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Research Article

Microwave Application in Petroleum Processing

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Abstract

Microwave energy is becoming the most diverse form of energy transfer, used in the petroleum industry for inspecting coiled tubing and line pipe, measuring multiphase flow, and the mobilization of asphaltic crude oil. Depletion of conventional crude oil reserves creates economic demand for various fuels; in Canada, efforts have intensified to develop microwave technology for in-situ enhanced oil recovery of heavy oil/bitumen; about 26 of the estimated 30 billion barrels of heavy oil are considered unrecoverable using current technology. Specific objectives included studying microwave process conditions affecting upgrading of heavy oil/bitumen to synthetic crude and achieve up to 50% desulphurization.

Keywords: *Microwave Irradiation; Oil Upgrading; Heavy Crude Oil; Bitumen Viscosity*

Introduction

Electromagnetic aspects of energy transfer between microwaves and other forms of matter are comprehended in processes where microwave energy is used to affect a chemical or physical change. Though its implications in petroleum applications are yet to be fully understood, the non-thermal aspects of energy transfer between microwaves and other forms of matter are always visible in processes where microwave energy is used to cause a chemical or physical change in the irradiated material. The depletion of conventional crude oil reserves is accompanied by growing economic demand for various types of fuel, biodiesels and petrochemical products creating the need for remediation of heavier asphaltenic crude [1]. Thus, the extraction, transportation and refining of this highly viscous, high paraffinic, high sulfur content crude oil and its wastes is becoming more prominent since heavy oil deposits exceed light oil deposits by two orders of magnitude [2]. In this work, multiple crude oils were studied for hydro-desulphurization (HDS) and defragmentation processes by a novel method of microwave irradiation. The specific objectives were to identify conditions that would upgrade the oil and simultaneously substantially reduced the sulphur content using microwave irradiation, and to obtain preliminary data on process economics. Results showed strong indications for the microwave technology to be employed not only for hydrocarbon extractions but also for in-situ and field upgrading of heavy oil, and reduction in sulphur content of crude oil. There was evidence of fragmentation and combination reactions present in the process, as well as high percent reduction in sulphur content. Overall, the microwave technology presents the best alternative, economically and environmentally, to the existing technologies for enhanced oil recovery operations and processing.

The microwave process employs specific frequency microwaves targeted into the formation containing heavy hydrocarbons to initiate conversion of the hydrocarbon into synthetic crude, with reduced discharge of greenhouse gas into the environment as natural gas or other fuels are not required to reduce viscosity [3]. The specific objectives were to identify conditions that would upgrade the oil and achieve up to 50% desulphurization using microwave irradiation, and to obtain preliminary data on process design and economics.

Typical reactions in the removal of various organic sulphur compounds have been identified as follows:

Thiols

$R—SH + H_2 \rightarrow RH + H_2S$

Naphthenes-, Aromatic-, and Alkyl- Suphides

$R—S—R' + 2H_2 \rightarrow RH + R'H + H_2S$

Disulphides

$R—SS—R' + 3H_2 \rightarrow RH + R'H + 2H_2S$

The process of the study was based upon expansion of Miadonye et al.'s 2009 article focusing upon crude oil desulphurization, however in the case of this project, acquiring a further array of oil compositions and loosely defining the limits of microwave exposure.

Experimental Methods

The process was carried out in a domestic microwave oven which was modified to allow for the accommodation of a mixer and a device to monitor temperature and pressure in the reactor and interfaced with a desktop computer for data recording. In a typical experiment, oil was mixed with one or more of additives (Table 1,2) and exposed to various dosages of microwave radiation at low pressure. The selection of microwave sensitizers was based on their dielectric constant obtained from literature [5]. The power level and irradiation intensity was at level high. Maximum irradiation period was 25 minutes (Figure 1,2). Irradiated samples were analyzed with GC-MS and distillation techniques. The distillation unit was provided by SGS lab at PointTupper; you may wish to visit and/or contact this lab to gather specifications and other details. For further details regarding analytical methods, refer to Miadonye et al., 2009.

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Table 1: Materials and Relative Properties (Adapted from Miadonye et al., 2009, page 457).

