Desulfurization of heavy crude oil by microwave irradiation

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Abstract

Heavy crude oils normally have a high sulfur content and are usually very viscous. To improve the quality of the refinery fractions and subsequent consumers' products, it is imperative to remove the impurities and contaminants and, where possible, upgrade the heavy crude oil. In this project, the desulphurization process of Arabian heavy sour crude oil was studied by a novel method of microwave irradiation. The heat transfer characteristics of various mineral additives were studied for use as microwave sensitizers. Crude oil samples containing various combinations of hydrogen donor additives, catalysts, and microwave sensitizers were studied. The samples were exposed to different irradiation periods at different power levels in a modified domestic microwave oven. The results indicate that crude oil microwave absorption characteristics can be improved fourfold with charcoal and doubled with polar solvents, but they showed negligible change with serpentine, due to poor hear transfer properties. The sulfur content of the original crude oil was reduced by 2.3% with H_2 at 20 atmosphere pressure and 5 minutes irradiation period; and by 33.8% with ethanolamine as the hydrogen donor and 25 minutes irradiation period. For the crude oil fractions, the sulfur reductions were up to 48% and 10% for lighter and heavier fractions respectively. Analysis with GC-FID showed strong evidence of fragmentation and recombination reactions in samples irradiated for 20 and 25 minutes with a temperature of 300°C and above.

Keywords: crude oil desulfurization, microwave irradiation, petroleum upgrading, hydro-desulfurization, microwave sensitizers.

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1 Introduction

The application of radiation chemistry in the oil industry gained prominence in the early 1960s when only light hydrocarbon substances were used as models in radiation processing experiments [1, 2]. Radiation processing was rather expensive then and it was not until the 1990s that the concept of the 'hydrocarbon enhancement electron-beam technology' (HEET) was developed. More recently, microwave irradiation has been used in the petroleum industry for inspecting coiled tubing and line pipes, measuring multiphase flow, and the mobilization of asphaltic crude oil [2–5]. Gunal and Islam [3] observed the permanent alteration of asphaltene in the colloidal structures of the crude oil molecules and an increase in viscosity when exposed to microwave irradiation, due to the re-orientation of molecular structures rather than thermal breakdown. They noted that when exposed to electromagnetic irradiation, the presence of asphaltene caused permanent changes in crude oil rheology due to the polar nature of asphaltene molecules. Zaykin et al. [6, 7] reported the evidence of much branching and breaking of the paraffin chain during irradiation of paraffinic oil. Thus, microwave heating has been identified to offer numerous advantages, such as short start up time, rapid heating, energy efficiency, and precise process control.

Microwave energy can be delivered directly to the reacting or processing species by using their dielectric properties or by adding absorbing material, which converts electromagnetic energy into heat. Thus, microwave energy has the ability to crack hydrocarbons and create a method of desulphurization. The sulfur content in heavy crude oil varies from 0.1% to 15%, and most is heavy molecular organic sulfur compounds – any dissolved elemental sulfur and/or hydrogen sulfide represent only a small part of the total sulfur. The sulfur containing compounds in crude oil have been identified to include the following compounds: sulfides, disulfides, mercaptans (thiophenes), benzothiophenes, dibenzothiophenes, benzonaphthothiophenes, and dinaphthothiophenes [8]. Desulphurization of crude oil is an important preliminary step to improve the quality and yield of gasoline products. Currently, the method of desulphurization in the chemical industry has fundamental limitations, such as costly energy and material consumption, extreme processing conditions and expensive catalysts. New products and processing routes are continually being sought including current methods in microwave irradiation. Through the use of microwave power, along with additives, hydrocarbons high in sulfur content and/or composed of primarily heavy hydrocarbons can be made into useful commercial products that can be burned cleanly and efficiently as a fuel oil, as demonstrated in several patents for the use of microwave irradiation [9].

2 Experimental methods

The experiments involved the reconstruction of a domestic microwave to accommodate the devices required for monitoring the irradiation process, and the analysis of the reaction products using appropriate analytical instrumentation.

