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THE UNIVERSITY of TULSA

Department of Chemical Engineering

Fundamentals of Delayed Coking Joint Industry Project

NON CONFIDENTIAL
Final Report

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Disclaimer

1. Executive Summary

Thirteen organizations were members of the Fundamentals of Delayed Coking JIP that started January 1, 1999: Baker-Petrolite, Chevron, Citgo, Conoco, Equilon, Exxon-Mobil, Foster Wheeler, Great Lakes Carbon, KBC Advanced Technologies, Marathon, Petrobras 6, Suncor, and the U.S. Department of Energy.

The coking test facilities include three reactors (or cokers) and ten utilities. Experiments were conducted using the micro-coker, pilot-coker, and stirred-batch coker. Gas products were analyzied using an on-line gas chromatograph. Liquid properties were analyzed in-house using simulated distillation (HP 5880a), high temperature gas chromatography (6890a), detailed hydrocarbon analysis, and ASTM fractionation. Coke analyses as well as feedstock analyses and some additional liquid analyses (including elemental analyses) were done off-site.

The micro-coker was an effective screening tool, producing small quantities of coke, liquids and gases for testing over a very short operating period. The results from the micro-coker compare favorably with pilot scale and commercial results in terms of product yields, liquid product distribution and properties, and coke properties. Some differences between the micro-coker and pilot unit results were noted, specifically the somewhat lower liquid yields and higher gas and coke yields, and higher gasoline yields in the micro-coker. These differences are due to the differences in the way the micro-coker and pilot-coker are run, resulting in higher temperatures in the micro-coker and thus some overcracking of the feed.

The pilot unit was successfully run to obtain reliable and reproducible coking data. Results from the pilot unit correspond well with results from refinery operation from the same feedstocks at similar operating conditions. Analysis of the gas, liquid and coke products have given valuable information on the liquid product subfraction yields, sulfur distributions, and coke morphology as a function of feedstock and operating conditions. Both shot and sponge morphologies were produced with this facility.

Preliminary studies have been carried out using the modified pilot unit for foam detection. Use of the gamma densitometer was successfully demonstrated to detect foam formation, foam collapse (both spontaneous and from antifoam addition), and to classify coke morphology.

Fouling tests were carried out with the pilot unit using two different application techniques for the anti-coking agent; one where the coil was pre-treated and one where it was only added to the feed. The pre-treating agent passivated the metal surface inhibiting the lay down of coke precursors. This pre-treatment resulted in energy savings due to quicker warm-up as well as from only having to apply a 5^oF delta T rather than 10^oF for the test where the coil wasn't pre-treated. A decrease in temperature by as much as 20^oF was observed when a combination of anti-coking agent was used with a stabilizer.

Kinetic studies were carried out using both the stirred-batch reactor and thermogravimetric analysis (TGA). The TGA studies gave excellent temperature control for a large data set (feed loss vs. time), but provide no information on product distributions. This data has resulted in a simple kinetic model of resid conversion. The stirred batch reactor gave good information on product distributions but has limited temperature control and a limited amount data over time for each run (typically four liquid samples are obtained during a coking run). Combined with information from the TGA, a more detailed kinetic model can be developed that includes prediction of the boiling point distribution of the products.

The stirred-batch reactor experiments were carried out until complete reaction occurred, i.e. until complete conversion of the feed to coke and vapor (condensate and gas) products. This aspect of the experiments allowed a comparison of the end products of the stirred-batch coking reactions to the results of the micro-coker and pilot unit studies. Results showed that the product yields (coke, liquid and gas) match very well with what was achieved in the pilot unit under comparable temperatures and pressures.

Correlations to predict the product yields for the micro-reactor were developed. Sets of correlations for several feedstocks (Fluid 5, Fluid 1, Fluid 4) were developed to predict product and liquid subfraction yields as a function of temperature, pressure, and liquid space velocity. A general correlation was also developed based on temperature, pressure, liquid space velocity, and feedstock microcarbon residue. Correlations were also produced to predict sulfur distribution among gas, liquid and coke products. All correlations show very good agreement between experiment and prediction. The product yield correlations were adjusted with correction factors, which account for the overcracking mentioned above, to allow prediction of the pilot unit results.

Correlations (both general and feedstock-specific) were also developed from the pilot unit studies to predict product distributions, with very good agreement between experiment and prediction. Results from the revised SimDis data were used to successfully correlate liquid product distribution data.

Results from the stirred-batch reactor were also used to develop some simple rule-of-thumb correlations for coke, liquid, and gas yields.

