between 1980 and 1990 when the coke flooded the market with over 70% production increase and slump in prices to as low as \$10 per ton despite its high heating value [3].

2. Methodology

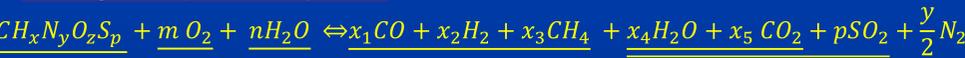
A. Analytical and experimental analysis of sample crude

Thermo-Gravimetric and elemental analyses are conducted on two types of crude oil samples. These samples are characterized with high naphtha upper distillates and low residuals, a typical characteristic of the locally produced crude oil in United Arab Emirates. These samples are brought from two different wells in UAE and used for educational purposes at Khalifa University laboratory. A multiple crucibles of ~18mg weight were prepared for thermo-gravimetric proximate analysis using Thermoscientific STDQ600 TGA machine. Following similar procedures of (Shabbar and Janajreh, 2013), the TGA experimental analyses were conducted under heambient condition, but purging in O2 instead of Air at flow rate of 100 ml/min. T sample crucibles are equilibrated at 30 °C for 2 min, then ramped to 750 °C at fixed heating rate of 5 C/min, and finally left in isothermal condition for 5 min before switching to air cooling back to ambient conditions. Another crucible sets of ~6mg used for the ultimate analysis of the crude oil utilizing the 5 element-CHNS&O FLASH200 appartus. This is required since carrying out thermodynamic and chemical analysis for crude oil provide enthalpy of formations that otherwise available for common liquid and gaseous fuels like jefuel, kerosine, and diesel etc, but not for the crude oil. Density, specific gravity and heat values are also evaluated following standard procedures using viscosity meters, hydrometer, and bomb calorimeter.

Sample	C(%)	H(%)	N(%)	S(%)	O(%)	Formula (CH _x N _y S _z O _w)	Viscosity (cP)	API Gravity	Bomb (MJ/kg)
No. 1	75.5±1.5	13.5±0.45	0.35±0.04	1.10±0.15	9.55±1.7	CH _{2.1457} N _{0.0004} S _{0.0055} O _{0.0949}	1.05±0.01	40.03±0.07	39.52±0.5
No. 2	76.3±1.3	12.5±0.55	0.33±0.03	0.98±0.13	9.89±1.3	CH _{1.9659} N _{0.0037} S _{0.0048} O _{0.0972}	1.11±0.1	38.01±2.1	38.87±0.4
Coal	0.7315	0.0531	0.0153	0.0101	0.1058	CH _{0.8711} N _{0.0179} S _{0.0052} O _{0.1085}	----	----	33.252*

B. Gasification Equilibrium Modeling

A thermodynamics analysis of gasification process is performed using equilibrium based modeling following the general gasification equation that formulated around 10 unknowns covering the species (m, n, x1 through x5 etc) and the temperature.



Feedstock Oxidizer Moderator Syngas Product Combustion Product

The solution is formulated from the below table representing independent set of equations:

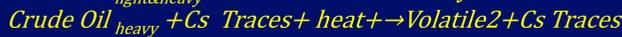
Equation	Description	Mathematical/Stoichiometric Formula
1,2,3	Element C, H, and O Balance	$\sum_{i=react}^{n \text{ of species}} C_i = \sum_{i=prod}^{n \text{ of species}} C_i$
4	Heat balance	$\sum_{i=react}^{n \text{ of species}} nh_i = \sum_{i=prod}^{n \text{ of species}} nh_i + Q$
5.a	Equilibrium: Gas Shift	$C + H_2O \rightleftharpoons CO + H_2 + 131 \text{ MJ/Kmol}$
5.b	Equilibrium: Boudouard	$C + CO_2 \rightleftharpoons 2CO + 172 \text{ MJ/Kmol}$
5.c	Equilibrium: Methanation	$C + 2H_2 \rightleftharpoons CH_4 - 75 \text{ MJ/Kmol}$
5.d	Equilibrium: CO shift	$CO + H_2O \rightleftharpoons CO_2 + H_2 - 41 \text{ MJ/Kmol}$
5.e	Equilibrium: Steam Reforming	$CH_4 + H_2O \rightleftharpoons CO + 3 H_2 + 206 \text{ MJ/Kmol}$
7	Product mole sum	$\sum_{i=prod}^{n \text{ of species}} X_i = 1$

C. Evaluation for Chemical Kinetics

The gasification of the crude oil differs from the solid coal as it consist of mainly volatile and characterized with two-event at low and high temperature. Gasification process is very complex inside the reactor with chemically intrinsic, unsteady flow of multiple-phase, highly turbulent, and multiple of chemically reacting flow species that all is driven by the devolatilization kinetics that needed for the development of more accurate gasification model.

