Fossil Fuel and Hydrocarbon Conversion Using Hydrogen-Rich Plasmas

**Topical Report
February 1994 - February 1995**

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Work Performed Under Contract No.: DE-FC21-93MC30126

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

MASTER

By
Western Research Institute
University of Wyoming Research Corporation
Laramie, Wyoming

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EXECUTIVE SUMMARY

Exploratory experiments have been conducted on the use of hydrogen and methane plasmas as a means of converting waste materials and heavy oils to hydrogen-rich transportation fuels. Experiments were conducted in batch and continuous operational modes with an industrial microwave generator and a commercially available microwave oven. A continuously circulating reactor was constructed for carrying out experiments on flowing oils.

Experiments on the decomposition of scrap tires demonstrated that microwave plasmas can be used to decompose scrap tires into potentially useful liquid products. In an experiment conducted in the batch mode using a commercial microwave oven, about 20% of the tire was converted to liquid products in about 9 minutes.

Methane was decomposed in a microwave plasma to yield a liquid product composed of a variety of compound types. Gas chromatography/mass spectrometry (GC/MS) analyses of the liquid product identified a wide variety of unsaturated compounds including benzene, toluene, ethyl benzene, methyl and ethyl naphthalene, small amounts of larger aromatic rings, and a number of olefinic compounds.

Experiments conducted on a crude oil in a continuously flowing reactor showed that distillate materials are produced using hydrogen and methane plasmas. In addition, the recycle oils had an overall carbon aromaticity that was lower than that of the starting feed material, indicating that some hydrogenation and methanation had taken place in the recycle oils.

INTRODUCTION

Objectives

The objectives of this project are to investigate the use of microwave-generated plasmas to develop an innovative, noncatalytic method for directly converting fossil fuel and hydrocarbon-containing materials to hydrogen-rich transportation fuels, while simultaneously reducing the nitrogen, sulfur, and oxygen heteroatom contents.

Background

The basic chemical problem in converting fossil fuels, such as coals, to liquids and in upgrading heavy oils is that of manipulating the atomic hydrogen-to-carbon ratio (H/C) during the process. Coals and petroleum resids typically have H/C ratios of less than unity because of their high carbon aromaticity. Therefore, to make a suitable liquid fuel with an H/C ratio between 1.6 and 2.0, either hydrogen must be added or carbon removed.

During coal liquefaction, hydrogen is added in the presence of a catalyst to assist with bond rupture and production and stabilization of small molecules. Literally hundreds of compounds and combinations have been tested and used as catalysts for coal liquefaction. With the passage of the Clean Air Act Amendments of 1990, a different strategy must be adopted for converting fossil fuels to liquid transportation fuels. Increased emphasis will be placed on producing liquids that have fewer aromatic compounds and more hydrogen-rich isoparaffins. Further, there must be a considerable reduction in the nitrogen, oxygen, and sulfur heteroatoms.

Some studies have been conducted on the reaction of coal with hydrogen atoms generated in a microwave discharge. These studies (Amano et al. 1984, 1985) could have enormous implications on coal liquefaction, resid upgrading, and on the requirements of future transportation fuels as dictated by the Clean Air Act Amendments of 1990. The coal liquids produced from these experiments were practically free of heteroatoms and were composed mainly of mono-, di-, and tricyclic paraffins in the carbon range C_5 to C_{22} . The atomic H/C ratio of the liquid was 1.82 and the oil specific gravity and refractive index were 0.855 and 1.447, respectively. These values are typical of highly hydrogenated light hydrocarbons.

A gas chromatographic simulated distillation showed that the coal liquid corresponded to a mixture of petroleum fractions consisting of 35% gasoline, 28% kerosene, 34% gas oil, and 3% fuel oil. Thus, H-atom induced coal liquefaction, as demonstrated by these experiments, can provide a method whereby coal can be directly converted to an eminently suitable feedstock for transportation fuels in a single step, without the use of catalysts or high pressure hydrogen. The fact that the process was applied to subbituminous coals is also noteworthy, because these coals are already low in sulfur and therefore, represent a desirable starting material.

