

# FUNDAMENTAL CHEMISTRY OF HEAVY OIL

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## INTRODUCTION

Worldwide demand for petroleum products continues to expand as the nations develop. However, if the demand is analyzed in terms of the three major classes of petroleum cuts: light products such as gasolines; petrochemical feedstocks, middle distillates such as jet fuels and diesels; and heavy products such as fuel-oils and lubricants; then there has been a drastic shift in emphasis toward the light end. Whereas in 1972, both the light products and the middle distillates accounted for approximately 30% of the market. By the turn of the century the light products are 38%, the middle distillates 40%, leaving only 22% for the 1973 major component the heavy-ends.

Whether it is an East Coast refinery importing crude oil from Nigeria, or a U.S. Gulf Coast refinery importing crude oil from Saudi Arabia, or even a U.S. West Coast refinery operating on Alaskan North Slope crude, over the last decade or more for which records are available (1986-96), the quality of the crude oil processed by refineries has declined. If the decline in the quality of crude processed in U.S. refineries is denoted in terms of the API gravity, the gravity has decreased by an average of  $0.15^\circ$  per year in the decade 1986-95. Furthermore, the decline appears to have accelerated back to the rate applicable in the early 1990's. Measured as a five-year average (1989-93), the API gravity had declined by  $0.22^\circ$  per year. After leveling at  $31.3^\circ$  for the next four years, in 1996 it was back on the line pointing to a value of  $30.5^\circ$  for the API gravity in the year 2000. As the API gravity of crude oil falls, the aromatic content (carbon content) increases and the correlations derived for the light crudes begins to break down. The failure of the correlations is well documented in the literature. New or revised correlations are necessary for continued high thermal efficiency in the refining of present and future crudes.

Within the petroleum industry, catalytic hydroprocessing continues to be the core method for upgrading of feedstocks with high aromatic content, as well as for heteroatom removal through HDS and HDN. Meetings such as the 3-day symposium, "Recent Advances in Heteroatom Removal," presented at the Division of Petroleum Chemistry meeting as part of the ACS biannual meeting held in Dallas, March 1998, demonstrate the extensive interest by the petroleum and catalysis industries in this area. In a review of fuel-quality specification for transportation fuels, Touvelle et al. of Exxon Research and Engineering discussed trends in the regulation of aromatics in fuels. Although benzene content is carefully scrutinized, the total aromatics content is not regulated specifically in the U.S.. In contrast, European environmental organizations have already established standards in this area and the U.S. is expected to follow in the near future.

The reduction of aromatics in petroleum and particularly in heavy petroleum will require careful management of hydrogen during hydroprocessing. Effective hydrogen management requires an understanding of the relationship between the distribution of the

hydrogenated products in the process streams and the conditions of their formation, i.e., temperature and pressure. To meet this need, a dual-track approach involving both state-of-the-art property measurement and advanced Ab Initio computations is proposed.

The property measurement program previously funded by DOE Fossil Energy in Oklahoma has accumulated extensive results for partially hydrogenated two, three and four-ring aromatics. The majority of these results have not been published; particularly those which allow calculation of hydroaromatic distributions under processing conditions. Ab Initio computational coding is in its infancy in this area. Accurate atomistic modeling of hydroaromatic systems will use the codes and techniques we have developed for parallel molecular simulations on the ORNL Paragons and other parallel supercomputers. Using our simulation capabilities, we believe we can substantially surpass the best prior efforts in realism and quantitative, predictive accuracy. These simulations will build on existing ORNL world-class efforts on simulating high temperature liquid and supercritical aqueous systems.

The experimental database and the fundamental understanding from the simulations will be brought together to develop useful models for correlating data and predicting stability under hydroprocessing conditions. The two fundamental questions to be addressed in this research are: (1) What are the “ideal condition” for meeting low aromatics levels and still meet sulfur levels, smoke point, etc., (2) How does the model react to changes in the complex heterogeneous and multi-component systems (i.e., addition of a new crude oil from, say, Nigeria to the refinery)?

Results from this research will allow the industrial participants to lead the field in catalyst development and process condition controls in processing particularly middle distillates. It can be anticipated that severe operating conditions such as high temperatures, low space velocities, and high pressures can be mediated as the result of insights developed with the program. For example, at low temperatures and high space velocities, the amount of monoaromatics in the product can be higher than in the original feed. This is not unexpected since every mole of triaromatic compound that is saturated would add a mole to the diaromatics, each diaromatic compound hydrogenated would add a mole to the monoaromatic category, and as the number of rings decrease, the rate of saturation should also decrease. Interaction between the various options can be simulated in the model and options such as increased catalytic activity balanced against two- or even three-stage process designs.