2.1 Microwave set-up and irradiation process

The desulphurization process was carried out in a domestic microwave oven which was modified to allow for the accommodation of high temperature and moderate pressure reactors, mixing device, and a device for reconstitution of volatile fractions. Also included in the modification was a provision for monitoring the temperature and pressure of the process. In a typical experiment, Saudi Arabia heavy crude was mixed with one or more of hydrogen, light hydrocarbon liquid, polar additives, hydrotreating catalysts, microwave sensitizers, 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 [10]. The power level and irradiation intensity was at level high (recorded in this microwave oven as Power Level 10), and the maximum irradiation period was 25 minutes. Table 1 illustrates the different samples used in the process. Polar additives used were ethanolamines, to examine their influence on desulphurization and, on the microwave radiation characteristics of the Saudi Arabia heavy crude oil.

Table 1: List of materials.

Arabian Heavy Crude Oil	°API (27.31); Sulfur content (3.066%)
Pure Hydrogen Gas	
Activated Charcoal	Sensitizer
Palladium Oxide	Catalyst
Serpentine	Sensitizer
Ethanolamines	Polar Additives
Mongstad, Norway Crude Oil	Model Compound

2.2 Analytical methods

The products formed after irradiation and the control samples were analyzed using Gas Chromatography with Flame Ionization Detector (GC-FID), GC with Mass Spectrometry (GC-MS), and Fourier Transform Infrared (FT-IR) spectroscopy among other analytical methods. The GC instrument is a 5890 Series II Plus Gas Chromatograph coupled with a FID and a 5872 Mass Selective Detector (MS) fitted with a fused silica capillary column. The column contained the non-polar stationary phase used for simulated distillation analyses (ICB-1, 30mx0.25mm ID, 0.25µm film thickness; J & K Scientific, Milton, Ontario, Canada). The initial column temperature 70°C, held for 1 minute, then increased at a rate of 30°C/min to 310°C and held for 1 minute. The injection volume was 0.5µl. The carrier gas was ultra-high purity hydrogen (from Air Liquide Canada, Sydney, Nova Scotia, Canada) at an initial pressure of 4.1 psi (at 70°C) and flow rate of 0.50ml/min. The FID was held at 350°C with H_2 at 35ml/min; air, 350

ml/min, make-up N_2, 25ml/min. The MS interface temperature was 320°C. It was operated in the scan mode (50-550 amu) with 1-minute solvent delay period. Each analysis was 10 minutes. Carbon standards were analyzed and retention times of n-C5, 10,15,20,25 and 30 were determined.

3 Results and discussion

The physical properties of the pure (original) heavy crude oil were determined. The ºAPI was obtained by hydrometer to be 27.31, with sulfur content of 3.066 per cent and viscosity of 34.84 cSt at 25.2°C. The distillation fractions of the pure heavy crude oil obtained between 154°C and 452°C for 50 gram sample and their mass per cent of sulfur contents before and after microwave irradiation are compared in Table 2. The sulfur contents of the light distillates were reduced to 39% and 48%, while those of heavy distillates were reduced to 0.9% and 10%. The results showed approximately 50% desulphurization can be achieved in the lighter fractions.

3.1 Effects of sensitizers and additives in hydro-desulfurization

The main purpose of hydro-desulphurization (HDS) is to improve the quality of the heavy crude oil and thus, meeting the required specifications for its particular

Table 2: Sulfur content analysis for the fractions.

