REACTIVE PLASMA UPGRADE OF SQUALANE - A HEAVY OIL SIMULANT

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ABSTRACT

U.S. light crude oil production has steadily declined over the last two decades. However, huge known heavy oil deposits in the North American continent remain largely untapped. In the past 10 years, the API gravity of crude oils has been decreasing by about 0.17% per year, and the sulfur content has been increasing by about 0.027% per year. As the API gravity of crude oil decreases, there will be an urgent need for economically viable new technologies to upgrade the heavy oil to a high API gravity feed stock for the refineries. The Idaho National Engineering Laboratory is investigating an innovative plasma process to upgrade heavy oil and refinery residuum. This paper will present some of the results and the implications of this technology for heavy oil upgrade and conversion.

INTRODUCTION

Enormous domestic petroleum stores in heavy oil and tar sands are currently under-used or unmarketable because of the cost of obtaining high-quality refinery feed stocks from them. At the same time, the United State's supply of light crude oil is in sharp decline, leading to a steadily increasing reliance of imported crude oil and refinery products. To maintain adequate domestic supplies and guarantee long-term U.S. energy security, the refinery industry is seeking better and more economical ways to use lower quality crude.

Applying advanced plasma processing techniques to low-quality crude oil feed stocks offers the possibility of economical refining. Plasma petroleum processing research at the Idaho National Engineering Laboratory is supported by the U.S. Department of Energy as part of its national mission to develop new industrial processes that improve energy efficiency and reduce pollution. Key outcomes of applying the new technology include:

- Use of currently uneconomical crude oil resources
- Use of currently unexploited residual byproducts in refinery waste streams
- Improved industrial competitiveness.

Advanced plasma petroleum processing employs two technologies (both U.S. patent pending) to upgrade heavy oil. The first technology is a reactive plasma process and the second is a plasma fast quench process. The first process uses a plasma to produce reactive hydrocarbon species and intense heat to crack and hydrogenate the heavy oil into feed stock suitable for refining. The plasma fast quench process applies the concept of aerodynamic super quenching to crack and convert the heavy oil to a lighter oil in a plasma. Heavy metals and sulfur in the heavy oil feed stock do not seem to affect either process. These technologies can be applied to bitumen tar sand, as well as to heavy oil, and are potentially suitable for environmental remediation applications. The economics of these processes should be attractive for several reasons:

- the processes are insensitive to the type of heavy oil used
- the processes will have simple, low maintenance, equipment requirements
- the processes will convert the bottom-of-the-barrel products that are environmental liabilities, i.e. the asphaltene or residuum, of existing refineries into more profitable products
- the processes will be applicable to remote locations (e.g. Alaskan North Slope) where huge heavy oil and natural gas resources are in close proximity to each other, which provides a different economic scenario than conventional refineries.

Successful use of the North Slope resources, 4.5 billion barrels of oil equivalent in natural gas and 1.5 billion barrels of heavy crude, converted at 80% efficiency, would be equivalent to almost two years of U. S. oil imports.

This paper will focus on the first process, reactive plasma technology, and present some of the bench-scale proof-of-concept results. Since the technology is in the U.S. Patent Application process, detailed information on the technology will not be discussed.

Experiment and Results

The technology is currently under going bench-scale testing. Positive results were observed with crude oil and kerosene. However, a well-controlled model material was needed to clearly demonstrate the concept at the bench-scale. To achieve that goal, a single compound was used. If cracking/conversion occurs, new compounds will be observed in the product. For the controlled model study, squalane (shark oil) was chosen as the starting feed stock. Squalane is a high boiling point, normal $C_{30}H_{62}$ heavy alkane that has six methyl groups attached to various carbon positions on the chain. Figure 1 shows the structure and gas chromatogram (GC) of the squalane used. Figure 2 is a block diagram for the bench-scale experimental system. Products are identified with a GC-MS system. Squalane cracking/conversion was tested with four plasma gases, Ar, CH_4, H_2, and CH_4/H_2. Of the four plasma gases, Ar is unreactive and only provides heat to process the squalane. The other, reactive, gases all participate in chemical reactions to process the squalane. Whether the plasma gas is reactive or unreactive, numerous new compounds were observed in the reactor, the cold trap, and the activated carbon trap. During the plasma run, the temperature of the reactor did not rise much above room temperature. Vapor temperature along the transfer line remained ambient.