Although the experiments of Amano were conducted on coals, these experiments suggest that, in general, fossil fuels and hydrocarbon-containing materials might be hydrogenated at low severity conditions without the use of catalysts and that the produced liquids might have remarkable qualities for a transportation feedstock. Methods that increase the product yields now need to be investigated.

Exploratory experiments have been conducted using microwave plasmas to determine whether high-quality liquid products can be obtained by reacting low-quality feedstock materials in various microwave plasmas. Feedstock materials included scrap tires and heavy crude oil. Microwave plasmas were generated using hydrogen (H_2) and methane (CH_4), with and without argon and helium. The results of those experiments are the subject of this topical report.

EXPERIMENTAL

Feedstock Materials

The crumb rubber waste tire material was obtained from the Western Research Institute (WRI) Asphalt and Heavy Oil Division. Originally, the material was supplied by Rubber Granulators, Inc. (Snohomish, Washington) for a WRI asphalt crumb rubber rheology study.

A crude oil, API gravity 23.1, from Chetopa, Kansas, was used as the liquid reactant. Experiments were performed using the whole crude oil and a preconditioned oil. The crude oil was preconditioned by vacuum distillation to remove the low-boiling (<369/<478K) fraction. Simulated distillations of the total crude and preconditioned crude oil, reported in terms of conventional distillate fractions, are given in Table 1. The preconditioned feedstock consisted mostly of material boiling above 478K, mostly in the heavy and vacuum gas oil boiling ranges.

Table 1. Simulated Distillation of Total and Preconditioned Chetopa Crude Oil

Distillate Fraction	Temperature Range, K	Total Oil, % Distilled	Preconditioned, % Distilled
Gasoline	305 - 361	0.02	0.02
Naphtha	361 - 466	7.32	0.02
Kerosene	466 - 544	18.60	2.46
Light Gas Oil	544 - 594	13.57	8.36
Heavy Gas Oil	594 - 700	26.76	33.75
Vacuum Gas Oil	700 - 839	24.12	37.41
Residue	839 +	9.61	17.98

Simulated Distillation

This procedure is a gas chromatographic technique for determining distillation profiles of materials that are not 100% distillable below 544 K. The chromatographic data are divided into desired distillate fractions from correlations between gas chromatography (GC) retention times and normal alkane boiling points. The concentration (weight percent) of each distillate fraction is determined using response factors obtained from standard samples. The results are reported as concentration (weight percent) of distillable material versus temperature. The boiling ranges are chosen to correspond to those of the true boiling point distillation (Gary and Handwerk 1975).

NMR Analyses

NMR measurements on solid reaction products were made on a Chemagnetics CMX solids NMR spectrometer using the technique of cross polarization with magic-angle spinning (CP/MAS). CP/MAS Nuclear Magnetic Resonance (NMR) measurements were made at a carbon frequency of 25 MHz using a low background ceramic probe. The ceramic probe reduces probe background signals that arise when recording spectra of samples having low levels of total organic carbon for which signal averaging over long periods of time is required. A 7.5 mm o.d. pencil sample spinner was used.

Spinning rates were ~4.5 kHz. Data were collected using a pulse delay of 1 s, a contact time of 1 ms, a pulse width of 5 μ s and a sweep width of 16 kHz. A 50 Hz exponential multiplier was applied to the free induction decay before Fourier transformation.

The NMR spectra were integrated between 90 and 260 ppm for the aromatic region and between -40 to 90 ppm for the aliphatic region. The spinning rates were sufficiently high so that contributions to the aliphatic integral from high field aromatic carbon spinning sidebands were negligible and were not included in the aliphatic carbon integral. The carbon aromaticity values can contain contributions from carbonyl (~210 ppm) and carboxyl carbons (~180 ppm) if present.

Liquid-state ^{13}C NMR spectra were also recorded on the WRI solids NMR spectrometer using a single pulse sequence with decoupling. Generally, the resolution is sufficient to obtain reliable carbon aromaticity measurements in this manner. Data were collected on non spinning samples using a pulse delay of 1 s, a pulse width of 5 μ s and a sweep width of 16 kHz. Typically, 1800 transients were collected. The NMR spectra were integrated between 90 and 260 ppm for the aromatic region and between -40 to 90 ppm for the aliphatic region.

