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Downstream Details

Physical and Chemical Property Measurements (Chemical Thermodynamics) On Pure Organic Compounds for the Refining, Petrochemical and Chemical Industries. The Bartlesville Thermodynamics Group, Bartlesville, Oklahoma, USA 1943 – 1998 and its Subsequent Reincarnations

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Historical Summary

In 1943, a program for the determination of the physical and chemical properties of the components of jet fuels and strategic chemicals (e.g., synthetic rubber) was inaugurated in the Petroleum Laboratories of the US Bureau of Mines in Bartlesville, Oklahoma. The renowned thermodynamist, Hugh M. Huffman, was persuaded by the importance of the task within the war effort to leave the comforts of university life in California and “Head East Young Man” into the “oil-patch”. Huffman gathered a group of exceptional talents, particularly in instrument making and careful exact property measurement, to initiate what became a world renowned center for thermochemical and

thermophysical property measurement on organic and organometallic compounds. For fifty-five years, the Bartlesville Thermodynamics Group (BTG) pushed the frontiers in instrumentation and precision, becoming a world-class, one-of-a-kind research group. The history and contributions of BTG are little recognized outside the world of thermodynamicists and the end users of the data, the chemical and process engineers who design and operate chemical plants and refineries worldwide. After World War II, the Group became part of the American Petroleum Institute (API) efforts to characterize the thermodynamic properties of the components of light petroleum. In subsequent decades, the range of compounds changed.

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Figure 1: Hugh M. Huffman sitting at a White potentiometer trying to follow the galvanometer spot just after ignition in a combustion bomb calorimeter. (circa 1950).



The 50s can be considered the smelly decade of sulfur-containing organics; the 60s was the NASA/organometallics decade; the 70s was the U.S. Air Force specialty fuels era and nitrogen containing organics; the 80s and 90s became the “heavy, bottom-of-the-barrel” fossil fuels years.

Throughout the Bartlesville years, the goal of the BTG was accurate and precise determination of the thermochemical and thermophysical properties of molecular entities, measuring all the properties necessary for the determination of the Gibbs Free Energy and any chemical equilibria involving that entity. To that end, the equipment designed for the property measurements was unique. It was designed by taking the instrument-making talent available and setting the goal of making a “state-of-the-art” piece which pushed the boundaries of the available technology. The following are four examples of cutting-edge technology developed and used within the laboratory.

1) In the 1940s/1950s **adiabatic calorimeters**, for

enthalpy/heat capacity measurements from liquid hydrogen temperature to 300°K, were built in-house (as was all the original equipment) using tube technology as it became available to control temperature equilibration to 10⁻³°K all across the temperature range! In the early 1980s the equipment was updated with solid-state electronics that replaced the tubes, helium replacing explosive hydrogen, and measurements converted to being under computer control. From 1984 through 1998 four adiabatic calorimeters operated 365 days a year (except in cases of power outages or tornados) producing enthalpy data, heats of transition and/or fusion derived heat capacities and entropies etc., all under the control of **one operator**, Dr. Robert (Rob) D. Chirico.

2) **Vapor pressure measurements** were made using twin ebulliometers designed to enable measurements from 20 mm Hg to 2026 mm Hg. To widen the available measurement range as the molecular weight of the substances studied increased, an ingenious rotat-



Figure 2: API research projects 48 & 52 meeting participants, Bartlesville, Oklahoma, March 8-9, 1966.



Figure 3: Rob Chirico at the adiabatic calorimeter console (circa 1984).

ing inclined piston apparatus was designed to enable measurements in the 0.1 to 30 mm Hg range. [An inclined piston was designed to be virtually frictionless, and during operation, knowing precisely the acceleration due to gravity in the laboratory immediately adjacent to the operating equipment, to balance the vapor pressure to be measured against the weight of the piston and the angle of inclination.] A WWII bomb-sight was used to determine the angle precisely, and the value of g was measured by two experts from the then Bureau of Standards brought in for the determination. In the 1980s, the procedure was revised to determine the balance angle of the piston, from the rate of fall of the piston when the angle of inclination was slightly too large and the rate of ascent when the angle was slightly too small by the same amount. This greatly improved the accuracy and speed with which the balance angle could be determined relative to the former static method. Previously, determining pressure required no lateral movement in the piston over a set time period that was difficult to delineate. In addition, the inclined piston measuring equipment was automated and operated under computer control. Angle adjustment and piston-locating systems were installed and were interfaced with a control computer. For angle adjustment, an inclinometer was mounted on the top of the (piston+cylinder) assembly. The inclinometer gener-

ated a potential difference proportional to the angle of inclination and was used in conjunction with a stepping motor to monitor the angle to better than 0.006 sec. To track the piston position, a non-contacting linear displacement transducer (LDT) was attached to the end of the (piston+cylinder) assembly, and a stainless steel target was placed on the moving piston. The LDT generated a low-level inductive field in front of the sensor (probe). As the piston moved, the target entered or left this field, and eddy currents were generated in the target that changed the impedance of the sensor. The output voltage from the transducer was linearly proportional to the distance from the piston to the conductive surface at the cylinder end.

3) A **rotating-bomb calorimeter** was designed in collaboration with Professor Sunner of the University of Lund Sweden. The equipment ensured the position of the Bartlesville Laboratory as the world



Figure 4: Bill Steele showing Dennis Ripley the fine detail of one of the adiabatic calorimeters. Note in the background the spools of fine wire needed to construct the temperature control portions of the equipment.

leader in the determination of the energy of combustion of organo-sulfur compounds. Energy of combustion measurements that are made using the equipment have both an accuracy and a precision of better than 1 part in a million.

4) In the 1980s it became apparent that the PVT equipment available was not ideal for the study of the heavier molecules of the research programs, and new ideas were necessary. [In 1983/4 one man-year of effort was consumed making PVT measurements on methanol in the critical region without complete success due to decomposition of the alcohol which appeared to be accelerated by the mercury used in the system to measure pressure. No research project can afford that luxury.] A brainstorming session led to revival of an earlier idea of Bruce E. Gammon to use a **differential scanning calorimeter** (DSC) to measure enthalpy increments (and hence heat capacities) at high temperature. The design and development of special sample cells capable of withstanding both high temperature (approximately 900°K) and pressure (approximately 7.6 MPa) without rupture was the cornerstone of the successful extension of the research capability. Initially, the DSC in conjunction with the newly developed cell was used to obtain enthalpy increments, and hence, heat capacity values to temperatures approaching the critical region. The DSC technique gives values of the temperature and density where each particular filling is converted from the two-phase (liquid + vapor) region to a single phase (fluid) region when the sample is sufficiently stable near the critical point. This led to the use of the technique to determine experimentally critical temperatures and critical densities rapidly, completely replacing the original PVT apparatus. Details of the initial successes of the methodology can be found in the 42nd Huffman Lecture (Group Publication 350).

Publication Highlights

A complete listing of the publications in the scientific literature of the BTG can be found in the Journal of Chemical & Engineering Data, Volume 47, Part 4, 2002, pp. 629-642. In addition to those 390 publications, more than 100 reports are available through NTIS.