Distillation Fractions (50 g)	Temp (°C)	Irradiation Time (mins)	Mass % sulfur	
			Non-irradiated	Irradiated for 10 mins with catalyst
1	154.5 to 250.0	10	1.859	0.9624 (**48.3%**)
2	260.0 to 306.2	10	0.3110	0.1902 (**38.8%**)
3	318.2 to 380.1	13	0.9030	0.8128 (**10%**)
4	396.4 to 452.2	25	2.528	2.506 (**0.89%**)

use. Depending on the process conditions the HDS process can be classified as "destructive" or "non-destructive". The destructive HDS process is characterized by molecular fragmentation and hydrogenation saturation of the fragments to produce lower boiling fractions, and the non-destructive HDS process requires milder conditions (referred to as hydrotreating) and provides a means of removing simple souring compounds [8]. In the microwave irradiation process it is difficult to meet the requirements of the HDS destructive process in the absence of sensitizers. The prevailing conditions in microwave process generally favor non-destructive HDS due to the low temperature conditions obtainable with microwave irradiation. Since crude oil absorbs little microwave radiation, sensitizers and other polar solvents have been used to improve its absorption. As indicated in Figure 1, the presence of sensitizers and additives improved absorption by the oil of microwave radiation, identified by the increase in the temperature of the oil.

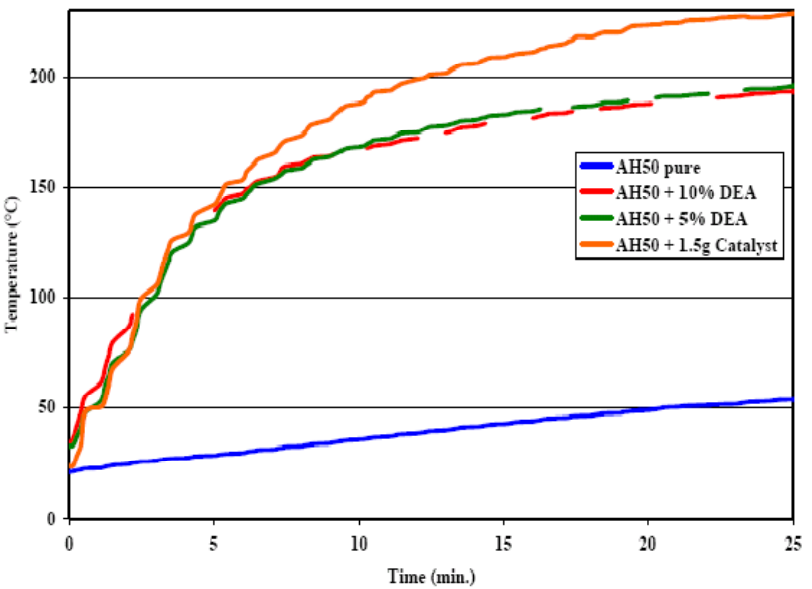

Figure 1: Microwave absorption characteristics of heavy crude oil with and without additives.

To ascertain the amount of power absorbed by the charcoal and serpentine used as sensitizers, the energy absorbed at Power Level 10 by 60 ml water core immersed in 650 ml crude oil jacket was measured. Each sensitizer was incrementally added into the crude oil jacket and irradiated for a prescribed period. Table 3 illustrates the microwave absorption characteristics of the sensitizers as given by the average power absorbed by the oil in the jacket. It is evident from the results that serpentine is a poor microwave sensitizer with 73 Watts (perhaps this is unique with the type of serpentine used for this experiment

Table 3: Microwave absorption characteristics of the sensitizers.

Samples	Composition	Final Temperature (ºC)	Irradiation Time(s)	Power (Watt)
AH50 (original crude) only	650 ml crude oil	32.2	90	100
AH50 + 60g charcoal	650 ml oil and charcoal	91.8	90	975
AH50 + 40g charcoal + 60ml water	water tube in 650 ml oil	oil: 33.2 water: 102.0	45	oil: 383 water: 461
AH50 + 20g charcoal + 60ml water	water tube in 650 ml oil	oil: 28.3 water: 101.0	43	oil: 241 water: 476
AH50+ 3.25g serpentine	650 ml oil + serpentine	30.8	90	73

as their composition varies depending on location). The activated charcoal however, improved the microwave absorption characteristics of the crude oil from 100 to 975 Watts and thus, one of the effective sensitizers for crude oil.