A preliminary model was developed to predict the two-phase flow regimes for the furnace tube, both for horizontal and inclined flow. The flow pattern in this case is a function of the resid properties (density, viscosity, and surface tension), which are estimated at the temperature and pressure of interest, as well as the angle of inclination of the pipe. Results show that the flow pattern in the pilot unit furnace changes from intermittent to annular due to vaporization of the feedstock. The vaporization results in a large increase in gas velocity, leading to the pattern transition from intermittent to annular flow. For the commercial delayed coking process, the high mixture velocity at the furnace outlet is expected to result in the annular flow regime.

2. Acknowledgements

Acknowledgements

The successful completion to a project of this type and magnitude requires significant contribution of time and other resources from a large number of individuals and organizations. We specifically acknowledge the following:

- Equilon for their donation of the pilot unit, the on-line GC and scrubber. This donation allowed the JIP to start-up quickly without the need for a large capital investment.

- Chris Paul of Great Lake Carbon for his assistance in training the technicians at the University of Tulsa in the operation of the pilot unit facility, for his assistance in trouble shooting the unit during the shakedown period as well as presenting a tutorial to the coking staff related to delayed coking.

- The United States Department of Energy for their donation of the micro reactor and some of the components used to construct the batch reactor. These donations also allowed the JIP to start-up quickly without the need for a large capital investment. We would also like to thank the United States Department of Energy for recognizing the importance of this project to the domestic refinery industry and for funding approximately 35% of the total cost.

- Phillips for the donation of two Hewlett Packard 5880A GC's that were utilized for the simulated distillation analyses of the produced liquids.

- The six companies and the United States Department of Energy for the donation of the resides that were utilized in the study and well as for providing the refinery data used in the model validation and scale-up efforts.

- Steven Klasnich of Chevron-Texaco for providing addition analyses of the resid samples as well as for the seminar presented to the coking staff related to safety.

- Kuwait National Oil Company for supporting Hamad Al-Merri as a Research Assistant for his PhD program.

- ARAMCO for supporting Majed Al-Gousi and Hamdan Al-Shammary as a Research Assistant for their MS program.

- Sonangol (National Oil Company of Angola) for supporting Zola Afonso as a Research Assistant for her MS program.

- The Woobanks Foundation for supporting Shack Hawkins as a Research Assistant for his MS program.

- The committee chairs: Chris Paul of Great Lakes Carbon who chaired the Coker and Facility Operation Committee, Weijian Mo of Equilon who chaired the Process Dynamics and Modeling Committee and James Blevins of Chevron-Texaco who chaired the Technology Transfer and Commercialization Committee for their leadership during the JIP.

In addition, the following University of Tulsa staff members deserve special recognition for their contributions throughout the JIP:

- Don Harris, Electronics Technician, for rewiring the pilot unit, developing the control software for the gamma densitometer utilized in the foaming studies as well as for trouble shooting electrical problems as they arose.

- Gene Derby, Pilot Unit Operator, whose dedication and determination generated the high quality data used to develop the correlations and models.

- Laura Young and John Corgan, Analytical Technicians, for processing the liquid and gas samples generated during the micro, pilot and batch reactor tests.

- Deborah Clancy, Project Assistant, for all tasks related to accounting, organization and preparation of material for meetings and reports, purchasing and communications with JIP members.

3. Table of Contents

List of Figures

List of Tables

4. Introduction

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 of any operation in a modern refinery. Large amounts of energy are required to heat the thick, poor-quality petroleum residuum to the 900 to 950 degrees F 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 (near zero economic value) byproduct, compared to transportation fuels, there is a significant worldwide trade and demand for coke as it is an economical fuel. Coke production has increased steadily over the last ten years, with further increases forecast for the foreseeable future. Current domestic production is near 111,000 tons per day. A major driving force behind this increase is the steady decline in crude quality available to refiners. Crude slates are expected to grow heavier with higher sulfur contents while environmental restrictions are expected to significantly reduce the demand for high-sulfur residual fuel oil. Light sweet crudes will continue to be available and in even greater demand than they are today. Refiners will be faced with the choice of purchasing light sweet crudes at a premium price, or adding bottom of the barrel upgrading capability, through additional new investments, to reduce the production of high-sulfur residual fuel oil and increase the production of low-sulfur distillate fuels. A second disadvantage is that liquid products from cokers frequently are unstable, i.e., they rapidly form gum and sediments. Because of intermediate investment and operating costs, delayed coking has increased in popularity among refiners worldwide. Based on the 2000 Worldwide Refining Survey published in the Oil and Gas Journal December 2000 issue, the coking capacity for 101 refineries around the world is 2,937,439 barrels/calendar day. These cokers produce 154,607 tons of coke per day and delayed coking accounts for 88% of the world capacity. The delayed coking charge capacity in the United States is 1,787,860 b/cd.