To illustrate contributions, a single paper or two has been selected to represent the genre of each of the important compound types studied at Bartlesville through its existence. A short description depicting the importance of the genre to energy and process research will follow each selection.

22. Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. 2,2,3,3-Tetramethylbutane: Heat Capacity, Heats of Transition, Fusion and Sublimation, Vapor Pressure, Entropy and Thermodynamic Functions. *J. Am. Chem. Soc.* 1952, 74, 883-887.

This paper is representative of highly branched hydrocarbons studied in the 1940's. Results from it and similar papers aided in the development of equations of state, etc., to generally represent alkanes in the development of refining processes.

84. McCullough, J. P.; Pennington, R. E.; Smith, J. C.; Hossenlopp, I. A.; Waddington, G. Thermodynamics of Cyclopentane, Methylcyclopentane, and 1,cis-3-Dimethylcyclopentane: Verification of the Concept of Pseudorotation. *J. Am. Chem. Soc.* 1959, 81, 5880-5883.

This paper is representative of naphthenes studied in the 1940s and 1950s. Results from it and similar papers aided in the development of equations of state, etc., to generally represent naphthenes in the development of refining processes. These papers formed the backbone of the Technical Data Book – Petroleum Refining published by API commencing in 1966.

25. McCullough, J. P.; Scott, D. W.; Finke, H. L.; Gross, M. E.; Williamson, K. D.; Pennington, R. E.; Waddington, G.; Huffman, H. M. Ethanethiol (Ethyl Mercaptan): Thermodynamic Properties in the Solid, Liquid, and Vapor States. Thermodynamic Functions to 1000 K. *J. Am. Chem. Soc.* 1952, 74, 2801-2804.

39. McCullough, J. P.; Sunner, S.; Finke, H. L.; Hubbard, W. N.; Gross, M. E.; Pennington, R. E.; Messerly, J. F.; Good, W. D.; Waddington, G. The Chemical Thermodynamic Properties of 3-Methylthiophene from 0 to 1000 K. *J. Am. Chem. Soc.* 1953, 75, 5075-5081.

These two papers are representative of the thiols, sulfides, disulfides, and thiophenes studied in the smelly 1950s. Results were instrumental in the development of energy efficient hydrodesulfurization (HDS) processes by refiners. **Figures 5, 6** and **7** depict boundaries between the kinetic and thermodynamic

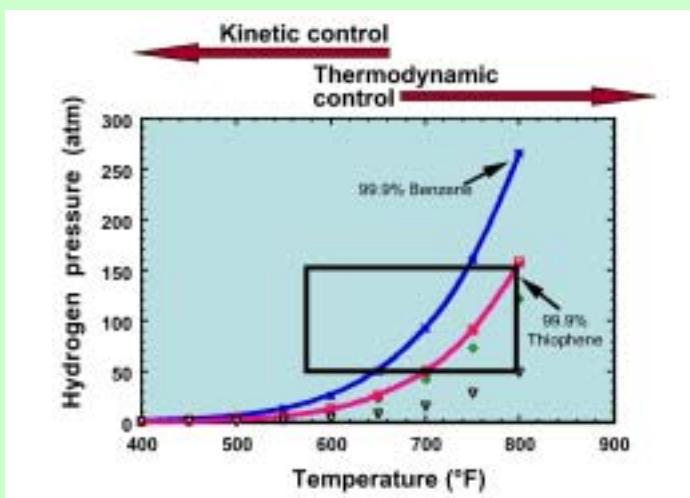


Figure 5: Each curve represents the percentage conversion marked theron. To the right of each curve, the reaction is under thermodynamic control. The box represents the “usual” limits of industrial HDS reactors.

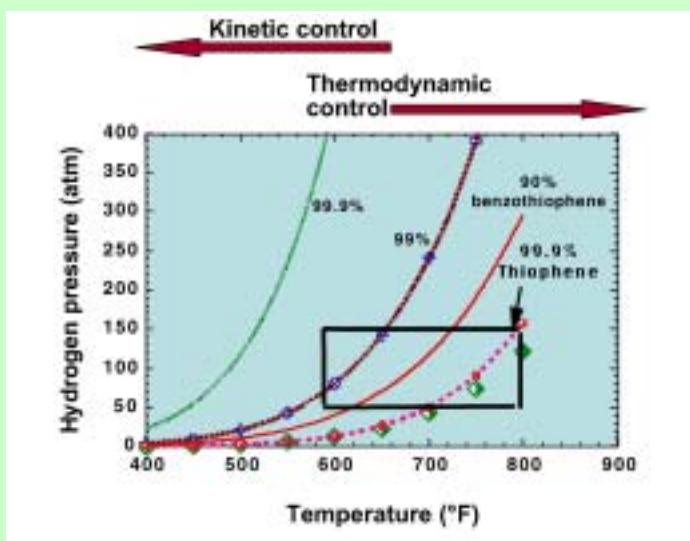


Figure 6: Note that removal of benzothiophenes via single-stage HDS is under thermodynamic control with possibly upwards of 10% of the original levels remaining after processing within the “usual” industrial limits.

control regions for HDS of thiophenes. Its importance has increased as the sulfur limits in fuels continue to be regulated to lower and lower levels.

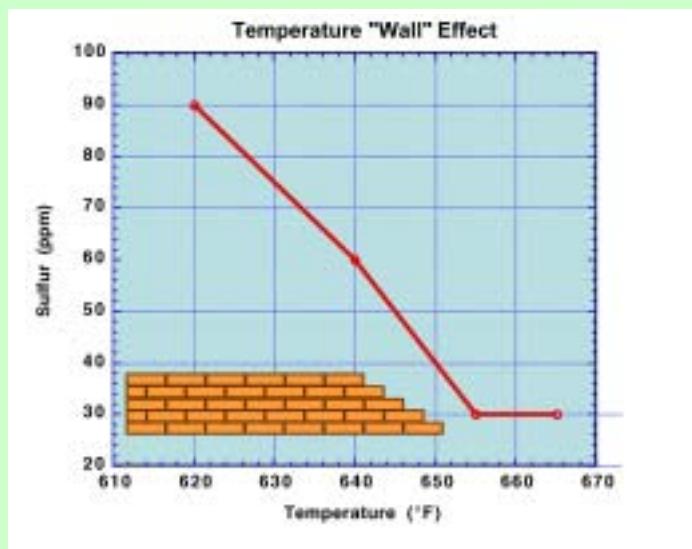


Figure 7: Thermodynamic control limitations for benzothiophenes (and dibenzothiophenes) removal via single-stage HDS can lead to the “brickwall effect” where increased severity (temperature) does not result in more sulfur removal: in this case 30 ppm sulfur remains in product.

63. McCullough, J. P.; Finke, H. L.; Messerly, J. F.; Todd, S. S.; Kincheloe, T. C.; Waddington, G. The Low-Temperature Thermodynamic Properties of Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, 1,2,3,4-Tetrahydronaphthalene, trans-Decahydronaphthalene, and cis-Decahydronaphthalene. *J. Phys. Chem.* 1957, 61, 1105-1116.

This paper is representative of diaromatics; these results were subsequently used in the development of the chemical engineering for the initial plant for the Exxon Donor Solvent coal liquefaction process.