Gas Analyses

Gas samples were analyzed using a Hewlett-Packard 5840A gas chromatograph. Hydrocarbon gases were analyzed on a Chemipac C-18 column with flame ionization detector. A helium flow rate of 30 cc/min. was used. The column was temperature programmed from 353 to 443 K at 25 K/min. A Chromosorb 102 column and thermal conductivity detector were used to provide an argon/methane ratio that was used to calculate the approximate outlet gas volume for some tests. The column was temperature programmed from 243 to 453 K at 25 K/min.

Process Procedures

The apparatus used to conduct the tests consisted of a recirculating reactor system, a microwave energy system, and a gas flow system. The recirculating reactor, shown schematically in Figure 1, was used for most of the testing. The plasma was contained within a 19-mm o.d. vycor tube that passed through the microwave applicator. A thin stainless steel rod with a pointed tip was sealed in the top of the plasma tube. This rod was sparked with a Tesla coil to provide the free electrons needed to initiate the plasma.

Figure 1. Schematic Diagram of Recirculating Flow Quartz Reactor System

The lower portion of the reactor served as a sump from which the oil was circulated by means of a peristaltic pump. The oil was pumped from the sump through a 5-mm i.d. pyrex tube sealed concentrically inside the vycor plasma tube. The oil flowed from the open top of the pyrex tube, down the outer surface of the tube, and back to the sump for recycle. By raising and lowering the reactor with respect to the fixed microwave applicator the distance between the liquid discharge and the plasma zone could be varied.

The sump and lower portion of the plasma tube were wrapped with a heat tape that was controlled by means of a variac. The heat tape was used to warm the oil so that it could be pumped. A type K thermocouple junction located a few centimeters below the discharge end of the pyrex circulation tube provided a measure of the bulk temperature of the oil as it approached the plasma zone.

The system used to deliver microwave energy to the terminated waveguide applicator consisted of a microwave generator, magnetic circulator, directional coupler, impedance matching device, and various waveguide sections. A block diagram of this system is shown in Figure 2.

Figure 2. Block Diagram of Microwave Apparatus

Microwave energy was supplied by a Cober S6F industrial microwave generator. The generator power output was adjustable from 0 to 6000 watts (J/s) at a fixed frequency of 2.45 GHz. The generator was connected via a magnetic circulator and a Microwave Techniques twin stub tuner to a terminated waveguide applicator (Haugsjaa 1986). The applicator was constructed by boring a 22-mm hole through the center of the broad faces of a standard WR284 waveguide termination. The distance from the center of the hole to the shorted end of the termination was equal to one half the width of the broad face. Hewlett-Packard 432 power meters were used in conjunction with the directional coupler to measure incident and reflected power.

The gas flow system is shown schematically in Figure 3. Precision needle valves were used to regulate the flow of reactant and inert gases. Flow rates were measured by rotameters that were calibrated using a soap bubble flow meter. A Wallace and Tiernan precision differential pressure gauge (0 to $1.06 \cdot 10^5$ Pa) was used to measure the system pressure.

Figure 3. Schematic Diagram of Gas Flow System

Condensable liquid products were collected from the outlet gas stream in a 10 mL cold trap immersed in a slurry of dry-ice and methanol. Downstream of the cold trap, a rubber septum was provided through which grab samples of the product gas could be withdrawn by means of a gastight syringe. A throttle valve, vacuum trap, and rotary pump completed the gas flow system.

Inert gases were high purity helium and argon supplied by United States Welding. Technical grade methane supplied by Scott Specialty Gases and hydrogen from an electrolytic generator were used as reactant gases.

For a typical test series, the distance between the top of the oil discharge tube and the bottom of the microwave applicator was established by moving the reactor up or down to the desired position. This distance remained set throughout the test series. The preconditioned crude was warmed in an oven to a temperature above the pour point, and approximately 10 g of the warm oil was placed in the sump. The heat tape was adjusted to maintain the oil temperature at about 329 K, and the circulation pump was started.

