Microwave Radiation Induced Visbreaking of Heavy Crude Oil

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Abstract
Microwave energy is slowly becoming the most diverse form of energy transfer and has been used in the petroleum industry for inspecting coiled tubing and line pipe, measuring multiphase flow, and the mobilization of asphaltic crude oil. In Canada, efforts have been intensified to develop microwave irradiation technology for in-situ enhanced oil recovery of the country’s large deposits of bitumen and heavy oil. The new technology employs specific frequency microwaves targeted into the formation containing heavy hydrocarbons to initiate conversion of the hydrocarbon into synthetic crude. The results of work presented in this report showed strong indications for the microwave technology to be employed not only for hydrocarbon extractions but also for in-situ induced visbreaking of heavy oil and bitumen (to drastically reduce oil viscosity for pipeline transportation without the use of diluents). Overall, the microwave technology presents the best alternative, economically and environmentally, to the existing visbreaking technologies for upgrading of heavy crude oil and bitumen.

Keywords
Heavy Crude Oil; Microwave Energy; Viscosity; Radiation Induced Cracking; Petroleum Visbreaking; Microwave Sensitizers

Introduction
The application of radiation chemistry in oil industry gained prominence in the early 1960s when only light hydrocarbon substances were used as models in radiation processing experiments (Panchenkov, and Erchenkov, 1980; and Ashton et. al, 1994). 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 pipe, measuring multiphase flow, and the mobilization of asphaltic crude oil (Gunal, and Islam, 2000; Stanley, 2001; and Zaykina, et. al, 2002). Gunal and Islam (2000) observed permanent alteration of asphaltene in the colloidal structures of the 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. Zaykina, et. al (2002) and Zaykin et al. (2004) 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. 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 which can be burned cleanly and efficiently as a fuel oil, as demonstrated in several patents for the use of microwave irradiation (US Patent 1979, 1988 and 1994).

Materials And Experimental Methods
The visbreaking process was carried out in a 1.1ft³ domestic microwave oven Dandy model DMW 1048SS
which had been modified to contain a water loop, a reactor (Pyrex glass and Teflon), thermocouples, and a mixer, connected to a products separation and collection system and a computer (for recording temperature and products volume percent during reaction). Also included in the modification was provision for monitoring the temperature and pressure of the process. Table 2 shows the properties of different samples used in the process, which also included refinery residuum and Lloydminster bitumen.

**TABLE 2 MATERIALS AND THEIR PROPERTIES**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabian heavy crude oil</td>
<td>°API 27.31, Sulfur content 3.066%</td>
</tr>
<tr>
<td>Australian Spirit crude oil</td>
<td>°API 61.2, Sulfur content 0.01%</td>
</tr>
<tr>
<td>Bonny light crude oil</td>
<td>°API 33.4, Sulfur content 0.16%</td>
</tr>
<tr>
<td>Activated Charcoal</td>
<td>Sensitizer (S2); 12-20 mesh, Laboratory grade; Sigma-Aldrich Canada Co. Oakville, ON.</td>
</tr>
<tr>
<td>Palladium Oxide</td>
<td>Catalyst; 99.9 % purity Sigma-Aldrich Inc. St. Louis. MO. USA.</td>
</tr>
<tr>
<td>Serpentine</td>
<td>Sensitizer (S1); 98.0% purity Sigma-Aldrich Canada Co. ON.</td>
</tr>
</tbody>
</table>

In a typical experiment, heavy crude was mixed with 5 and 10 percent of various proportions of hydrocarbon additives, catalysts and microwave sensitizers (see Table 3).

**TABLE 3 TYPICAL FORMULATIONS OF SAMPLES FOR IRRADIATION AND ANALYSES**

<table>
<thead>
<tr>
<th>Oil</th>
<th>Diluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arab Heavy Non-Microwaved</td>
<td>-</td>
</tr>
<tr>
<td>Arab Heavy Microwaved</td>
<td>10% Diethanolamine</td>
</tr>
<tr>
<td>Arab Heavy Microwaved</td>
<td>10% Diethanolamine + Sensitizer 1 or 2 (DEA + S1 or S2)</td>
</tr>
<tr>
<td>Arabian Spirit Non-Microwaved</td>
<td>-</td>
</tr>
<tr>
<td>Arabian Spirit Microwaved</td>
<td>10% Diethanolamine</td>
</tr>
<tr>
<td>Arabian Spirit Microwaved</td>
<td>10% Diethanolamine + Sensitizer 1 or 2 (DEA + S1 or S2)</td>
</tr>
<tr>
<td>Bonny Light Non-Microwaved</td>
<td>-</td>
</tr>
<tr>
<td>Bonny Light Microwaved</td>
<td>10% Diethanolamine</td>
</tr>
<tr>
<td>Bonny Light Microwaved</td>
<td>10% Diethanolamine + Sensitizer 1 or 2 (DEA + S1 or S2)</td>
</tr>
</tbody>
</table>

A 40 gram sample of each formulation was subjected to microwave irradiation for different time periods. The power level and irradiation intensity was at a high level (recorded in this microwave oven as Power Level 10), and the maximum possible irradiation period was 20 minutes. The samples were then examined with GC-MS, to allow for an understanding of compound mass changes along with reduction of compounds upon microwaving. The percent reduction in sulphur contents of the crude oil was also determined. The sample mixtures that were very viscous charred at prolong irradiation periods. Thus, the maximum irradiation period was limited to 20 minutes to avoid excessive loss of volatile components of the samples. 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.