48. Scott, D. W.; Good, W. D.; Waddington, G. Heat of Formation of Tetrafluoromethane from Combustion Calorimetry of Polytetrafluoroethylene. *J. Am. Chem. Soc.* 1955, 77, 245.

Again, a definitive paper that developed the rotating-bomb calorimetric method for the measurement of the enthalpy of formation of organo-fluorine compounds. Enthalpy of reaction calculations throughout the whole fluorocarbon industry can be traced back to these definitive measurements for perfluoromethane and teflon.



129. Good, W. D.; Lacina, J. L.; DePrater, B. L.; McCullough, J. P. A New Approach to the Combustion Calorimetry of Silicon and Organosilicon Compounds. Heats of Formation of Quartz, Fluorosilicic Acid, and Hexamethyldisiloxane. *J. Chem. Phys.* 1964, **68**, 579-586.

141. Good, W. D.; Måansson, M. The Thermochemistry of Boron and Some of Its Compounds. The Enthalpies of Formation of Orthoboric Acid, Trimethylamineborane and Diammonium Decaborane. *J. Phys. Chem.* 1966, **70**, 97-101.

These definitive papers developed the rotating-bomb calorimetric method for the measurement of the enthalpy of formation of organo-silicon and organo-boron compounds respectively. In the silicon case, it has led to the acknowledgement of subsequent data abstractors that all previous energy of combustion measurements on silicon compounds not using rotating-bomb calorimetry and auxiliary fluorine-containing combustion aids are all irrelevant and of historic interest only.

214. Douslin, D. R.; Harrison, R. H. Pressure, Volume, Temperature Relations of Ethylene. *J. Chem. Thermodyn.* 1976, **8**, 301-330.

220. Harrison, R. H.; Douslin, D. R. Derived Thermodynamic Properties of Ethylene. *J. Chem. Eng. Data* 1977, **22**, 24.

These papers are twin examples of the painstaking measurements required in the subsequent development at National Institute of Standards and Technology (NIST) of an equation of state for this staple compound of the petrochemical industry.

234. Smith, N. K.; Good, W. D. Enthalpies of Combustion of Ramjet Fuels. *American Institute of Aeronautics and Astronautics Journal* 1979, **17**, 905-907.

Publication of a little piece of the NASA/US Air Force research program of the 1960s/1970s. Precise and accurate measurements of such energies of combustion aided significantly in the acceptance of JP-10 as the “fuel of choice” for the cruise missile program.

288. Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. The Vapor Pressure of n-Alkanes Revisited. New Vapor Pressure Data on n-Decane, n-Eicosane and n-Octacosane. *J. Chem. Eng. Data* 1989, **34**, 149-156.

This paper detailed accurate and precise measure-

ments of the vapor pressure of two representative heavy alkanes. It continues to be a paper of choice for researchers deriving equations of state or vapor pressure correlations for heavy oil fractions in refining. Exxon partially funded the measurements within their coal liquefaction program.

307. Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E; Smith, N. K. *High-Temperature Heat-Capacity Measurements and Critical Property Determination Using a Differential Scanning Calorimeter. Results of Measurements on Toluene, Tetralin, and JP-10*; NIPER-395 (NTIS Report No. DE89000749); DOE Fossil Energy: Bartlesville Project Office, June 1989.

This report was one of the first detailing the new DSC methodology for high temperature enthalpy measurements and critical property determinations. Most chemical property prediction schemes are based on critical properties. To quote Palmer, (Palmer, D. A. *Handbook of Applied Thermodynamics*. CRC Press: Boca Raton, Fl. 1987), critical properties are needed “because the principle of corresponding states predicts that all properties related to intermolecular forces can be predicted based on the relationship between the critical properties of both model compounds and the component under study.” Development of predictive methods has been hampered by a scarcity of critical-property data.

342. Steele, W. V.; Chirico, R. D.; Nguyen, A.; Knipmeyer, S. E. The Thermodynamic Properties of 2-Methylaniline and trans-(R,S)-Decahydroquinoline. *J. Chem. Thermodyn.* 1994, **26**, 515-544.

This paper represents the wide range of nitrogen-containing organics studied. Details are given of the thermodynamic restrictions to hydrodenitrogenation at high temperature and moderate hydrogen pressures. Interest in this work is increasing as several refining groups are finding the presence of nitrogen organics can, under certain circumstances, prevent the attainment of low sulfur fuels via HDS.

377. Collier, W. B.; Magdó, I.; Klots, T. D. Infrared and Raman Spectra of bicyclic molecules using scaled non-correlated and correlated ab

initio force fields. *J. Chem. Phys.* 1999, 110, 5710-5720.

This paper highlights a research program of the early 90s, funded by DOE Basic Energy Sciences (BES), which applied the new area of computational chemistry, especially Density Functional Theory (DFT), to the determination of entropies of substances of interest. Gibbs free energies and equilibria determinations via computation based on the laws of statistical thermodynamics was the goal. Funding was cut when the BTG became a for-profit research institute and BES could no longer legally fund it. Papers on DFT now deluge the literature.

365. Chirico, R. D.; Steele, W. V. Thermodynamic Equilibria in Xylene Isomerization. 5. Xylene Isomerization Equilibria from Thermodynamic Studies and Reconciliation of Calculated and Experimental Product Distributions. *J. Chem. Eng. Data* 1997, 42, 784-790.

This paper and the earlier Parts I to IV form a set defining the thermodynamic equilibria for the C10 aromatics. The ability to accurately calculate product yields aided the American chemical industry in its defense of patent rights and worldwide income from patent licenses. In addition, the results of this research for xylenes provide the basis for the accurate estimation of properties for broad families of alkyl-substituted aromatic compounds. Results are presently being used to derive isomerization distributions for alkyl naphthalenes to help “fingerprint” crude oils obtained from various fields. This “fingerprinting” will aid in the development of customized methods for refining crudes to produce specialty fuels.

372. Chirico, R. D.; Klots, T. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. Reconciliation of calorimetrically and spectroscopically derived standard entropies for the six dimethylpyridines between the temperatures 250 K and 650 K; a stringent test of thermodynamic consistency. *J. Chem. Thermodyn.* 1998, 30, 535-556.

This paper and others in the ilk highlight the coming together of calorimetric measurements and statistical thermodynamics over wide temperature ranges

when accurate and precise measurements are compared to similarly accurate and precise gas-phase vibrational spectral frequencies and molecular structure. In these papers, agreement between spectroscopic and calorimetric entropies is better than 0.1% over several hundred °K every time. This, in turn, shows the capabilities of the virial equation of state and extended corresponding states to represent organic compound thermodynamics.

356. Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Nguyen, A.; Knipmeyer, S. E. Possible precursors and products of deep hydrodesulfurization of distillate fuels. I. The thermodynamic properties of diphenylsulfide and revised values for dibenzothiophene. *J. Chem. Thermodyn.* 1995, 27, 1407-1428.

378. Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Nguyen, A.; Knipmeyer, S. E. Possible precursors and products of deep hydrodesulfurization of gasoline and distillate fuels. II. The thermodynamic properties of 2,3-dihydrobenzo[b]thiophene. In press *J. Chem. Thermodyn.* 2003.