With the oil circulating, the vacuum pump was started, and the system was pumped down to the test pressure. After the desired pressure was attained, inlet gas flow was begun by opening the appropriate flow control valve or valves. After allowing several minutes for the system to purge and equilibrate, the microwave generator was turned on at a preset power, the stainless steel rod was sparked with a Tesla coil to initiate the plasma, and the beginning time, pressure, gas flows, oil temperature, and generator power output were recorded.

Pressure, flows, and temperature were recorded, and grab samples of the product gas stream were taken at intervals as the test progressed. After the test the generator was shut off, and the system was brought up to atmospheric pressure with inert gas. The cold trap was allowed to warm up and samples of the condensed liquid product and recycle oil were saved for analysis.

RESULTS AND DISCUSSION

Plasma Reactions with Waste Materials

Exploratory experiments were conducted on the use of microwave-induced hydrogen plasmas for converting scrap tires to useful products. Two experimental arrangements were employed. In one arrangement, a small glass thimble containing ~0.5 gram of -40 + 80 mesh Rubber Granulators, Inc. scrap tire was placed inside a 19-mm (o.d.) Vycor tube. This assembly was then placed in the waveguide of a Cober Electronics model S6F industrial microwave generator. The contents were evacuated to $\sim 2.7 \cdot 10^3$ Pa pressure and a flow of hydrogen maintained at this pressure. A hydrogen plasma was induced by discharging a Tesla coil onto a thin metal rod that extended into the plasma region. The rod was removed after plasma initiation.

The crumb rubber was irradiated for about 15 minutes under these conditions and produced about an 8% weight loss. For this preliminary experiment, gases and liquids were not trapped. However, there was a noticeable change in the color of the residue from black to brown. Solid state ^{13}C NMR measurements were made on the residue material (Figure 4b). The spectrum clearly shows the loss of natural rubber (133, 124, 22 ppm) and styrene-butadiene (128, 25 ppm), and butyl rubber (128, and 32 ppm) components as a result of chemical reactions in the plasma.

Figure 4. Single Pulse Solid-State ^{13}C NMR Spectra of: (a) Scrap Tire, (b) Tire Residue after Hydrogen Plasma Reaction in Cober Unit, (c) Tire Residue after Hydrogen Plasma Reaction in Kenmore Oven

The residual component at ~ 110 ppm has not been identified. Typically, carbon resonances in this spectral region are due to various protonated aromatic carbons, alkenes and vinyl and substituted vinyl structures. The carbon at 28 ppm in the residue does not appear in the spectrum of the original scrap tire. This carbon could be due to a methyl group β to an aromatic ring, which would form as a result of cleavage of the styrene butadiene copolymer. No attempts were made to positively identify the residue carbons in these exploratory experiments. However, it is interesting to note that the most prominent carbon type in the residue is a minor component of the starting material. The origin of the broadening of the resonances was not determined.

Another scrap tire/hydrogen plasma experiment was conducted using a Kenmore microwave oven. In this experiment ~3 grams of scrap tire were placed in a round bottom flask which was configured to maintain a flow of hydrogen at ~20 torr. The scrap tire was irradiated for ~9 minutes in the hydrogen plasma, during which there was a 53% conversion to gas and liquid products. Most of the conversion occurred during the first few minutes. Liquids accounted for 37.5% of the amount converted.

The residue from this experiment was examined by solid-state ^{13}C NMR (Figure 4c). This residue resembled the starting material in terms of color; however, the residue severely detuned the NMR probe, presumably because of increased electrical conductivity of the residue carbon. Comparison of the NMR spectra of both residues show removal of most of the carbons in the polyisoprene (natural rubber) and polystyrene-butadiene components.

Produced liquids were trapped in a dry ice/methanol bath. Simulated distillation was performed on the liquid product to assess its quality (Figure 5). The distillation curve was bimodal with almost one third (31.5%) of the material boiling in the gasoline and diesel boiling ranges. Residue accounted for about 10% of the liquid material.

Figure 5. Distillation Curve of Pyrolysis Liquids Resulting from Microwave-Plasma Induced Decomposition of Scrap Tire Material.