Catalytic hydroprocessing continues to be the core method for upgrading of feedstocks with high aromatic content. European environmental organizations have already established standards in this area and the U.S. is expected to follow in the near future. The reduction of aromatics in heavy petroleum upgrading will require careful management of hydrogen during hydroprocessing. Effective hydrogen management requires an understanding of the relationship between the distribution of the hydrogenated products in the process streams and the conditions of their formation, i.e., temperature and pressure.

To counteract the adverse effects of carbon rejection methods, refiners have the option of hydrogen-addition (hydroprocessing) methods. However, hydroprocessing consumes large quantities of hydrogen. As refineries reconfigure to produce the new “clean fuels” (“reformulated fuels,” i.e., those with oxygenates present), hydrogen shortages are occurring, and new sources of supply are required. The addition of oxygenates to gasoline means that less octane is required from the reformer, lowering the severity of the operation and the amount of hydrogen formed. Also, the mandated reduction of aromatics content by the U.S. government in the 1990 Clean Air Act Amendments has resulted in a further reduction of reformer operating severity, hence, severely reducing hydrogen production. Other contributions to the problem in managing hydrogen result from mandated lower gasoline temperature endpoints and reduced sulfur levels. Hence, the use of hydrogen exactly where it will “do the most good” is paramount. Over-hydrogenation will have to be minimized.

## **HYDROGEN**

Hydrogen has continued to fascinate the generations of people for at least the last two centuries. It is the stuff of Science Fiction expounded by visionaries like Jules Verne. The “Hydrogen Economy” is often touted as the ultimate solution for energy and environment.

In his 2003 State of the Union address, President Bush announced a \$1.2 billion initiative to reverse America's growing dependence on foreign oil by developing the technology for commercially viable hydrogen-powered fuel cells to power the nation with no pollution or greenhouse gases. The DOE Fossil Energy website states

“A key element of the President's hydrogen initiative is to develop advanced hydrogen production and delivery technologies that can supply tomorrow's energy and transportation systems with affordable hydrogen with significantly reduced or near-zero emissions. Fossil fuels (e.g., natural gas and coal) can provide the transition to a hydrogen economy by delivering a near- to mid-term source of hydrogen. With carbon sequestration, coal could be used to produce hydrogen for many decades without adding to concerns over the buildup of carbon gases in the atmosphere.”

In a “Hydrogen Economy,” hydrogen is produced from some hydrogen containing entity, to be packaged by compression or liquefaction, transported by vehicles or pipeline, stored, and transferred to the end user. Hydrogen, the most common chemical element in the Universe, does not exist on this planet in its elemental form. It has to be separated from chemical compounds by electrolysis from water, or by a chemical process from hydrocarbons or other hydrogen carriers. In the past “Hydrogen Economy” proponents have, for example, propounded the electricity for electrolysis coming from renewable sources such as solar radiation, wind power, water-power, or geothermal heat. Therefore, hydrogen is then the all-important link between renewable physical energy and chemical energy carriers. But have the physics and chemistry been considered in a “proper” scientific manner? The “upstream” aspects of a “Hydrogen Economy” are seldom

addressed. It is the goal of this project to do exactly that in detail, grounded on thermodynamic and scientific principles.

In this project we will consider the main stages of “Hydrogen Economy” - production, packaging, transport, storage and transfer of elemental hydrogen – and relate the energy consumed for these functions to the energy content of the deliverable hydrogen. All the process analyses will be based on either ideal physics or chemistry or actual data from industry. Hence, the results will stand the test of time and are unlikely to be bettered significantly in the future.

#### **PUBLICATION OF STATE-OF-THE-ART UNPUBLISHED PROPERTY MEASUREMENTS**

The lead editorial for 2002 in the Journal of Chemical and Engineering Data [2002, 47(4)] stated:

“In 1943 a laboratory was established in Bartlesville, Oklahoma, by Hugh M. Huffman, to measure the thermophysical properties of components of petroleum, jet fuels, and other strategic chemicals. Over the next 55 years this laboratory established an undisputed world renowned reputation for the highest quality measurements on the thermochemical and thermophysical properties of organic and organometallic compounds. The Bartlesville Thermodynamics Group ceased to exist on Nov 8, 1998.”