This duo of papers discusses thermodynamic equilibria related to the HDS of aromatic thiophenic components of crude oils. These papers and others to be published in 2003, will define the boundaries between the kinetic and thermodynamic control regions for HDS of benzothiophenes and dibenzothiophenes. The importance of this data has increased as the sulfur limits in fuels continue to be regulated to lower and lower levels.

DIPPR CRADA

DIPPR (Design Institute for Physical Property Research), now in its 23rd year of funded research, is the oldest of the America Institute of Chemical Engineers' (AIChE) active industry technology alliances. In 2002, DIPPR had 36 sponsors from industry and government. Its purpose is to make possible, through joint sponsorship, thermophysical property data measurement, correlation, and dissemination.



Dr. Mary Good (then Senior Vice President, Technology, Allied Signal, Inc.):

"The U.S. chemical process industry had a record trade surplus of \$19 billion in 1991, with indications it will be close to that for 1992 demonstrating its continued global leadership position. One of the key factors contributing to this is the development and use of leading edge chemical process technology. Allied Signal has relied heavily on the DIPPR databases in design of its chemical and polymer processes, and finds great value in sharing the costs of developing and verifying data."

DIPPR in conjunction with DOE/FE conducts two measurement projects at Oak Ridge National Laboratory:

- Project 821 - Pure Component Liquid Vapor Pressure.
- Project 871 - Determination of Pure Component Ideal Gas Heat of Formation.

DIPPR describes these projects using the words: "We use top national research facilities to carry out specific projects." DIPPR's Project Steering Committees recognized the BTG as the only remaining thermodynamics laboratory in the U.S. with the full range capability to obtain the type and quality of data required by the sponsors.

Over the lifetime of the two DIPPR projects, greater than 150 compounds have been studied. All the compounds appear in the listing of the top 1000 compounds produced by the US chemical industry.

The Fifth edition of the "Chemical Engineers Bible" *The Properties of Gases and Liquids* by B. E. Poling, J. M. Prausnitz, and J. P. O'Connell was recently published by McGraw-Hill. The appended Property Databank is used throughout the chemical industry by engineers in process design. The seven DIPPR publications previous to 2000 are highlighted in the refer-

ences to the database as sources of reliable and accurate property measurements. Six papers (Group Publications 382-387) were published in the Journal of Chemical & Engineering Data, Volume 47, Part 4, 2002, pp. 629-739. The 110 pages of Journal's articles showcase both the wide range of measurements made and the wide range of compounds studied by BTG.

Future

The Bartlesville Thermodynamic Group ceased to exist on 8th November 1998. In what resembles Fred Rossini's discussion of his 1950 move from what was then the National Bureau of Standards in Washington, D.C., to the then Carnegie Institute of Technology in Pittsburgh, Pennsylvania, the BTG equipment, standard chemicals, and library were transported in one large highway van from Oklahoma to the Oak Ridge National Laboratory. Rossini in the inaugural Rossini Lecture [F. D. Rossini Fifty years of thermodynamics and thermochemistry, *J. Chem. Thermodyn.*, 8, 805-834, (1976)], reminisces that his move took six or seven such large highway vans. At Oak Ridge, the laboratories were originally housed within the Chemical Technology Division, which later became the Nuclear Science & Technology Division under the new laboratory contractor, UT Battelle. This year, 2003, the laboratories are moving again. This time the move is to the Chemical Engineering Department of the University of Tennessee, Knoxville (UTK). Positioning the laboratories at UTK will encourage collaboration between university and laboratory scientists, while opening the range of industry interactions. Graduate and postdoctoral students can be trained in thermophysical property research, providing future personnel for the unique technological challenges associated with the refining, petrochemical, and chemical industries of the 21st century.

The "Phoenix is rising from the ashes", and shortly,

detailed thermochemical and thermophysical property measurements papers of the ilk of Group Publications 357/358 and 375/376 will again begin appearing in the scientific literature.

Financial support of the DOE/FE within the Emerging Processing Technology Applications program is gratefully acknowledged. During my (WVS) sojourn at Bartlesville, the continued support (moral etc.,) of DOE Project Manager Alex Crawley, William (Pinky) Peters, Dexter Sutterfield, and Art Harstein was greatly appreciated. At Oak Ridge National Laboratory (ORNL), I would add Kathy Stirling of the National Energy Technology Laboratory (NETL), Tulsa, Oklahoma to that list. ORNL is managed by UT-Battelle for the DOE under contract DE-AC05-000R22725.

The future would not be possible but for the dedication and expertise of not only the thermodynamicists in the BTG but also the extremely skilled instrument makers, including Steve Knipmeyer who built instrumentation that was beyond state-of-the-art and have proven to be extremely stable and rugged to have survived all the recent moves.

For more information on this project, contact Dr. William (Bill) Steele, ORNL, at (865) 576-7696 or email at steelewv@ornl.gov.

Downstream Details

Downstream Details is an annual newsletter devoted to providing information about DOE's Downstream Projects. For more information on these projects, contact **Kathy Stirling**, Project Manager, DOE's National Energy Technology Laboratory:

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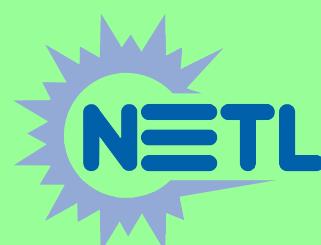
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This is the final issue of **Downstream Details** as
DOE's new research focus will be on
conversion of Natural Gas to Hydrogen.



Advance Process to Remove Naphthenic Acid from Crude Oil

Yongchun Tang, Ph.D. and William A. Goddard III, Ph.D.,
Power, Energy, Environmental Research (PEER) Center,
California Institute of Technology

Goal

Development of low-temperature (~200°C) and cost-effective processes for removing naphthenic acids (NA) compounds from heavy crude oil will significantly help the US petroleum industry to improve refining processing for heavy crude oils. Success in this project could encourage development of the Nation's heavy oil resources.

The main goal of this project is to develop cost-effective methods to remove NA from crude oil. Two different targeted approaches are:

(1) Develop a catalytic system to decarboxylate cleanly, simple aliphatic and aromatic acids under mild conditions. In particular, develop a system readily adaptable to remove naphthenic acid from crude oil. Combined experimental and theoretical efforts are being used to obtain an understanding about the chemistry of NA and to develop an efficient and low cost catalyst system.

(2) Remove NA via solid filters, such as by custom designed polymer resins and/or clays.

Background

NA are a broad group of organic acids found in crude oils. They are important to the petroleum industry because they cause corrosion problems for distillation units in the refinery. They have adverse impacts in wastewater treatments and environmental compliance. In the upstream phases of oil production and transportation to refineries, NA can form sludge and gum, thus plugging pipelines and fouling pumps. High acid crude oils form stable, highly-viscous emulsions and cause tremendous problems for oil-water separation. NA reactivity translates to increased metal corrosion in refineries and lower

high-value product yield. On a positive note, NA find commercial usages in the wood-preservation industry.

