FUNDAMENTAL CHEMISTRY OF HEAVY OIL

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INTRODUCTION

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.

The purpose of the cooperative work between the Design Institute of Physical Property Data (DIPPR)® and the Thermophysical Property Group within the Separations and Materials Research Group at ORNL is to develop thermodynamic and thermophysical property data for use in leading edge chemical technology. The property measurements are directed by the DIPPR Project Steering Committees responsible for Project 821-Pure Component Liquid-Phase Vapor Pressure Measurements and Project 871-Pure Component Ideal-Gas Enthalpies of Formation. The objective of Project 821 is to obtain precise and accurate liquid-phase vapor pressure data for selected pure components. The objective of Project 871 is to measure the enthalpies of combustion and derive the enthalpies of formation in both the condensed and the idea-gas phases of "key" compounds that have been chosen to elucidate the enthalpy of particular atomic groupings. These group contributions can then be used to estimate data on large families of related compounds each containing that particular atomic arrangement.

DIPPR, now in its 24th year of funded research, is the oldest of the American Institute of Chemical Engineers' (AIChE) active Industry Technology Alliances. In 2003, DIPPR has 30 sponsors from industry and government bodies. Its purpose is to make possible, through joint sponsorship,

thermophysical property data measurement, correlation, and dissemination. The objective of the Design Institute for Physical Property Data (DIPPR)® is to develop the world's best set of critically evaluated thermophysical and environmental property data to satisfy industry needs. Data developed in DIPPR projects have become the data of choice for leading chemical process simulators and are used throughout the world.

DISCUSSION OF CURRENT ACTIVITIES

BACKGROUND

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° per year in the decade 1986–95.[1] 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° per year. After leveling at 31.3° for the next four years, in 1996 it was back on the line pointing to a value of 30.5° 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 again two- or even three-stage process designs.

The project has been set up in the CRADA form with an initial lifetime of three years. Subcommittees comprised of DIPPR Project supporters, DOE Fossil Energy Staff, and ORNL staff will decide at the

annual AIChE/DIPPR meeting in November a list of compounds for study in the following year in each of the two project areas. Compounds will be chosen to represent whole families containing the necessary functionalities and to facilitate extension of available data bases, rather than to fulfill the specific needs of any single member company.

PROGRESS

Work is in progress on a number of fronts within this project. An initial literature search is being 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 will be 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.

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%	+15F	120%
200 ppm	190%	+30F	170%
100 ppm	300%	+55F	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 FY 2001 will expand on these initial ideas.

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_2SO_4. Fuels would be manufactured via olefin formation and upgrading. Possibilities then increase of producing "zero sulfur" gasoline and even cleaner-burning naphthenic fuels.

In the reporting period, DIPPR)® project committees met during the AIChE meeting in November 2002. Lists of possible compounds for measurements were tentatively drawn up at those meetings and finalized after subsequent literature surveys were conducted to ensure the quantity and quality of any available data. Samples of each of the chemicals chosen for study were obtained and purification via spinning-band distillation or (in case of solid samples) zone-refining are in progress. The property measurements are due to commence in early May 2003.

Results from earlier work completed at Bartlesville, Oklahoma, have cleared full committee review and were published in the *Journal of Chemical & Engineering Data* in May 2002. The titles of the 6 papers are:

Steele, W. V., R. D. Chirico, S. E. Knipmeyer, and A. Nguyen. Vapor pressure, heat capacity, and density along the saturation line: Measurements for benzenamine, butylbenzene, sec-butylbenzene, tert-butylbenzene, 2,2-dimethylbutanoic acid, tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, and 1-chloro-2-propanol. J. Chem. Eng. Data v. 47, 2002, 648–666.

Steele, W. V, R. D. Chirico, A. B. Cowell, S. E. Knipmeyer, and A. Nguyen. Thermodynamic properties and ideal-gas enthalpies of formation for methyl benzoate, ethyl benzoate, (R)-(+)-limonene, tert-amyl methyl ether, trans-crotonaldehyde, and diethylene glycol. J. Chem. Eng. Data v. 47, 2002, 667–688.

Steele, W. V., R. D. Chirico, S. E. Knipmeyer, and A. Nguyen Vapor pressure, heat capacity, and density along the saturation line measurements for ε-caprolactam, pyrazine, 1,2-propanediol, triethylene glycol, phenyl acetylene and diphenyl acetylene. J. Chem. Eng. Data v. 47, 2002, 689–699.

Steele, W. V., R. D. Chirico, A. B. Cowell, R. D. Chirico, S. E. Knipmeyer, and A. Nguyen Thermodynamic properties and ideal-gas enthalpies of formation for trans-methyl cinnamate, α–methyl cinnamaldehyde, methyl methacrylate, 1-nonyne, trimethylacetic acid, trimethylacetic anhydride, and ethyl trimethylacetate. J. Chem. Eng. Data v. 47, 2002, 700–714.

Steele, W. V., R. D. Chirico, S. E. Knipmeyer, and A. Nguyen Vapor pressure, heat capacity, and density along the saturation line measurements for cyclopropane carboxylic acid, N,N'-diethyl-ethanolamine, 2,3-dihydrofuran, 5-hexen-2-one, perfluorobutanoic acid, and 2-phenylpropionaldehyde. J. Chem. Eng. Data v. 47, 2002, 715–724.

Steele, W. V., R. D. Chirico, A. B. Cowell, S. E. Knipmeyer, and A. Nguyen Thermodynamic properties and ideal-gas enthalpies of formation for 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, cyclohexanone oxime, dimethyl malonate, glutaric acid, and pimelic acid. J. Chem. Eng. Data v. 47, 2002, 725–739.

In addition a bibliography of the publications of the Bartlesville Thermodynamics Group from its inception in 1943 through the present was given in the *Journal of Chemical & Engineering Data* May 2002 issue. In all, the papers and bibliography took up **over 100 pages** of the issue.

In addition, during this reporting period, two papers on the thermodynamic properties of naphthalene and benzophenone respectively, were published in the *Journal of Chemical Thermodynamics* and a further paper on the properties of dihydrobenzo[b]thiophene was accepted for publication:

Chirico, R. D., S. E. Knipmeyer, and W. V. Steele. Heat capacities, enthalpy increments, and derived thermodynamic functions for naphthalene between the temperatures of 5 K and 440 K. J. Chem. Thermodynamics v. 34, 2002, 1873–1874.

Chirico, R. D., S. E. Knipmeyer, and W. V. Steele. Heat capacities, enthalpy increments, and derived thermodynamic functions for benzophenone between the temperatures of 5 K and 440 K. J. Chem. Thermodynamics v. 34, 2002, 1885–1895.

Steele, W. V., R. D. Chirico, A. B. Cowell, A. Nguyen, S. E. Knipmeyer, J. W. Reynolds, and 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. Accepted for publication in Journal of Chemical Thermodynamics, November 2002.

REFERENCE

1. S. W. Benson, *Thermochemical Kinetics*, 2nd Edition; Wiley: New York, 1976.