**Results And Discussion**

**Irradiation Effects on Crude Oil Composition**

In a typical experiment, heavy crude was mixed with 5 and 10 percent of various proportions of hydrocarbon additives, catalysts and microwave sensitizers (see Table 3).
various hydrocarbon additives, catalysts and microwave sensitizers (S1 and S2). These samples were subjected to microwave irradiation for different time periods. Figures 1 and 2 are the typical distillation fractions of irradiated samples, illustrating the distributions of fractions at different temperature ranges.

As evidenced in the graphs, there were remarkable changes in the composition of each fraction. The irradiated samples containing ethanolamine, sensitizer, and catalyst show reduction in the percentages of lower temperature fractions. In Figure 2, an increase in the heavy fraction (>450°C) is more apparent with samples that contained the sensitizers. As indicated in Figures 1 and 2, the presence of sensitizers and additives improved absorption characteristics of the oil to microwave radiation; identified by the significant shift in molecules distribution to the largest fraction (> 450°C each fraction) with sensitizers and an increase in the volume percent of mid-fractions for sample with only polar solvent.

Serpentine (S1) was found to be a poor microwave sensitizer compared to activated charcoal (S2) which gave a better microwave absorption characteristics for the crude oil. The shift to higher molecular weight distribution for crude oil samples is also shown in the GC-MS micrographs (Figures 3-6). The GC-MS micrographs comparing various irradiated and non-irradiated oil samples showed the irradiated samples to shift more towards the high scale, which is an indication an increment in higher molecular weight fractions in the sample. This phenomenon is more noticeable in the chromatograms of heavy crude than those of light crude oil as reported in our previous work (Miadonye et. al, 2008). Figures 3 to 6 compare micrographs of samples irradiated for 20 minutes with non-irradiated ones for Bonny Light oil (Figure 3), Australian spirit crude oil (Figure 4) and Arabian heavy crude (Figures 5 and 6). Figures 3 and 4 showed no significant change in distribution of fractions before and after 20 minutes exposure of the samples to microwave radiation.

The irradiated samples containing ethanolamine, charcoal, and catalyst show reduction in lower hydrocarbon fractions and an increase in higher hydrocarbon fractions (Figure 2) This is in agreement with Figure 5 which showed a shift in the micrograph of irradiated sample to high scale, an indication of an increase in the higher molecular weight fractions in the sample. This effect is well highlighted in Figure 6 for heavy oil with no additives or sensitizers.

![Fig. 3 Comparison of Micrographs of Bonny Light Crude Oil Samples](image1)

![Fig. 4 Comparison of Micrographs of Australian Spirit Crude Oil Samples](image2)

The prevailing conditions in microwave process generally favor non-destructive process due to the low temperature conditions which characterise microwave irradiation. Since crude oil absorbs little microwave radiation, sensitizers and other polar solvents have been used to improve its absorption characteristics. In our previous work (Miadonye et. al, 2008), we indicated that two processes of fragmentation and recombination are present during crude oil irradiation. The irradiated samples containing ethanolamine, sensitizer, and catalyst showed a reduction in the light fractions of the heavy crude oils (Figures 5 and 6). This is an indication of the occurrence of recombination reactions by the lower molecular weight fractions. This is in agreement with Figures 1 and 2 which showed a substantive percent increase in heavier fraction. However, fragmentation reaction appeared to be dominant in the light crude oil samples shown in Figures 3 and 4, and in heavy Arabian crude
containing only 10wt% ethanolamine (Figure 2). It is worthy to mention that at high temperature there was a high rate of evaporation of the light fractions which arguably will significantly affect a recombination reaction in the microwave process.