Materials	Properties
Arabian Heavy Crude Oil	°API 27.31, Sulfur content 3.066%
Australian Spirit Crude Oil	°API 61.2, Sulfur content 0.01%
Bonny Light Crude Oil	°API 33.4, Sulfur content 0.16%
Hibernia Light Oil	°API 30-32, Sulfur content 0.38%
Activated Charcoal	Sensitizer (S2); 12-20 mesh
Palladium Oxide	Catalyst, 99.9% purity
Serpentine	Sensitizer (S1), 98.0% purity
Di-ethanolamine (DEA)	Polar Additive

Table 2: Typical Formulations of Samples for Irradiation and Analyses.

Oil	Additives
Non-Irradiated	-
Arab Heavy Irradiated	Pure and 10% DEA
Australian Spirit Irradiated	Pure and 10% DEA + S1 or S2
Bonny Light Irradiated	Pure and 10% DEA
Hibernia Light Irradiated	Pure

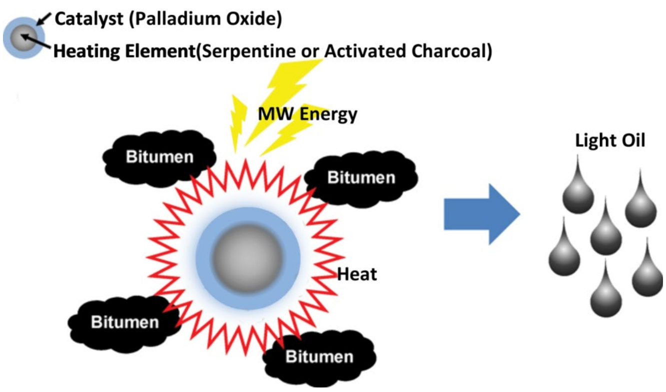


Figure 1: Typical process mechanism for the microwave irradiation of crude oils.

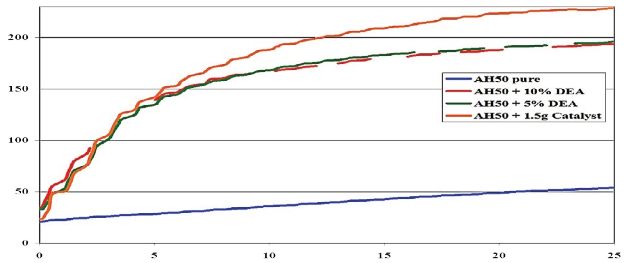


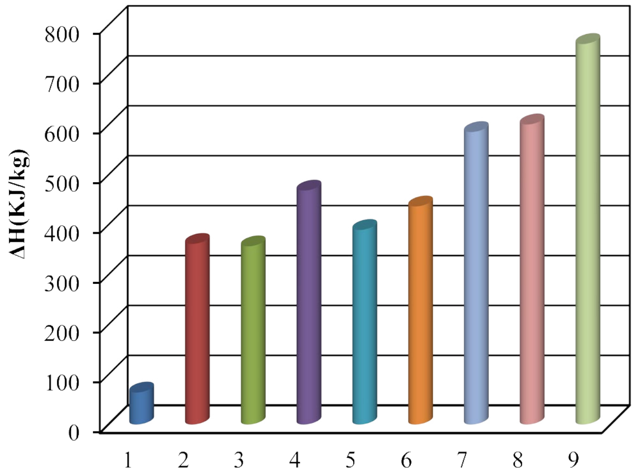
Figure 2: Microwave Absorption characteristics of samples for 25 minutes [4].

Results

Change in the sulfur content for the oil samples subjected to high pressure hydrogenation reaction was negligible (between 1.8% and 2.3%); sulfur contents of the light distillates were reduced to 39% and 48%, while those of heavy distillates were reduced to 0.9% and 10% (Table 3). At high temperatures, a high rate of evaporation of the light fractions was noted, which in turn reduced the overall mass of remaining product and allowed for disruption of long chain hydrocarbons and release of sulfur. The irradiated samples containing ethanolamine, sensitizer, and catalyst show reduction in sulfur content of between 16% and 39.4%; this provides solid proof that sensitizers improve absorption of microwave radiation (Figures 2 - 4). To ascertain the amount of power absorbed by the sensitizers, the energy absorbed at Power Level 10 by 650 ml crude oil samples were measured (Figure 3). Samples in some cases were found to be slightly charred, indicative of over-microwaving to reverse the intended

Table 3: Sulfur content analysis for irradiated and non-irradiated AH50 fractions [4].