A "blank" experiment was run on the scrap tire in the hydrogen gas with the microwave oven turned on, but without generating a plasma. In this experiment there was no noticeable weight loss for the same reaction time of about 9 minutes.

Although these experiments were exploratory, they did illustrate that microwave-induced plasmas could be used to decompose waste tires into potentially useful liquid products. In the exploratory experiments, the rubber tire was placed in the region where the plasma was generated. However, this arrangement tends to produce more gases than liquids. Additional studies are necessary to more completely determine the feasibility of the process. Such studies include *inter alia* varying the geometry of the sample/plasma arrangement, the use of magnetic fields to concentrate the reactive species, and the use of other gases (e.g., methane) to alter the reaction chemistry and final value-added product distribution.

Plasma Experiments with Total Chetopa Crude Oil

Microwave plasma experiments were conducted on the unrefined Chetopa crude oil to test the circulating reactor system. Experiments were conducted for different periods of time using hydrogen and methane plasmas at pressures of ~5 torr, flow rates of 5 cc/minutes and microwave power of 200 watts (J/s) (Table 2).

Table 2. Summary of Microwave Plasma Experiments on Chetopa Crude Oil

Sample	Pressure, Pa	Gas	Flow, cc/minutes	Microwave Power, watts (J/s)	Temperature, K	Duration, minutes
865-50	1012	He/H ₂	5/5	200	312 - 332	98
865-52	1012	He/H ₂	5/5	200	312 - 332	98
865-54	733	He	5	0	311 - 323	287
865-56	733	He/H ₂	5/5	200	317 - 345	180
865-60	613	He	5	200	331	75
865-62	547	He	5	200	307 - 339	60
865-64	747	He/CH ₄	5/5	100-150	316 - 334	260

A portion of the starting material was distillable under the low pressure at which the plasma experiments were conducted. As a result, some distillate material was collected in the dry ice/methanol trap when the microwave generator was off and when there was no hydrogen or methane in the plasma. Run 865-54 (Table 2) represents a blank run when the microwaves were turned off and there was no plasma, and run 865-60 represents a blank in which there was microwave power in the cavity and a helium plasma was generated.

The distillate and resid from these runs were collected, and simulated distillations were performed to obtain an assessment of the quality of the liquids. The results for the distillates are shown in Figure 6. The data indicate that up to the temperature at which about 50 vol % of the liquid product is distilled, the boiling temperatures of the plasma-produced distillates are lower than the distillate fraction of the crude oil produced in the absence of the plasma. A bar graph comparing the initial boiling points for the four distillate fractions is shown in Figure 7. The distillates collected from exposure to hydrogen and methane plasmas had initial boiling points lower than the materials generated during the blank runs. The distillate from the crude oil in the absence of any plasma had the highest initial boiling point. These data suggest that some improvement of distillate quality may have been obtained during irradiation of the crude oil in the hydrogen and methane plasmas. However, material balances were not obtained, so the results are not quantitative.

During experiments on the generation of plasmas from methane, some liquids were produced and were collected in the dry ice/methanol trap. It was estimated that between 5 and 10% of the methane was converted to liquids from recombination reactions of the reactive radical and ion species in the methane plasma. Gas chromatography/mass spectrometry (GC/MS) and ^1H NMR analyses were made on the liquid product. The GC/MS analyses identified a wide variety of unsaturated compounds including benzene, toluene, ethyl benzene, methyl and ethyl naphthalene, small amounts of larger aromatic rings, and a number of olefinic compounds. These types of compounds are also formed during high temperature pyrolysis and aromatization of methane (Marcelin et al. 1993). A ^1H NMR spectrum of the liquid product is shown in Figure 8. The spectrum clearly shows a large number of aliphatic hydrogens (0 to 4 ppm) and aromatic hydrogens (6 to 8 ppm) in the sample. Olefinic hydrogens (4 to 6 ppm) represent a small amount of the total hydrogen composition of the sample.