NA are present in most crude oils, and are especially prevalent in heavy and biodegraded oils. Their uniqueness stems from their unparalleled chemical activity, not approached by other components in crude oil. NA are natural products of petroleum oxidation that have developed over a geologic time. Biodegradation is considered to be the main process producing high concentrations of carboxylic acids in crude oils.

NA are usually a mixture of carboxylic acid compounds—which may be polycyclic—with or without unsaturated bonds, aromatic rings, hydroxyl and/or phenol groups attached. **Table 1** shows a typical distribution of naphthenic acids from the lube oil boiling range.

Table 1:
Type Distribution of Naphthenic Acids from Lube Oil Fractions

Type	Mol Weight of Oil Fractions		
	281	384	470
Saturates	68	58	45
Monoaromatics	15	18	16
Diaromatics	6	12	23
Benzothiophenes	5	8	
Resins	6	4	16

The complex compositional heterogeneity of NA, makes it very difficult to predict corrosion severity

based on analytic measurements of an individual NA compound or a small group of NA compounds. Consequently, the most commonly adopted criteria for predicting NA effects (such as the corrosive potential) of a crude oil are the total acidity number (TAN) and the neutralization number (Neut Number). Both are defined by the number of milligrams of KOH required to neutralize the acidity in one gram of oil. Oils can vary in TAN from <0.1 to as high as 8 mg KOH/g. High TAN oils (>0.5mg KOH/g) are less desirable than low TAN oils because they increase corrosion and cause refinery problems. Consequently, high TAN crudes sell at a lower price.

The occurrence of high TAN oils is widespread. Many oil fields at late stages of production have higher TAN.

Decarboxylation of naphthenic acid

Many approaches have been reported to mitigate NA problems, but none is entirely satisfactory. The most straightforward method is to neutralize the acid. The problem is that this treatment produces stable emulsions.

The objective of Phase-I of this project is to develop a system for the low-temperature catalytic decarboxylation reactions. The strategy is to establish the fundamentals of the catalyzed decarboxylation reaction using results from both computational modeling and experimental studies.

Copper catalysts are commonly used for laboratory-scale decarboxylation. The presence of an organic nitrogen base is generally required. Several precious metal complexes have also been demonstrated to be effective for decarboxylation. However, none of them show potential applicability in a practical process on a refinery scale.

Progress of the Project

A laboratory-scale catalyst evaluation apparatus has been set up (**Figure 8**) and a primary catalyst screening method established. Milligram amounts of NA sample, solid catalyst, and other additives (if any) are sealed in a glass tube under vacuum conditions. The sealed glass tubes are placed in an oven to undergo reaction under controlled conditions. Products are collected in a vacuum line via standard gas transfer methods and quantified by a gas chromatograph (GC). Reaction residuum is recovered by washing the glass tube with organic solvent. The residue is then subjected to GC analysis. Based on the GC analysis data, NA conversion and CO₂ yield can be calculated.

Model compounds chosen for these experiments included a mixture of naphthoic acid and cyclohexane carboxylic acid as well as a mixture of five carboxylic acids, all dissolved in a hydrocarbon solvent. Catalyst screening focused on metal oxide catalysts, but the addition of active transition metals and mixtures of other active components were also tested. Magnesium oxide (MgO) and several oxidative metal oxides show promising catalytic activity towards decarboxylation. For a reaction time of 4 hours at 200°C, acid conversion could reach 60-70% while



Figure 8: Experimental Setup for the Decarboxylation Reaction

CO_2 yields reached nearly 20%. For the mixed acid sample, MgO also showed high acid removal activity. At 200°C for 4 hr reaction, acid conversions reached 40-90% depending on the acid structures. Introducing an active transition metal improved acid removal efficiencies to 70-98%.

Catalyst screening is being conducted. The design concept is to search for a basic center to abstract a proton from the carboxylic acid group, while at the same time introducing a carbon-carbon activation component to break the C-C bond. We will also investigate more supported transition metal catalysts (in addition to the alkali-earth metal oxides), zeolites, and hybrid systems. Optimizing reaction condition is an important issue for process development. Promising catalysts from the model compounds study will be directly applied to crude oils to measure their TAN change. For this purpose, several high acidity oils, with TAN ~ 4 , have been chosen.

The mechanisms and kinetics of the oxidative decarboxylation process in the presence of the metal oxides have been widely studied, but alpha-hydroxy, alpha-carbonyl, and dicarboxylic acids have received far more attention than monocarboxylic acid. Depending on the experimental conditions (moisture and air), various products and by-products, including benzene, biphenyl, phenol, diphenyl ether, benzoic acid, salicylic acid and phenyl benzoate, have been identified. Several plausible oxidative decarboxylation mechanisms, such as concerted, radical, formation of carbenes or benzyne, as well as one-electron and two-electron transfer mechanism, have been proposed (**Figure 9**). However, a detailed mechanistic understanding of the overall reaction network, particularly that at the atomic level, has not been obtained. One of the major ingredients of this project is to apply state-of-art computational simulation techniques to obtain fundamental insight to the mechanisms and kinetics

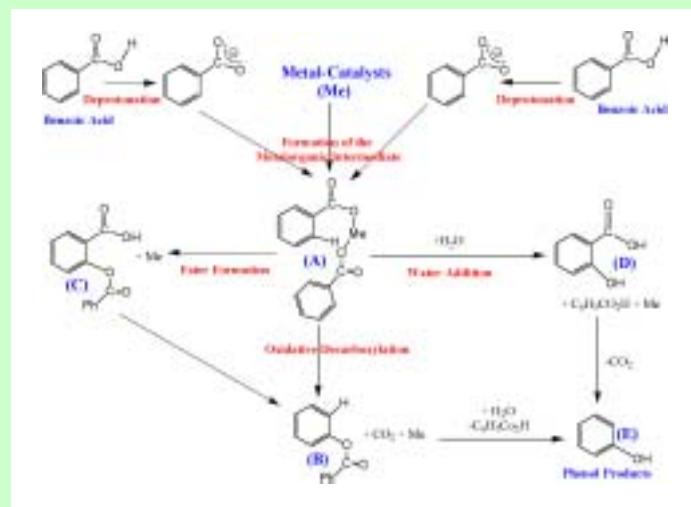


Figure 9: Decarboxylation reaction sequence.

of the oxidative decarboxylation process, which will provide theoretical guidance to the experimental efforts.

Cooperation with industry is underway. ChevronTexaco and Conoco are providing technical consulting and information about industrial experience.

For more information on this project, contact Dr. Yongchun Tang at 909-468-9310 or e-mail: tang@peer.caltech.edu.

Fundamentals of Delayed Coking

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Background

Delayed coking evolved steadily over the early to mid-1900s to enable refiners to convert high boiling, residual petroleum fractions to light products such as gasoline. Pound for pound, coking is the most energy intensive operation in a modern refinery. Large amounts of energy are required to heat the thick, poor-quality petroleum residuum to the 900 to 950°F range required to crack the heavy hydrocarbon molecules into lighter, more valuable products.

One common misconception of delayed coking is that the product coke is a disadvantage. Although coke is a low-valued product compared to transportation fuels, there is significant worldwide trade and demand for coke as solid fuel competing with coal.