![Irradiated Sample with DEA and S2](image)

**FIG. 5 COMPARISON OF MICROGRAPHS OF ARABIAN HEAVY CRUDE OIL SAMPLES**

![Irradiated Sample](image)

**FIG. 6 COMPARISON OF MICROGRAPHS OF HEAVY OIL SAMPLES WITH NO ADDITIVES**

**Viscosity Characteristics of Irradiated Samples**

Viscosity measurements at different temperatures were made for the irradiated samples to examine their flow characteristics. The results are compared in Figure 7 with a pure unmicrowaved sample. Viscosity results illustrate the presence of light fractions at prolonged irradiation time and the strong possibility of the abundance of high molecular weight hydrocarbons at shorter irradiation time. From Figure 7, it is evident that the addition of 10wt% diethanolamine (DEA) lowered the viscosity of the heavy oil to approximately 70cSt at 20°C, but after 10 minute exposure to microwave radiation the viscosity increases to above 95cSt. This is an indication of the domination of recombination reactions over fragmentation reactions at low irradiation time in microwave process. However, when the irradiation time was increased to 25 minutes a lower viscosity of approximately 35cSt was obtained at 20°C. Addition of a microwave sensitizer (charcoal) only made a minimal difference in viscosity reduction. The results from viscosity measurements (Figure 7) and distillation (Figure 1) do not explicitly confirm the degrees of fragmentation and recombination reactions present in a typical irradiated sample, but show a strong dependency of reaction pattern on irradiation time of the sample in the microwave process.

![Viscosity of Heavy Crude Oil Samples at Different Temperatures](image)

**FIG. 7 VISCOSITY OF HEAVY CRUDE OIL SAMPLES AT DIFFERENT TEMPERATURES.**

**Energy and Cost Efficiency**

To determine the amount of power dissipated by the microwave per unit electric field and the energy costs related to this method the equation suggested by Wang and Yang (1994) applies.

\[ P = 55.63 \times 10^{-12} \times F \times E^2 \]

Where \( P \) is the power absorbed per unit volume of mineral (w/m²), \( F \) is the frequency of the microwave (Hz), and \( E \) is the imaginary part of the complex dielectric constant (dimensionless). Before being able to determine the amount of power dissipated by the microwave, first an experiment to determine the value of \( E \), the imaginary part of the dielectric constant, had to be conducted. Since this experiment can not be carried out in its explicit form the enthalpy data for
each sample was calculated by calorimetric method. Figure 8 shows the energy per kg of different samples irradiated for 25 minutes. For pure crude oil sample, the energy was approximately 50KJ/kg and increased by 7 to 15 fold depending on the types of additives and sensitzers used. The results on enthalpy values (Figure 8) gave an indication on the absorption of sensitzers in inhomogeneous mixtures to determine localized and selective heating in the reaction mixture. It is evident from the results that charcoal has the potential as a good sensitizer in crude oil microwave process. It is worthy to mention here that experiments on samples with both charcoal and catalyst did not yield conclusive results. The energy required to effect reactions in microwave process arguably depend mostly upon property of the sensitzers to improve the microwave absorption characteristics of the crude oil.

![Enthalpy of Heavy Crude Oil with Various Additives Irradiated for 25 Minutes](image)

**FIG. 8 ENTHALPY OF HEAVY CRUDE OIL WITH VARIOUS ADDITIVES IRRADIATE FOR 25 MINUTES**

The results from the analysis using GC-MS showed no significant change in molecular structure for majority of the light crude oil samples after being subjected to microwave irradiation. At temperatures of up to 300°C, corresponding to approximately 490KJ/kg, results obtained from microwave irradiation of these samples showed there was no noticeable change in molecular structure as displayed by the GC-MS analysis (Figures 3 and 4). The desired enthalpy to achieve breaking of the hydrocarbon bonds may not have been obtained at these temperatures. Bond energy or enthalpy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. For the methane molecule for instance, (CH₄), 435KJ is required to break a single C-H bond for a mole of methane. From Figure 8, it is apparent that only a few reaction medium attained the energy necessary to bring about bond cleavage.

**Conclusions**

The study showed that microwave irradiation in combination with the appropriate catalyst, sensitizer, and/or additives and other process parameters can be used for upgrading of heavy crude oil. It is shown that microwave radiation promotes both fragmentation and recombination reactions simultaneously for upgrading of heavy oil at low temperatures. The crude oil viscosity and irradiation time mostly control the type of reactions that dominate in the microwave process. The results from GC-MS for heavy oil sample suggest that the molecular structure of the sample has changed and higher molecular weight hydrocarbon chains were formed through bonding; an indication of the domination of recombination reactions over fragmentation reactions for high viscosity samples in the microwave process. However, the optimum dose and reaction kinetics for microwave process of crude oil irradiation need to be established.

**ACKNOWLEDGMENT**

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Adango Miadonye is a Professor of Chemical Engineering and the Chair of Department of Chemistry at Cape Breton University. He joined Cape Breton University in 1998 after many years of university teaching and research experience in Chemistry, Chemical Engineering and Petroleum Engineering in several countries. He is a member of editorial boards of several journals for chemical engineering, and petroleum science and engineering, and served as Chair in several Research Award Selection Committees for Government and Private sectors. Dr. Miadonye is an adjunct Professor at the Department of Process Engineering and Applied Science, Dalhousie University.

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