TGA and DSC techniques are used extensively to evaluate reactions kinetics, including devolatalization, pyrolysis and combustion and offer the advantage of using small sample size, reproducible results of a few samples and can be done over a long temperature range

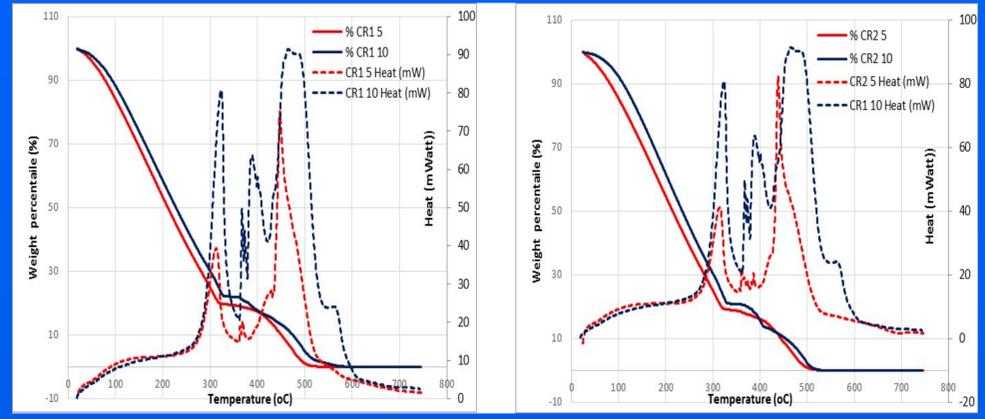
The crude thermal degradation will be represented by the two main devolatalization reactions successively and are constrained by the elemental mass and energy balance



The overall devolatalization reaction can be modeled via mass loss fraction ($X = w - w_0 / w_f - w_0$) and A and E kinetic pair are evaluated:

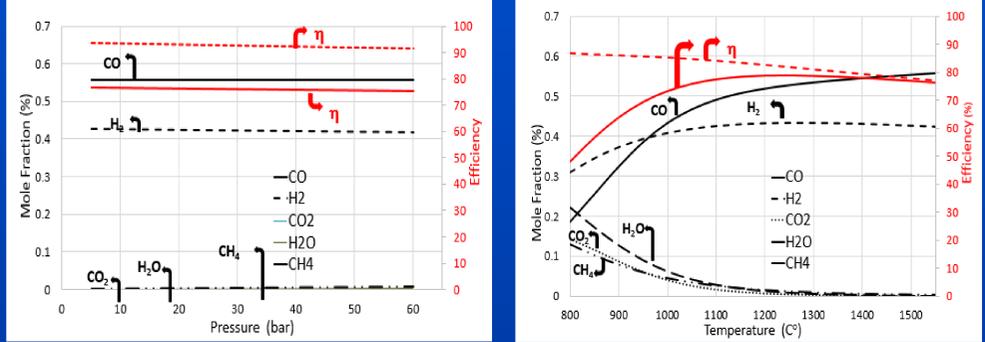
$$\frac{dX}{dt} = Ae^{-E/RT} (1-X)^n \quad \text{or} \quad \frac{dX}{(1-X)^n} = \beta Ae^{-E/RT} dt$$

A. TGA of Crude Oil 1 & 2 at 5C/min and 10C/min



The results of the TGA of the two different yet similar crude samples (CR1 and CR2) are depicted above. The purity of the samples renders excellent repeatability of the experimental data analysis following three repetitions and resulted in less than 0.5 C temperature-weight deviations. It is obvious that using higher heating value pushes the temperature to a higher value to yield similar pyrolytic compounds this is because the shorter or the insufficient residence time that is consumed at higher temperature to devolatilize a similar and equivalent sample. The heat release is also obvious at the end of the first devolatilization and lower temperature event. It is due to the heat of combustion that generated once the sample or its eluted compounds reach to their ignition point. This energy release first peak is centered around 320 C and is slightly pushed at higher heating value. This also marked the beginning of the higher temperature devolatilization event. This event is lesser smooth than the first event suggestion the inhomogeneous composition of the heavier portion of the crude oil which consists of asphaltene, xylene and toluene etc. This is also more obvious in the multiple appearing heat release peaks centered near 360 C, 385 C and broader one near 475C at higher heating rate while more confined and pronounced at lower heating rate. Similar observation applied to the second crude sample..