Coke production has increased steadily over the last ten years, with further increases forecast. The Oil and Gas Journal's Annual Worldwide Refining Survey, December 2002, shows world coking charge capacity (101 refineries) of 3 million barrels per calendar day (b/cd) producing 154,607 t/d coke. Delayed coking accounts for 88% of the world's coke capacity. Delayed coking charge capacity in the United States is 1,787,860 b/cd producing 111,000 t/d coke. A major driving force behind the increase is the steady decline in crude quality.

Future crude slates are expected to grow even heavier and have higher sulfur content. Future environmental restrictions are expected to reduce significantly the demand for high-sulfur residual and bunker fuel oil will increase the volume charged to cokers. The

restrictions simultaneously increase the demand for light, low sulfur refined products. Refiners will be faced with the choice of purchasing light sweet crudes at a premium price or adding bottom of the barrel upgrading capability.

With lower expenditures for heavier crudes and lower operating costs, delayed coking has increased in popularity worldwide. Despite its wide commercial use, relatively few contractors and refiners are truly knowledgeable in delayed-coking design and operations, so that this process carries with it a "black art" connotation. The University of Tulsa is drawing on its downstream expertise to better understand the coking process.

Facilities

Tulsa University has two small scale facilities (micro and batch reactor) and a pilot unit. The micro-coker is shown in **Figure 10**. It consists of a syringe pump with stirrer, preheater (corresponding to the commercial furnace), a coke drum with liner, three cooled liquid traps, a wet-gas test meter and an on-line GC. The process flow can be varied between 50 and 220 cc/hr with about 150 g of material processed.

The main objective for utilizing this reactor are to act as a screening tool to characterize coker resid



Figure 10: Micro-coker.

feedstocks' tendency to make liquid, gas, and coke products and to do so via a small feed sample and minimal set-up and run time.

The stirred batch reactor used in the kinetic studies is shown in **Figures 11** and **12**. This apparatus is utilized to identify coke precursors, to study the heat rate effect on yields (simulates furnace tube), and to study the thermal cracking kinetics of reactions. Resid samples are drawn to identify coke precursors; the vapor from the reactor is condensed as lights and heavies; the gas is analyzed via an online gas chromalograph (GC).

The pilot-coker obtained from Equilon Enterprises, LLC is shown in **Figures 13**. It consists of a feed tank with circulation system and a furnace with both the pre-heater and the coke drum. The feed drum holds approximately 15 gallons and is mounted on a scale. The drum outlet goes to a pump and then to the furnace. In the



Figure 11: Batch reactor.

furnace, the resid flows first to a pre-heater coil (mimicking the commercial furnace) and then to a coke drum. The coke drum is 3-inch x 40-inch with a volume of 4,750 cc and is located in a furnace that prevents heat loss. Operating variables include temperature, pressure, steam injection rate, and charge flow rate. The foaming studies are conducted using a 78-inch drum rather than the 40-inch drum. A gamma densitometer is used to measure the density of gas, foam, liquid and coke layers in the drum as a function of time.

The objectives for utilizing this reactor are to reproducibly mimic commercial operation. The reactor produces sufficient quantities of coke; liquids and gases for testing and investigation to correlate the

effect of feedstock composition and reactor conditions on product rates compositions; sulfur and sub-product distributions and coke morphology. The reactor is also used in the study of maximizing distillate prod-

uct production and minimizing coke and gas production.. The reactor was used to study foaming; find ways to reduce tube fouling; and used to investigate scale-up.



Figure 12: Batch reactor sample systems.



Figure 13: Pilot unit test facility.

Types of Studies

Many experiments can be run with small scale reac-

tors in a short period of time. The micro-reactor is utilized as a screening tool. The batch reactor is utilized to understand the reaction kinetics in the furnace tube and coke drum. Both tools have been useful in studying ways to enhance liquid production, as well as ways to reduce sulfur in the liquids to help refiners meet the upcoming stringent sulfur requirements.

The pilot unit generates data that is utilized to enhance the process optimization model and to better understand the foaming process, thus minimizing or eliminating process upsets as well as optimizing the use of antifoams to increase refinery margins. The produced coke studies conducted have provided a better understanding of the parameters that affect coke morphology and the reasons why settling, poor drainage and hot spots occur.

Experimental Insights

A significant amount of data and model development has occurred from the small-scale studies; however, the main focus is based on the data and model development effort from the pilot unit. Studies to date have provided:

- an understanding as to why and how shot and sponge coke are made,
- determined the efficiency of overhead vs. bottom drum quenching,
- determined what are the foaming tendencies of different types of resids and what impact operating conditions have on foaming,
- and, determined what are optimum concentrations and strategies to inject antifoam, as well as how antifoam partitions.

Illustrations of the type of data generated are provided below for one of the resids utilized in the study.

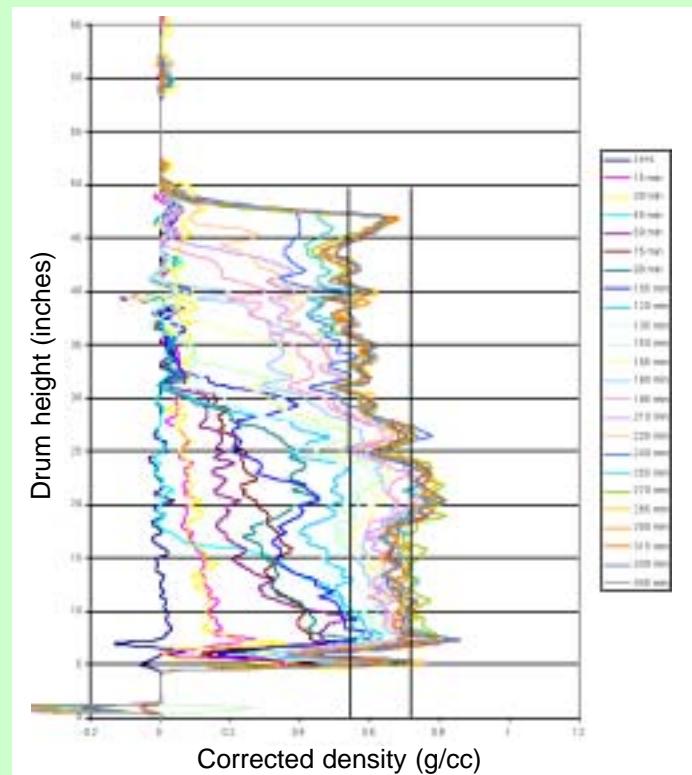


Figure 14: Density in coke drum as a function of height.