Distillation Fractions	Temp (°C)	Irradiation Time (mins)	Mass (g)	Mass % sulfur	
				Non-irradiated	Irradiated sample with 10% DEA, 15% charcoal cat.
1	154.5 – 250.0	10	6.75	1.859	0.9624 (48.3%)
2	260.0 – 306.2	10	3.96	0.3110	0.1902 (38.8%)
3	318.2 – 380.1	13	7.23	0.9030	0.8128 (10%)
4	396.4 – 452.2	25	18.31	2.528	2.506 (0.89%)
Residue	-	n/a	12.34	-	-
Loses	-	n/a	1.41	-	-



1: Pure Crude Oil
2: Crude+ 10wt%DEA
3: Crude +5wt% charcoal
4: Crude + 10wt% charcoal
5: Crude +1 gr catalyst
6: Crude + 1.5gr catalyst
7: Crude + 10wt% DEA+1gr catalyst
8: Crude + 10wt% charcoal+10wt% DEA
9: Crude+ 15wt% charcoal+10wt% DEA

Figure 3: Effect of Sensitizers on enthalpy of Arab Heavy crude oil irradiated for 20 minutes [3].

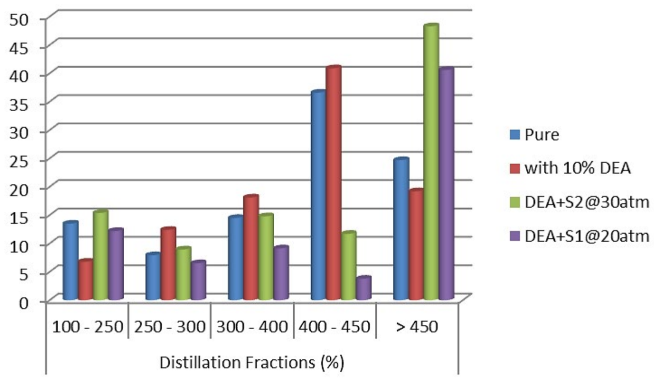


Figure 4: Distillation fractions of different irradiated samples of Arab Heavy crude for 20 minutes with various degrees of additives [3].

effects of irradiation. Serpentine was found to be a poor microwave sensitizer compared to activated charcoal; it should also be noted that past studies activated carbon products have proven preferable due to the lack of vaporisation seen during microwaving, however, regrettably become a composite of the resulting mixture [6]. Results obtained with GC-MS showed little significant change in molecular structure (Figure 5) for majority of the light crude oil samples after being subjected to microwave irradiation. Again, this is likely due to

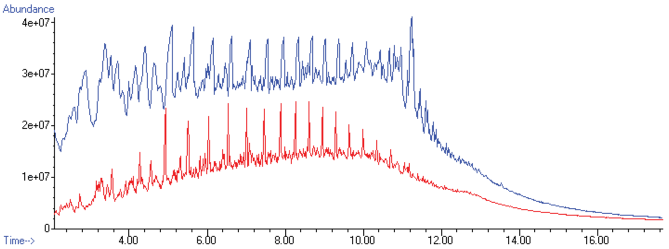


Figure 5: GC-MS analysis of (in blue) Australian Spirit pure crude non-microwaved (in red) Australian Spirit pure crude microwaved.

choice of microwaving time and ratios of sensitizer to crude sample used.

Conclusions

Microwave irradiation presents a potential alternative to the highly costly desulphurization process presently used in the industries promoting simultaneous fragmentation and recombination of molecules. When used in combination with the appropriate catalyst, sensitizer and other process parameters, microwave irradiation can be used for desulphurization and upgrading of heavy sour crude oil; the sensitizers and additives promote simultaneous fragmentation and recombination of molecules. Up to 39% desulphurization of the original heavy crude oil, mainly at the light fractions can be obtained with an increased expectancy through further investigation. Regarding future work there is a need for further trial regarding optimization of microwave time as well as identification of a possible retention time which may present the greatest issue as numerous samples were indicative of such changes; if this problem endures, investigation must be taken to ensure this is mitigated for the purposes of future industrial application.

Acknowledgements

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