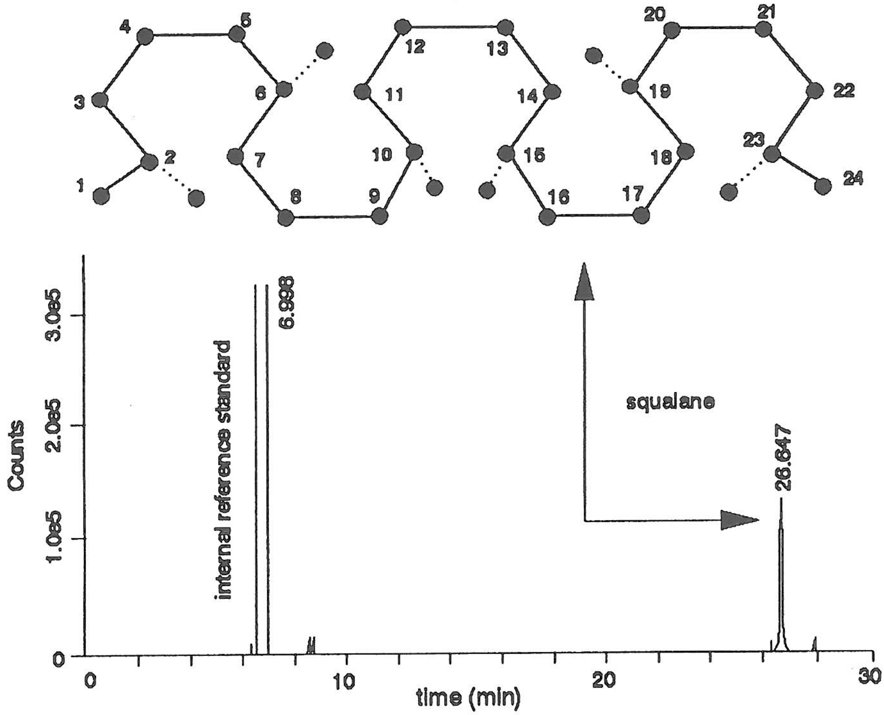

Fig. 1 Molecular structure and gas chromatogram of starting squalane

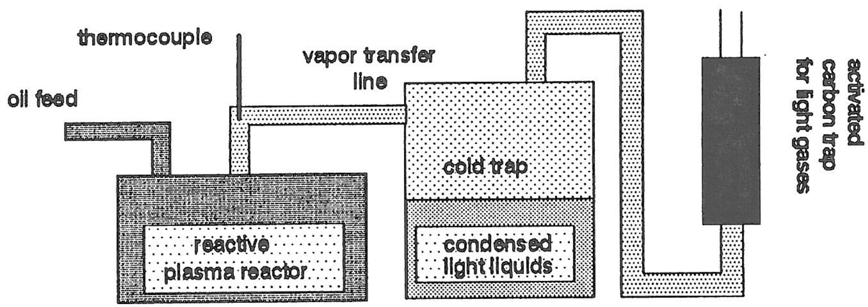

Fig. 2 Block diagram of the bench-scale system for heavy oil upgrade

Figure 3 shows GCs of the processed material for different plasma gases. Figure 4 shows the GCs for the trapped gases from these runs. In all cases, the processed liquid changed from colorless to some degree of amber. The amber color is indicative of forming conjugated unsaturated bonds in the compounds. Carbon precipitation was observed with all four plasma gas conditions. Argon plasma gas induced more carbon precipitation than the reactive plasma gases. Aromatics, highly branched alkanes, alkenes, and a smaller fraction of alkynes were observed in the product with GC-MS. New isomers of squalane were also formed. However, the composition of the products differed according to the plasma gases used. Table 1 is a partial list of the products commonly identified.

ethylene	ethane	ethanol
propylene	propyne	butene isomers
butyne isomers	butadiene isomers	butadiyne isomers
1-buten-3-yne	toluene	nonane
eicosane	7,9-dimethylhexadecane	heptadecane
2,6-dimethylnonane	4-methyldecane	2,5,5-trimethylheptane
2,6-dimethylundecane	6-methyldodecane	2,7,10-trimethyldodecane
pentadecane	6,10-dimethyl-2 undecanoane	2,6,10-trimethyldodecane

Table 1. Partial list of gas phase and liquid phase products formed by reactive plasma processing of squalane.