Figure 6. Simulated Distillation for Plasma-Produced Distillates from Total Chetopa Crude Oil

Figure 7. Initial Boiling Points for Plasma-Produced Distillates from Total Chetopa Crude Oil

Figure 8. ¹H NMR Spectrum of Liquids Produced from a Methane Plasma
Plasma Experiments with Vacuum Distilled Chetopa Crude Oil

A summary of the microwave plasma experiments conducted on the Chetopa crude oil is listed in Table 3. These experiments were mostly exploratory experiments to see what effects different combinations of plasmas might have on changing the composition of the resid. As a result, the amount of conversion was not obtained. In future experiments, a batch reactor will be employed to obtain conversion data.

The recycle oils from the plasma experiments exhibited similar distillation profiles. However, the simulated distillation chromatograms of the recycle oils all showed an enhanced normal alkane peak compared to the starting material (Figure 9). The origin of this peak is not known. Generally, plasma reactions lead to a variety of different products. As noted earlier, even for liquids produced from methane the product distribution was a complex mixture of compounds. The C₂₅ peak could also be an artifact due to some type of contamination. However, we have not been able to validate this. The C₂₅ peak was identified by comparing its retention time with that of a known standard.

Table 3. Summary of Plasma Experiments Using Preconditioned Chetopa Crude Oil

Sample	Pressure, Pa	Gas	Flow, cm ³ minutes ⁻¹	Temperature, K	Power, watts (J/s)	Duration, minutes	Distance from wave guide, cm
086576-R ^a	750-7200	He	7	325-331	0	135	0.3 cm
086582-R	625-890	He/H ₂	5/10	329-332	50	275	0.3 cm
086582-O ^b	---	---	---	---	---	---	---
086584-R	460-660	He	5	324-336	50	285	0.3 cm
086584-O	---	---	---	---	---	---	---
086584-C ^c	---	---	---	---	---	---	---
086587-R	600-865	H ₂	10	327-338	50	185	0.3 cm
086587-O	---	---	---	---	---	---	---
086590-R	600-865	He/Me	4/10	330-336	50	538	0.3 cm
086590-O1	---	---	---	---	---	215	0.3 cm
086590-O2	600-865	Me	10	330-336	---	323	0.3 cm
086594-R	425-690	Ar/Me	2.5/10	330-335	50	259	0.3 cm
086594-O	---	---	---	---	---	---	---
086598-R	720-850	Ar/Me	5/10	330-336	50	223	0
086598-O	---	---	---	---	---	---	---
0865100-R	950-1200	Ar/H ₂	4/8	333-341	50	117	0
0865100-O	---	---	---	---	---	---	---
0865100-F	feed						

^aR- Recycle Oil, ^bO- Product Oil, ^cSolid Reaction Product

In general, the simulated distillation curves of the oils produced from various combinations of plasmas were similar. Most of the product oils were distillable in the range of 369 to 400 K (Table 4). Figure 10 shows the simulated distillation boiling point curve for sample 82-O, which was generated in a He/H₂ plasma. This curve is typical of the oils produced from the microwave plasma reactions.

Figure 9. Simulated Distillation Chromatogram of Preconditioned Chetopa Oil (top) and Recycle Oil from Helium/Methane Plasma Experiment with Preconditioned Chetopa Oil (bottom)

Table 4. Simulated Distillations of Produced Oils from Plasma Experiments with Preconditioned Chetopa Crude Oil, K

% distilled	Sample							
	865-82	865-84	865-87	865-90.1	865-90.2	865-94	865-98	865-100
0.5	411	385	419	397	370	377	367	388
10	474	459	481	466	439	453	422	454
20	490	479	497	485	485	482	462	472
30	500	491	507	496	500	495	481	484
40	507	501	514	505	508	504	493	491
50	514	508	522	512	515	511	503	499
60	522	515	527	522	523	520	512	505
70	527	524	533	528	528	525	522	512
80	535	531	540	538	537	532	530	521
90	544	543	548	549	549	542	5433	530
99.5	726	630	614	618	705	616	765	708

Figure 10. Simulated Distillation Curve of Product from Helium/Hydrogen Plasma Reaction with Preconditioned Chetopa Crude Oil

One series of experiments behaved differently from the others. This was an argon/methane plasma reaction in which the recycle oil was placed at the bottom of the wave guide and thus closer to the plasma region. The distillate oil (98-O) produced from this experiment had an amber color. The oil (94-O) produced when the recycle oil was positioned below the wave guide was colorless. In addition, the distillation properties of the two oils were different (Figure 11). The oil produced when the reactor was placed at the bottom of the wave guide had an overall lower boiling point curve than the oil produced when the reactor was placed below the wave guide.