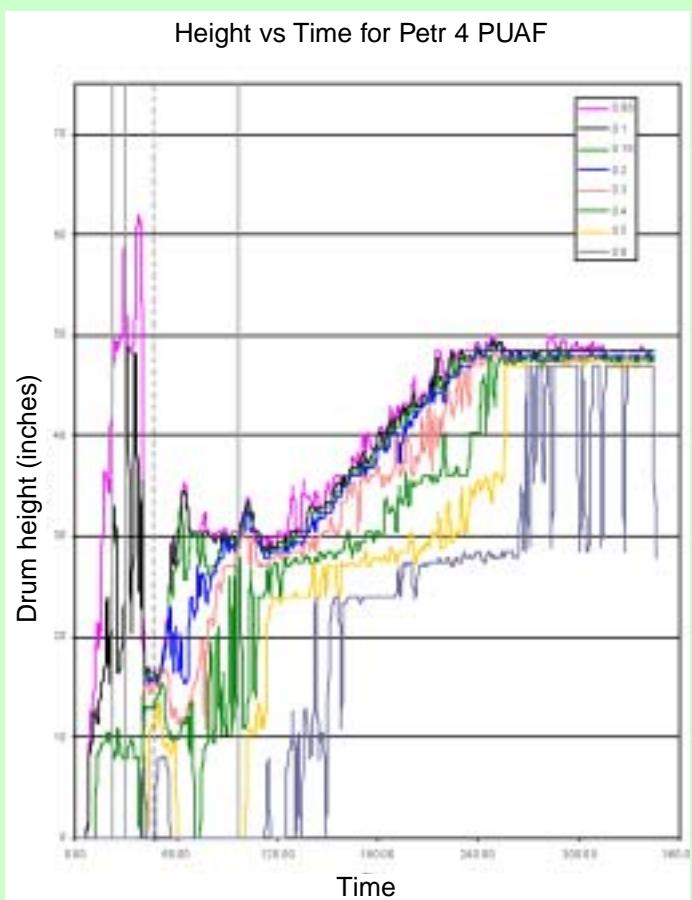


Figure 15: Foaming tendency.

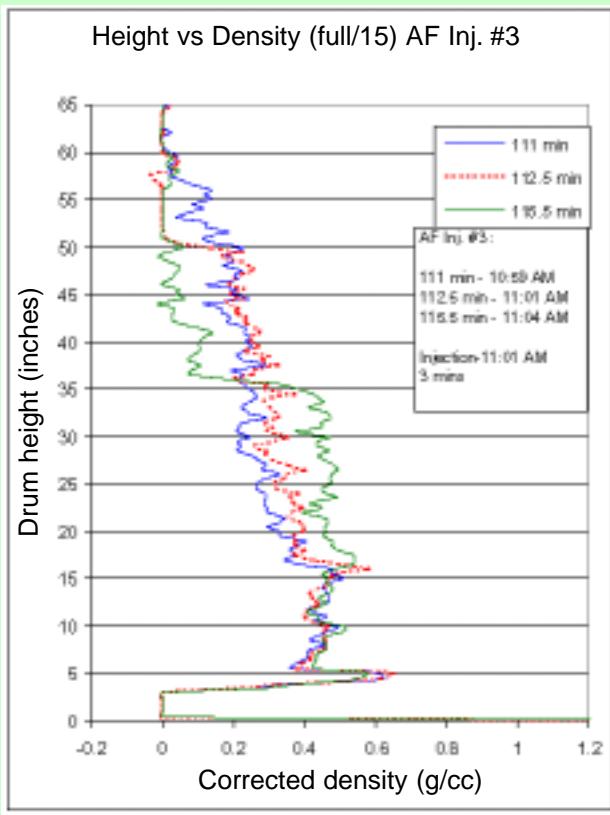


Figure 16: Foam collapse.

Figure 14 shows the density of contents in the coke drum. This coking run experienced a significant amount of foaming as shown in **Figure 15**. In this figure, foam is defined as having a density < 0.2 gm/cc,

the liquid layer as having a density > 0.2 but < 0.5 gm/cc while the solidified coke has densities > 0.5 gm/cc. Antifoam was injected several times throughout the run. **Figure 16** illustrates the collapse of the foam column after 2 hours of operation. Foam growth and collapse are better illustrated in **Figure 17**. Note that when foaming occurs, the density of the bubbly liquid layer decreased as the foam height increased. When antifoam was injected, the density of the bubbly layer increased, and the foam layer was collapsed.



Sponge coke.



Shot Coke

Upon completion of the coking process, the contents of the drum were steamed stripped. The gamma densitometer traces in **Figure 18** show the loss of mass from the stripping. The loss of material resulted in the coke bed slumping by approximately 10%. This

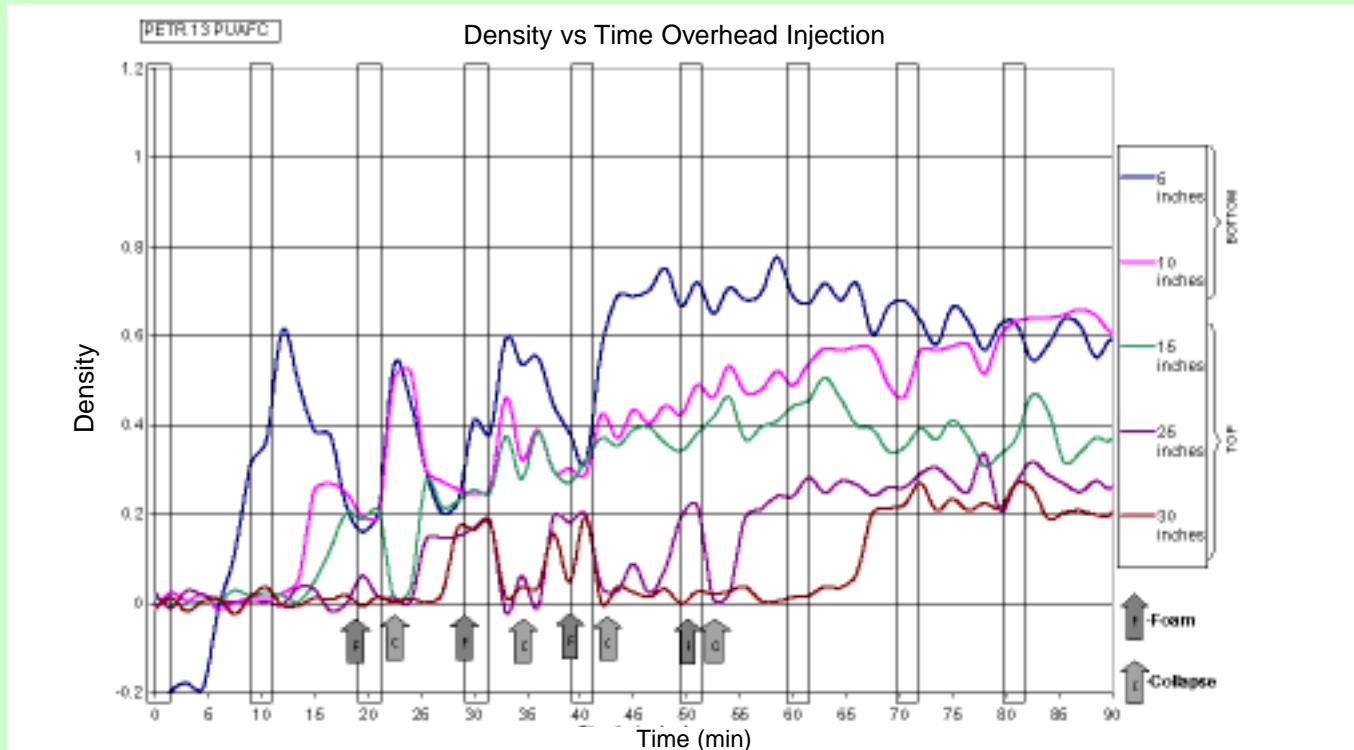


Figure 17: Foaming tendency.