In general, coking belongs to a class of thermal decomposition, free radical chemical reactions that have been extensively studied, except for the last stages of coke formation itself. The engineering of thermal processes has been well developed. Recent efforts to minimize the environmental impacts of furnace processes have lead to significant improvements.

As the coke product has declined in value, alternate coking processes have been developed to consume the coke produced in-house (e.g., burn it). The values of these processes are intimately associated with the utility needs of a particular refinery. Delayed coking is still the preferred process in new construction.

Despite the high quality of post World War II research into thermal chemistry, delayed coking remains a development mainly of plant engineers, technicians, and contractors. Since only a few contractors and refiners are truly knowledgeable in delayed-coking design, this process carries with it a “black art” connotation. Until recently, the expected yield from cokers was determined by a simple laboratory test on the feedstock.

It is important to gain a better understanding of the process and be able to model the process to optimize the cokers to reduce the amount of contaminants in coke, making it better suited for commercial use in the metals or chemistry industry, as well as ways to reduce the amount of sulfur in the gasoline and diesel fractions, reduce the amount of energy to process the resid which will result in a corresponding reduction in associated greenhouse gases, to design appropriate chemical treatments for foaming that minimize the amount of anti-foam used to eliminate upsets, and to be able to better predict shot coke formation and minimize HES related concerns by providing insight as to why settling, poor drainage and hotspots occur in drums.

5. Scope of Problem

SCOPE OF WORK

The usual basis for predicting coke yield in commercial units is by measuring the carbon residue from standardized pyrolysis procedures (Conradson, Ramsbottom and Microcarbon residue methods). In fact, carbon residue “content” had become accepted as the minimum attainable coke value. Yet, thermal cracking in the presence of hydrogen, as in the Veba Combi or HDH processes, yields lower coke levels, with coke formation being extremely low with many feedstocks. In these processes, hydrogen is believed to “cap off” aromatic radicals before they can couple with other aromatics to form high molecular weight coke precursors. The high temperature and pressure that are required for these processes make them capital-intensive.

An alternate, more economically attractive approach to minimize the formation of coke yield would be to carry out thermal cracking under conditions where the formation of (or coupling of) aromatic radicals is minimized. Use of lower coking temperatures or greater feedstock dispersion could be used toward these aims. Abstraction of aryl hydrogen atoms to form aromatic radicals has a higher activation energy that most thermal processes and thus becomes significant only a higher temperatures. Similarly, larger aromatic molecules couple in conventional ways because of close proximity as heavy liquid or semi-solid phases. This heavy liquid phase has been observed visually using Hot-Stage Microscopy by Rahimi et al., (1998).[1]

This program will examine methods for sustaining thermal cracking at lower temperatures and dispersing high molecular weight coke precursors (asphaltenes). Potential approaches could include the use of additives (free radical initiators of dispersants), modified furnaces or coke drum preheaters, augers, venture aspirators, co-solvents, and the like.

Concurrent work on the fundamentals of coking and development of mathematical models will aim toward identifying limiting factors for conversion and maximizing liquid yield. Once these factors have been identified, appropriate chemical and/or engineering modifications to the system will be proposed and evaluated. Data from even unsuccessful modifications will in turn be used to refine mathematical models and the fundamental understanding of the coking process.

Specific component processes and issues which likely impact operation and product slate for delayed coking include the following:

a. Paraffin and paraffinic side chain cracking
b. Phase behavior of napthenic/aromatic “cores” remaining after side chain cleavage.
c. Precipitation of residual asphaltene induced by formation of light product liquids.
d. Three-dimensional structure of molecules in vacuum resides.
e. Surface effects between existing coke and heavy liquids.
f. Thermal requirements for volatilization and recovery of heavier liquid products.

This project seeks to identify, quantify, and increase control over the component processes that make up the delayed coking process. The success of the project will depend on input from the industrial participants. It is expected that program variations will focus on the real problems encountered in coking in the current marketplace as well as seeking validation of new concepts in coking such as the theory that micelles present in the coker feed can change the solids yield from the process. They preliminary program given here reflects University of Tulsa research experience and information given by potential participants.

PROGRAM CHRONOLOGY

The program proposed was to begin with the stirred batch coker unit built with Department of Energy funds. The ultra-small batch coker unit used in the Department of Energy coker additives program will also be used. The program proceeds to the first batch system and continues with a combination of batch and flow experiments. A chronology of event's on a year by year basis, is provided below. Coke will be produced and characterized, as will the stream samples. A committee was to determine the complete list of analytical procedures as the program unfolds.