Liquid-state ^{13}C NMR spectra were also obtained on the produced and recycle oils from the argon/methane plasma experiment (Figure 12). The oil produced at the bottom of the wave guide gave a very broad NMR spectrum, which is characteristic of a solid rather than a liquid. This spectrum was almost identical to that of a solid reaction product (84-C, also amber in color) that was scraped from the reactor walls after a plasma experiment was conducted using only helium (Figure 12). Free radicals are known to broaden NMR lines. Free radicals are also involved in plasma reactions. Therefore, the severe broadening of the liquid-state NMR spectrum could be due to free radicals in the liquid product.

Figure 11. Simulated Distillation Curves for Plasma-Produced Oils, 94-O and 98-O

The NMR spectra of the recycle oils are similar to those of the starting material. This is expected, as the amount of conversion, although not measured, was estimated to be <5%. The NMR spectrum of the produced oil (94-O) shows greater resolution in the aromatic (100 to 160 ppm) and aliphatic regions (0 to 60 ppm) than does that of the corresponding recycle oils. This spectrum is typical of the oils produced by the plasmas. In particular, the aliphatic region is characteristic of materials containing short chains, branching, and naphthenic compounds.

The carbon aromaticities of the recycle oils were slightly lower than those of the feedstock material, suggesting that some hydrogenation and methanation had taken place (Table 5). This was true for all cases except for the experiment that was conducted in only a helium plasma. In this case, the aromaticity was about the same as the feed material. This is to be expected because there are no reactive hydrogen or methyl radicals present in the helium plasma. The aromaticities of the product oils do not appear to show any correlation with reaction conditions.

Figure 12. Liquid-State ^{13}C NMR Spectra of Produced and Recycle Oils from Argon/Methane Plasma Experiments with Preconditioned Chetopa Crude Oil

Table 5. Summary of Carbon Aromaticity Measurements on Produced Oils From Plasma Experiments with Preconditioned Chetopa Crude Oil

Sample #	Plasma	Carbon Aromaticity	
		Product Oil	Recycle Oil
086576	He	--	0.134
087682	He/H ₂	0.108	0.111
086584	He	0.133	0.148
086587	H ₂	0.117	0.136
086590	He/CH ₄	0.132	0.124
086594	Ar/CH ₄	0.154	0.115
086598	Ar/CH ₄	0.159	0.126
0865100	Ar/H ₂	--	0.142
0865100	Feed	--	0.147

SUMMARY AND CONCLUSIONS

Exploratory experiments have been conducted on the use of hydrogen and methane plasmas to upgrade waste materials and heavy oils. Most of the exploratory experiments were conducted in a configuration in which the reacting materials were in close proximity to the plasma region. In these cases, there was generally some reaction of the plasma species and the starting material.

Irradiation of scrap tire material for ~9 minutes in a microwave-generated hydrogen plasma produced a 53% conversion to gas and liquid products. Most of the conversion occurred in the first few minutes of irradiation. Liquid product accounted for 37.5% of the product. About a third of the liquid product boiled in the gasoline and diesel boiling ranges. In the absence of the plasma, there was no noticeable decomposition of the tire. Thus, plasma irradiation of scrap tire materials has the potential to produce useful liquid products from waste materials.

Irradiation of a heavy crude oil in a continuously flowing reactor using hydrogen or methane plasmas produced some distillate material. The amount of conversion in these experiments was low because of the high paraffinic and low heteroatom content of the feed material. Nevertheless, the lowering of the carbon aromaticity of the recycled oils gave some indication that the recycled feed material had been hydrogenated and methanated.

DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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