Results of numerous state-of-the-art thermodynamic-property measurements remained unpublished at the time the laboratory was closed. From the late 1970s until closing of the laboratory, the Department of Energy invested more than \$1,000,000 per year in support of this world-class research. Unpublished results exist for a variety of organic compound types, which are key to the production of high quality, environmentally-acceptable fuels. Compound types include saturated and unsaturated aromatic hydrocarbons as well as their sulfur and nitrogen-containing analogs. These “benchmark quality” results will aid the development of new processing technologies through provision of required properties for specific key materials, as well as for numerous related substances by serving as benchmarks for improved computational chemistry methods, estimations, and correlations

#### **DISCUSSION OF CURRENT ACTIVITIES**

Work is in progress on a number of fronts within this project. The studies related to the Hydrogen section of the Introduction are in their initial stages and will form the basis of a Topical report due for completion in September 2005.

An initial literature search was performed to ascertain the relative importance of various aromatic compounds and sulfur-containing compounds in the range of heavy petroleum being imported to refineries in the U.S. Emphasis was placed on finding the degrees of condensation and substitution of the compound types. The results of the study will be used to define the scope of the experimental work and the reaction schemes to be studied. Available literature data are being collected and process conditions defined where applicable. Properties for the majority of the species have not been published in the open

literature, particularly those that allow calculation of hydroaromatic distributions under processing conditions. Hydroaromatic distributions will be derived where possible and a list of gaps in the database highlighted. This work will conclude with the reporting of sets of compounds to be studied to widen the applicability of the derived correlations. A Topical Report on the synergies between sulfur and other heteroatom removal and aromatic formation and/or mitigation in the development of “carbon-saver fuels” from heavy oil is in preparation and will be completed in September 2004.

Work is also in progress to ascertain the practicality of using the range of heavy petroleum being imported to refineries in the U.S. to produce both 5 ppm sulfur gasoline and a “clean diesel” with the following specifications: 50 ppm sulfur with lower density, lower PAH (polyaromatic hydrocarbons), lower boiling point, and higher cetane number than the “best diesel being produced for the California market. Preliminary results of calculations of the conditions necessary to obtain various sulfur levels in diesel using hydrodesulfurization are given in Table 1. In the table the baseline is assumed to be the conditions (temperature/pressure/catalyst activity) required to produce 500 ppm sulfur diesel.

**Table 1. Conditions necessary to produce certain sulfur ppm levels in diesel**

Sulfur content	Catalyst activity	Temperature F	Hydrogen pressure
Baseline 500 ppm	100%	Baseline	Baseline
350 ppm	130%	+15 F	120%
200 ppm	190%	+30F	170%
100 ppm	300%	+55 F	300%
50 ppm	450%	+70F	600%

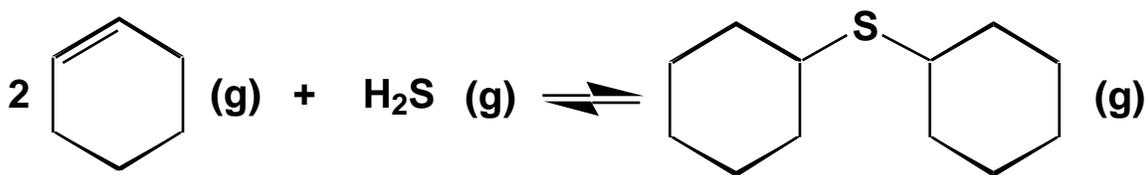
To obtain the required sulfur level, only one of the listed options would be required. Obviously, the hydrogen pressure increase option is not realistic. Note also that the increase in temperature would mean that the amount of aromatics would increase, requiring even greater hydrogen pressure to premeditate the effect.

Another option other than hydrodesulfurization to meet the sulfur level is alkylation of the sulfur-containing molecules raising the boiling point of sulfur-containing fraction and removing the sulfur in the resid. Or, in yet a further option, the sulfur-containing compounds can be removed by selective adsorption using a catalyst containing a zero-valent transition metal. Presently, both methods of sulfur removal are being presented by refiners as new technology options. Results from this research project will aid in both research areas (property measurements will give examples of boiling point of substituted benzothiophenes with both degree of substitution and actual position of substitution). Initial calculations point to several metals being particularly capable of reversible adsorption of benzothiophenes and dibenzothiophenes under very moderate reaction conditions. Further computational chemical calculation during FY2005 will expand on these initial ideas.