Discussion

An advanced reactive plasma process being developed at the Idaho National Engineering Laboratory to upgrade heavy oil has shown preliminary feasibility. Further testing on heavy oil and residuum upgrade/conversion is ongoing with an industrial partner. New reactor configurations are being evaluated against process throughput, stability, and efficiency. Economics of the process is assessed based on energy consumption and the value of upgraded products. Development of a viable technology will permit expanded use of domestic resources, thereby decreasing the cost of oil imports, which are currently more than $40 billion per year; revitalize U.S. global competitiveness in energy products; enhance national security; and reduce the national trade deficit.

Acknowledgment

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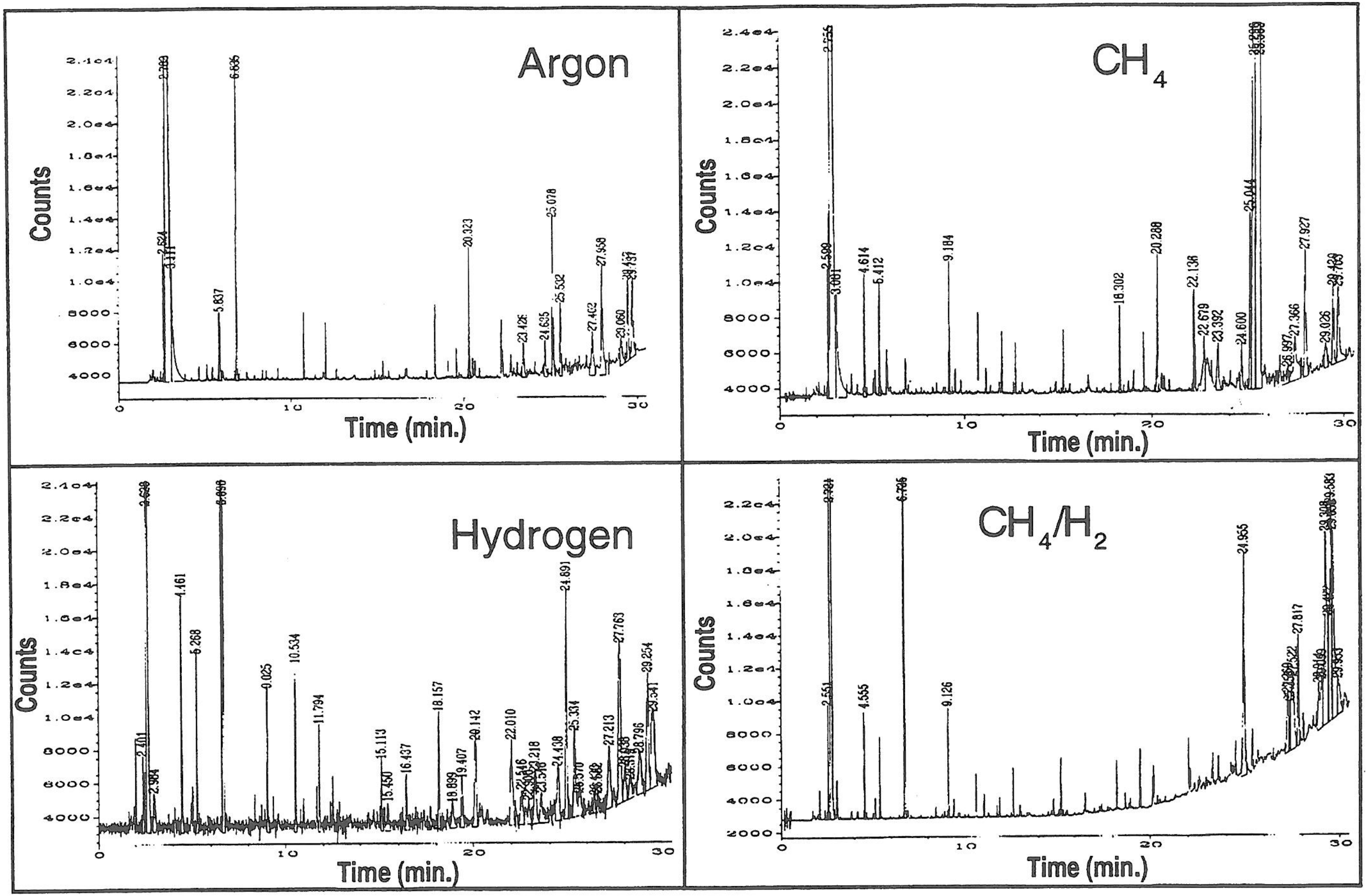