B. Effect of Pressure and Temperature on Gasification



As can be seen in the figure above, the conversion efficiency is slightly influenced by the process pressure while in general favors the lower process pressure. It marks near 76.7% (and 81.5% including CH₄) for the maximum attained conversion at 5bars for the three and two reactions process, respectively and these drops down to 75.3% and 77.66% at 60bars which is 1.5 and 2.8 percentile point drop in the efficiency for respectively the three and two process reactions. This is attributed to the generation of more methane at higher pressure that follows the steam the methanation and reforming reaction which is in line with le Chatelier's principle, i.e. "higher pressure reaction favors the least number of moles".

B. Kinetic evaluation

The evaluated kinetic data based on Arrhenius, and Coats-Redfern, 1st, 2nd and 3rd order models and for the 1st and 2nd devolatilization events

Model	Slope	Intercept	R ²	E (KJ/mole) A (1/sec) ^β	
				E (KJ/mole)	A (1/sec) ^β
Crude1 5C/min 1 st Event					
Arrhenius	-447.56	1.2725	0.9394	8.569494874	3.12E-01
Coats-Redfern 1st	-81.842	-11.952	0.7129	0.680434388	8.793E-05
Coats-Redfern 2nd	-693.05	-9.9784	0.9393	5.7620177	5.359E-03
Coats-Redfern 3rd	-1469.3	-7.5371	0.9482	12.2157602	1.305E-01
Crude1 5C/min 2 nd Event					
Arrhenius	-6534.3	7.3989	0.9192	125.11317	4.18E+05
Coats-Redfern 1st	-621.72	-11.242	0.7196	5.16898008	1.359E-03
Coats-Redfern 2nd	-4290	-4.3982	0.9208	35.66706	8.794E+00
Coats-Redfern 3rd	-9194.5	4.6347	0.9355	76.443073	1.578E+05
Crude1 10C/min 1 st Event					
Arrhenius	-471.54	-1.2476	0.9757	9.028643339	9.42E-04
Coats-Redfern 1st	-129.48	-11.955	0.851	1.07649672	1.387E-04
Coats-Redfern 2nd	-447.2	-10.757	0.9681	3.7180208	1.587E-03
Coats-Redfern 3rd	-1404.8	-7.9416	0.9493	11.6795072	8.327E-02
Crude1 10C/min 2 nd Event					
Arrhenius	-4240.1	4.002	0.4541	81.18579679	1.67E+02
Coats-Redfern 1st	120.26	12.304	0.5167	0.99984164	4.421E+06
Coats-Redfern 2nd	-1946	-7.7568	0.9588	16.179044	1.388E-01
Coats-Redfern 3d	-19936	24.045	0.3408	165.747904	9.207E+13

4. Conclusions

A comprehensive, predictive gasification modeling of the crude oil was carried out. Results are comparable to those obtained for the gasification of coal and showed favorability of crude oil gasification. As kinetics is missing for crude oil, kinetic investigation for the most important TGA events was conducted. This study has shown the feasibility of gasification of crude oil to give high quality syngas (CO₂ & H₂) and potentially using the result syngas as fuel stream to operate the IGCC.

References

- Shabbar S, Qudus R, Taha I, Janajreh I. Kinetics of pyrolysis and combustion of oil shale sample from thermogravimetric data. Fuel 90 (4): 1631-1637, 2011.
 Alkhatib I, Janajreh I, Azeem I, Ghani, G. (2019). Gasification behavior of coal and wood biomass: Validation and parametric study. Applied Energy, 195, 1007-1019.
 Almazrouei M, Janajreh I. Thermogravimetric Study of the Combustion Characteristics of Biodiesel and Petroleum Diesel. Journal of Thermal Analysis and Calorimetry, in the press 2018.