The hydrodesulfurization of thiols (mercaptans), sulfides, and disulfides is exothermic and there is no thermodynamic limitation under industrial reaction conditions where the

equilibrium constants all decrease with an increase in temperature and have values greater than unity. In contrast, the equilibrium constant for hydrogenation of thiophene to tetrahydrothiophene is less than unity above 600 K, indicating that a HDS pathway via the hydrogenation of the thiophene ring may be restricted under industrial reaction conditions because of the low equilibrium concentration of tetrahydrothiophene. Prior to the results published [see list of publications below] no corresponding analysis for the hydrogenation of the thiophenic ring in benzothiophene or dibenzothiophene could be made without estimation of the properties of the hydrogenated species. A paper is in preparation that will provide an overall analysis of the thermodynamics of hydrodesulfurization of dibenzothiophene over a wide range of temperature and hydrogen pressures. Initial calculations support the earlier conclusions of this Group that deep HDS may require two-stage catalytic hydrotreating or even, for some crude oils, multi-staged HDS reactors.

In the paper on the properties of dicyclohexylsulfide (see list of publications below) attention is drawn to the thermodynamic favorability for the formation of dicyclohexylsulfide in the reaction between cyclohexene and hydrogen sulfide. This highlights the reversibility of the hydrodesulfurization reaction. Under high pressure the addition of hydrogen sulfide to olefins can result in a net production of sulfur-containing compounds, defeating the intent of the hydrodesulfurization reaction. Thermodynamic equilibrium calculations for the reaction:



for 1 bar pressure results in mole fractions of dicyclohexylsulfide of 0.99998, 0.946, and 0.025, at 300 K, 400 K and 500 K respectively. Under higher pressures of hydrogen sulfide the formation/stability of the sulfide increases. Optimization of HDS processes in the future will need to consider such reactions if the proposed requirements of very low sulfur-content are to be met.

Work on the publication of the property measurements performed at Bartlesville proceeds at an even pace of 4 publications per year. In preparation at present are papers on (A) phenanthrene, 9,10-dihydrophenanthrene, and 1,2,3,4-tetrahydrophenanthrene; (B) diphenylmethane; (C) 1,2-dihydronaphthalene and hydrogenation equilibria in the naphthalene system; and (D) 2-methyl and 8-methylquinolines.

Finally, work is also in progress on what the PI of this project calls “The 2015 Refinery” where all processes within the bounds of the refinery are as environmentally sound as possible. The 2015 refinery would for example not have any alkylation units with the associated problems of HF-or H<sub>2</sub>SO<sub>4</sub>. Fuels would be manufactured via olefin formation

and upgrading. Possibilities then increase of producing “zero sulfur” gasoline and even cleaner-burning naphthenic fuels.

During this reporting period, the following papers on the thermodynamic properties of 2,3-dihydrobenzo[b]thiophene, pyrazine, 1,2,3,4-tetrahydrodibenzothiophene, dicyclohexyl sulfide and bicyclopentyl respectively, were published or accepted for publication in the *Journal of Chemical Thermodynamics*:

Steele W. V., R. D. Chirico, A. B. Cowell, A. Nguyen, S. E. Knipmeyer, A. P. Rau, Possible precursors and products of deep hydrodesulfurization of gasoline and distillate fuels II. The thermodynamic properties of 2,3-dihydrobenzo[b]thiophene. *J. Chem. Thermodynamics* v. 35, 2003, 1253-1276.

Chirico, R. D., S. E. Knipmeyer, W. V. Steele Heat capacities, enthalpy increments, and derived thermodynamic functions for pyrazine between the temperatures of 5 K and 380 K. *J. Chem. Thermodynamics* v. 35, 2003, 1059-1072.

Steele, W. V., R. D. Chirico, S. E. Knipmeyer. Possible precursors and products of deep hydrodesulfurization of gasoline and distillate fuels III. Thermodynamic properties of 1,2,3,4-tetrahydrodibenzothiophene between the temperatures of 5 K and 600 K. *J. Chem. Thermodynamics* v. 36, 2004, 497-509.

Steele, W. V., R. D. Chirico, S. E. Knipmeyer. Possible precursors and products of deep hydrodesulfurization of gasoline and distillate fuels IV. Heat capacities, enthalpy increments, and derived thermodynamic functions for dicyclohexyl sulfide between the temperatures of 5 K and 520 K. In press *J. Chem. Thermodynamics* June 2004.

Chirico, R. D., W. V. Steele. High energy components of "Designer Gasoline" I. Heat capacities, enthalpy increments, and derived thermodynamic functions for bicyclopentyl. In press *J. Chem. Thermodynamics* June 2004.