Figure 3. Gas chromatograms of reactive plasma processed squalane liquids

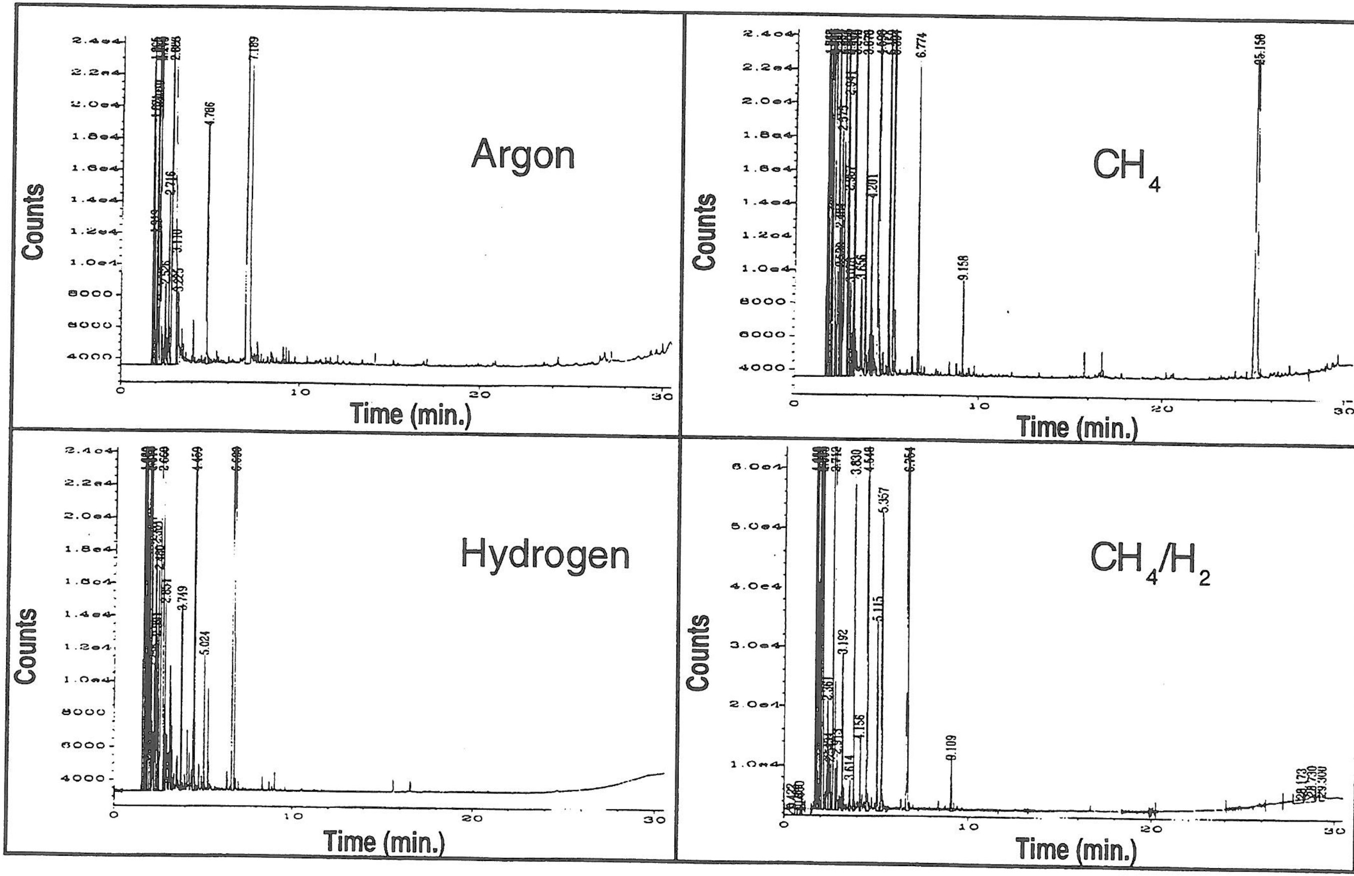

Figure 4. Gas chromatograms of trapped gasses from the reactive plasma processed squalane reactions.