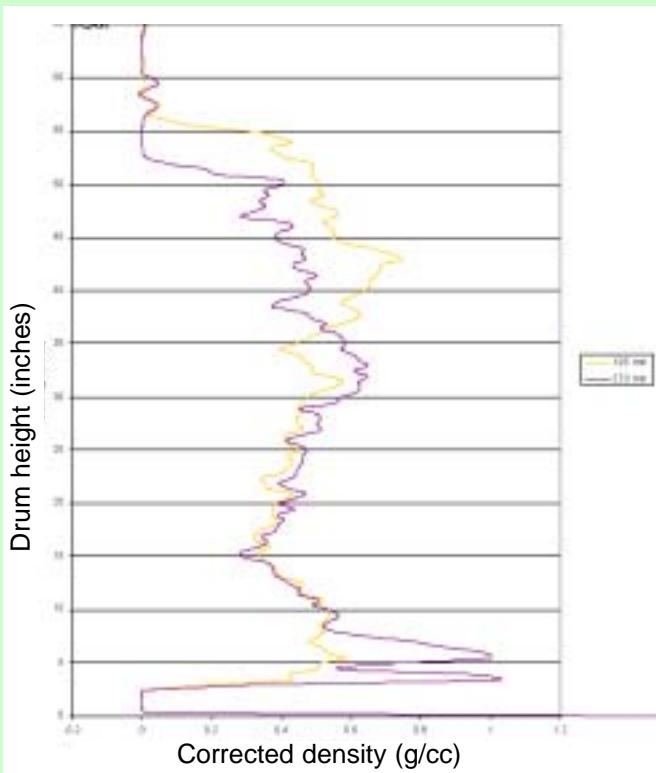


Figure 18: Slumping of Coke bed after steam stripping.

slumping actually caused an increase in the coke bed density, mostly at the bottom of the bed and to a lesser extent in the middle of the bed. After steam stripping the coker, water injection is increased in a controlled manner to cool the drum contents.

Several models have been developed whose robustness are continually being updated. These models are: a screening model, a process optimization model, a kinetic model and a quench model. In general, because the data is scaled up to industry data, the models are doing a good job of predicting behavior. The cooling curves along with the model predictions are shown in **Figure 19**. The differences are due to the assumption of using the same porosity, heat capacity, and thermal conductivity throughout the coke bed in the calculations.

Project sponsors include Baker-Petrolite, ChevronTexaco, Citgo, ConocoPhillips, ExxonMobil, Foster Wheeler, KBC, Great Lakes Carbon, Petrobras, Marathon-Ashland, Shell, Suncor and U.S. DOE.

For additional information regarding the project contact Dr. Michael Volk at the University of Tulsa by phone at 918-631-5127, via email at Michael-volk@utulsa.edu, or visit the web site at <http://www.tudcp.utulsa.edu>.

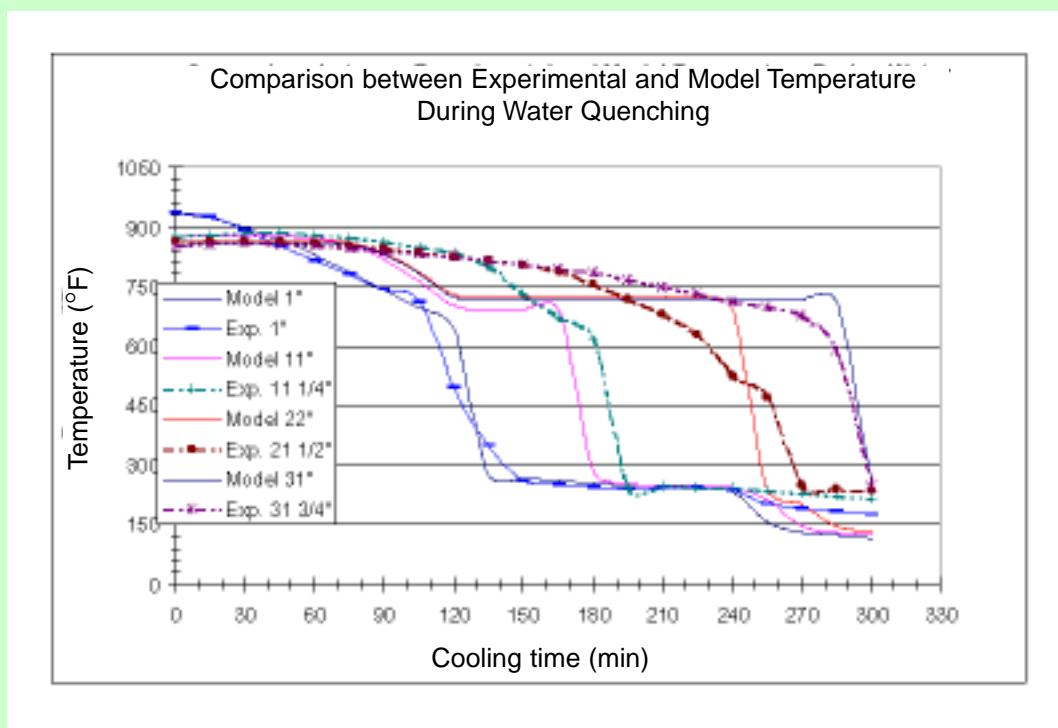


Figure 19: Quench results and prediction comparison.



API Research Project 48 members arriving for a group meeting (circa 1956).

MEETINGS CALENDAR

2003

August 12-13, 2003

National Petrochemical and Refiners Association (NPRA)

Clean Fuels Challenge
Westin Galleria
Houston, TX

Web: www.npradc.org/meetings/clean_fuels

September 7-11, 2003

American Chemical Society
226th ACS National Meeting
New York, NY

E-mail: natlmtgs@acs.org
Web: www.chemistry.org

September 14-19, 2003

International Association for Stability and Handling of Liquid Fuels

8th International Conference on Stability and Handling of Liquid Fuel
Steamboat Springs, CO

Web: www.iah.net

September 22-24, 2003

National Centre for Upgrading Technology (NCUT)

3rd Meeting on Upgrading and Refining of Heavy Oil, Bitumen and Synthetic Crude Oil and the Symposium on Stability & Compatibility during Production, Transportation and Refining of Petroleum
Westin Hotel
Edmonton, Alberta, Canada

Web: www.ncut.org

November 13-14, 2003

National Petrochemical and Refiners Association (NPRA)

Lubricants & Waxes Meeting
Omni Houston Hotel
Houston, TX

Web: www.npradc.org/meetings/lubes

November 16-21, 2003

American Institute of Chemical Engineers
2003 Annual Meeting

San Francisco Hilton
San Francisco, CA
Web: www.aiche.org

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
National Petroleum Technology Office
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DownstreamDetails



Summer 2003