The non-irradiated sample was also pressurized with pure hydrogen gas at 20 and 30 atmosphere pressure and then heated in a high pressure steel reactor and maintained at 84.5ºC and 100ºC respectively for 30 minutes over a palladium-silica based catalyst. The results of sulfur analysis are given in Table 4 for the heavy oil and Table 2 for the fractions. The change in the sulfur content for the samples that were subjected to high pressure hydro-desulphurization reaction in the autoclave heating was negligible, between 1.8% and 2.3%, compared to 16% and 33% for irradiated samples as shown in Table 4.

In agreement with the required process conditions for hydro-desulphurization discussed above, it is obvious that the temperatures for the autoclave process were too low to initiate the reaction for effective reduction in sulfur content of the heavy oil. On the other hand, for irradiated samples desulphurization was not much affected by high temperature as it was with irradiation periods, with the optimum period being 25 minutes for 33.8% desulphurization. The results showed that ethanolamine has potential as a desulphurization agent for sour crude oil.

3.2 Effects of irradiation on heavy oil composition

The samples exposed to five different microwave irradiation periods; 0, 5, 10, 15, 20, and 25 minutes were analyzed using GC-FID and GC-MS. The results

from the analysis showed no change in molecular structure for majority of the samples after being subjected to microwave irradiation. At irradiation temperatures of up to 300°C, corresponding to approximately 590KJ/kg, there was no noticeable change in molecular structure for the different samples as shown with the GC-FID analysis (Figure 2). The desired enthalpy to achieve breaking of the hydrocarbon bonds may not have been obtained at these temperatures.

Table 4: Sulfur content of the heavy crude after irradiation.

Samples	Temp. (ºC)	Irradiation Time(min)	Sulfur Content (%)	% Sulfur Reduction
Heavy oil (AH50) only	-	-	3.066	-
AH50-PM(10%)H_2=30atm	84.5	autoclave heating	3.011	1.8
AH50-PM(10%)H_2=20atm	100	autoclave heating	3.012	1.8
AH50-PM(5%)H_2=20atm	84.5	autoclave heating	2.997	2.3
AH50+1.5g Palladium cat	228.8	25	3.06	No change
AH50+10% charcoal on cat	243.7	25	No observation	-
AH50+10%DEA+15% charcoal on cat	381.6	25	2.574	16.1
AH50-(10%DEA)	193.6	25	2.062	32.8
AH50-(5%DEA)	196.1	25	2.031	33.8

Bond energy or enthalpy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. Looking at the enthalpy attained in each reaction media (samples 1 to 6 in Table 5), it is apparent that only a few reaction medium attained the energy necessary to bring about bond cleavage. Samples number 5 and 6 have enthalpies of 601.3 KJ/kg and 762.5 KJ/kg respectively. The highest temperature achieved when using charcoal as the sensitizer was 381.6°C (sample number 6). The GC-FID chromatogram of this sample showed a noticeable change in molecular structure (Figure 3) compared to the chromatogram for the pure crude (sample #1). There was an evident shift in the peaks of the chromatogram of this sample compared to that of the original heavy

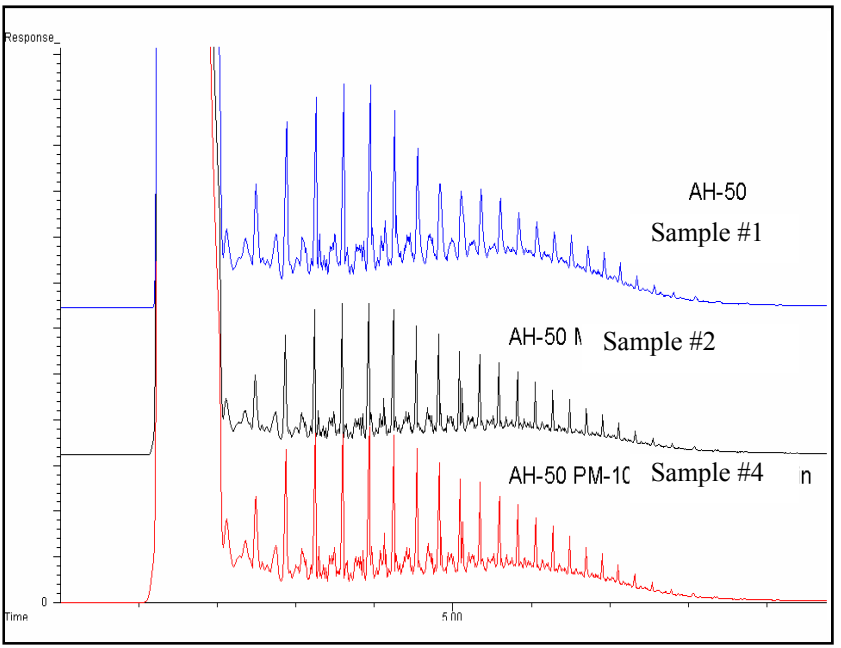

Figure 2: GC-FID of microwave irradiated samples.

Table 5: Energies of the reaction medium after 25 minutes microwave irradiation.

Sample number	Sample composition	Final Temperature (°C)	ΔH (KJ/kg)
1	AH50 Pure Crude 100g	53.80	-
2	AH50 Pure Crude 100g + 10% DEA	193.6	362.1
3	AH50 pure crude 100g + 1.5g palladium catalyst	228.8	437.1
4	AH50 pure crude 100g + 10% DEA/1g palladium catalyst	298.8	586.2
5	AH50 pure crude 100g + 10% DEA/ 10% charcoal/ 1g palladium catalyst	305.9	601.3
6	AH50 pure crude 100g + 10% DEA/ 15% charcoal/ 1g palladium catalyst	381.6	762.5

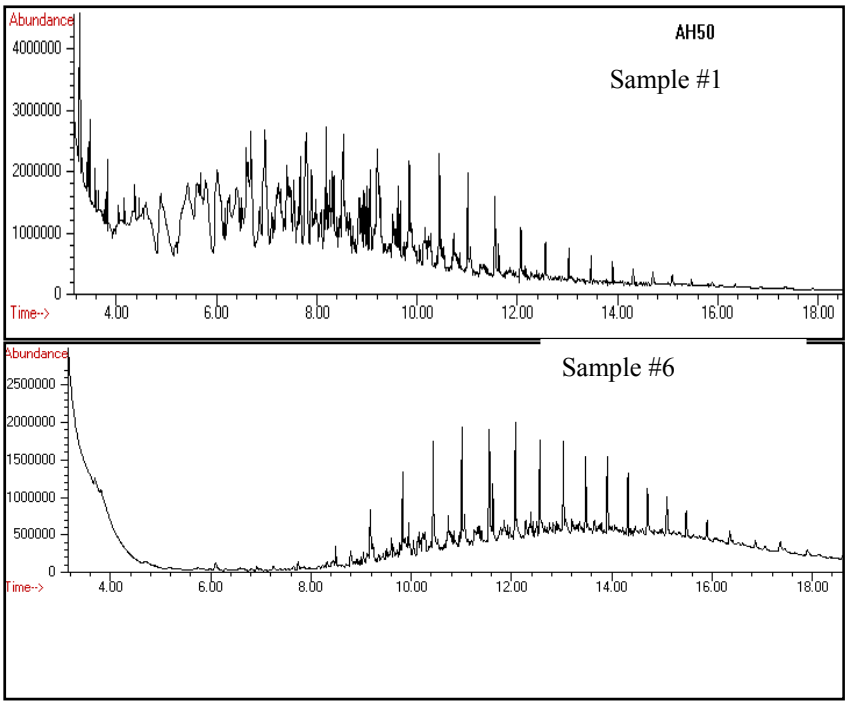

Figure 3: Comparison of GC-FID of pure heavy crude oil and crude oil sample containing additives irradiated for 25 minutes.

crude and other samples with lower reaction temperatures. These results suggest that the molecular structure of the sample has changed and higher molecular weight hydrocarbon chains were formed through chemical bonding.

With 15 per cent charcoal on palladium catalyst (sample #6), the highest temperature of 381.6°C was obtained approximately 10 minutes into the set irradiation time of 25 minutes. Once this temperature was achieved, it decreased to 346.1ºC over the remaining 15 minutes. The extra irradiation time allowed the reaction to proceed further causing the hydrocarbons to bond and create a higher molecular weight material. It appears that the optimum microwave irradiation time for this sample is 10 minutes which is when the highest temperature was reached. At this time, there might have been some breaking of the heavier hydrocarbons. Similar trend was obtained with sample #5, attaining the temperature of 305.9°C in approximately 17 minutes before reducing to slightly lower temperature. Viscosity tests were conducted at 30°C for each microwave sample to verify and compare the changes in molecular nature of the crude at different microwave irradiation time. The results are shown in Figure 4 for three samples. Viscosity results do not explicitly confirm the presence of light fractions, but illustrate the strong possibility of abundance of high molecular weight hydrocarbons. This is an indication of the domination of recombination

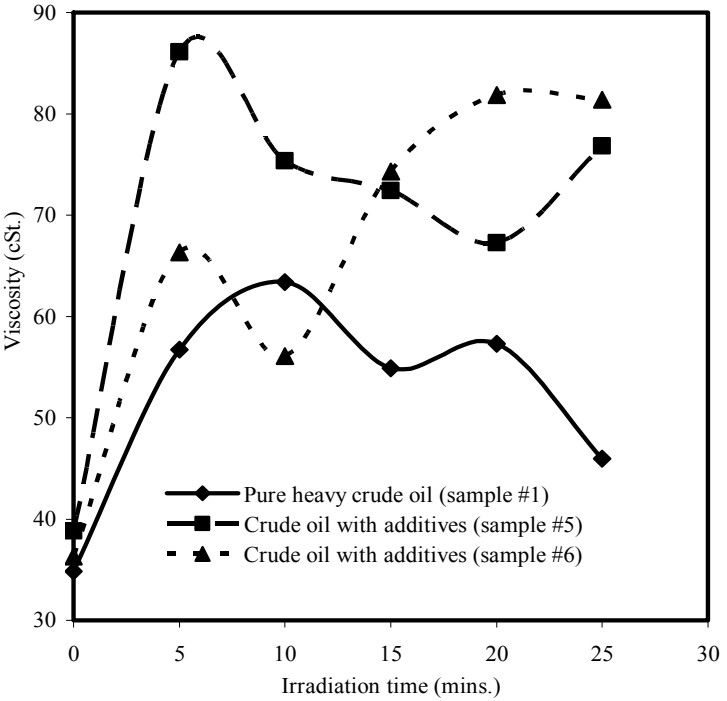

Figure 4: Comparison of viscosity of different samples exposed to different irradiation times.

reactions over fragmentation reactions in microwave process. This observation is in agreement with the GC-FID chromatogram obtained for irradiated and pure samples given in Figure 3.

4 Conclusion

The application of microwave irradiation process for desulphurization and upgrading of heavy crude oil is illustrated. The results show that sensitizers improve crude oil absorption of microwave radiation and that with appropriate composition of polar additive, catalyst and sensitizer up to 40% desulphurization is achievable. Erratic change in the viscosity of the heavy crude oil indicates the occurrence of fragmentation and recombination reactions at different irradiation time. Overall, the viscosity of irradiated samples is slightly higher than that of non-irradiated sample which means that recombination reaction is prevalent. This study shows that microwave radiation promotes both desulphurization and upgrading of heavy oil at low temperatures where similar reactions are not feasible by the thermal process. The optimum condition for desulphurization and upgrading of heavy crude oil by microwave irradiation depends on the composition and type of catalyst, microwave sensitizer, polar additive and

irradiation period. For concurrent desulphurization and upgrading process 25 minutes irradiation time, 381°C, 10% ethanolamine, and 15% activated charcoal on palladium catalyst were identified as the optimum.

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