Year 1 Phase I Program: Experimental Systems Development

1. Reassemble & commission customized stirred batch coke unit at University of Tulsa site.
2. Reassemble existing ultra-small batch coker for base runs at University of Tulsa site.
3. Run existing ultra-small batch coker for base runs.
4. Obtain Hot-Stage Microscopy result from National Centre for Upgrading Technology for base runs.
5. Begin analysis of donated data and math models.
6. Begin initial program studies on stirred batch coker
7. Reassemble, commission, and testing of a continuous furnace tube coker.
8. Add coke drum to the flow system.
9. Issue report on first year construction and testing, including data comparing the stirred batch and flow systems.

Year2 Phase II Program: Data Acquisition and System Comparisons

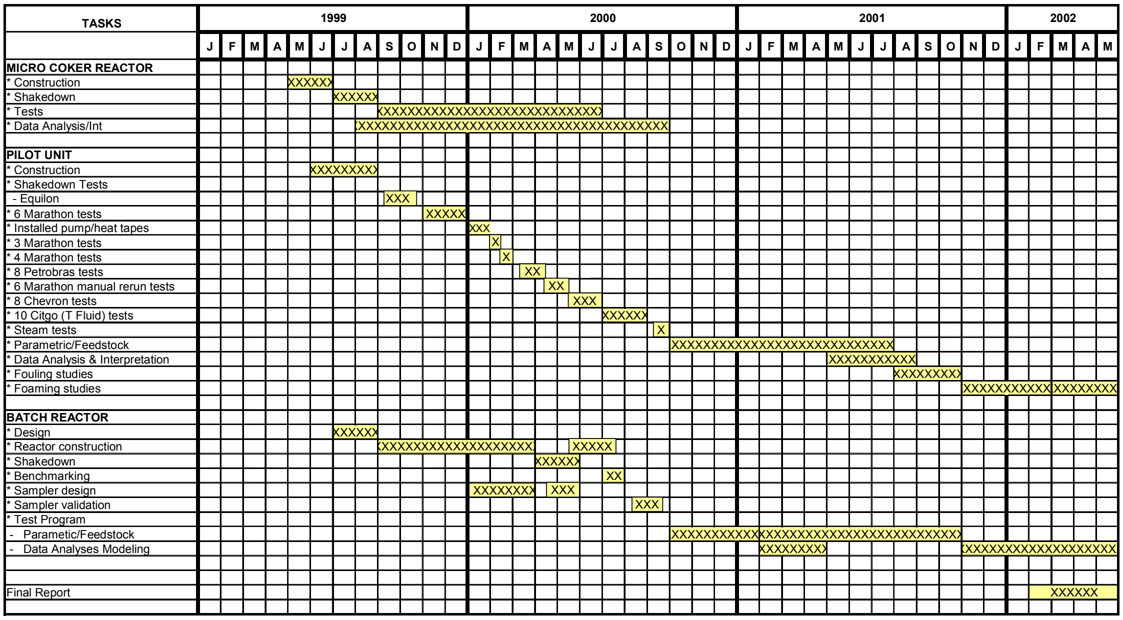
1. Start Phase II Program in the stirred batch system.
    a. Continue feedstock program with emphasis on liquid yield and quality.
    b. Study secondary processes
        - Lights/heavy ratio
        - Foaming
        - Improved correlations
2. In the stirred batch coker vary temperature and agitation to simulate the events in the last few feet of furnace tube length. Analyze for coke precursors, polymers, meso phase.

3. In tubular reactor vary sample and quench liquid from the last few feet of furnace tube length. Analyze for coke precursors, polymer, meso phase and compare to stirred batch reactor.
4. Correlate furnace tube chemistry with coke drum conditions and coke properties.
5. Develop from basic principles of chemistry/physics, a mathematical model of events taking place in the furnace tube.
6. Begin Pilot program to test the scale-up of results from the batch coker and tubular coker to pilot scale.
7. Write a report on Phase II research with data, correlations, and math models.

Year 3 Phase III Program: Advanced Flow Experiments & Theory Developments

1. Run coordinated programs in the stirred batch and flow systems:
    a. Parameteric studies
    b. Additive studies
    c. Test micelle theory
    d. Test special additives
2. Upgrade drum experimental system.
3. Continue Pilot Program investigating scale-up of the batch and the tubular coker results to pilot scale.
4. Construct advanced math model for furnace/drum/liquids interrelations.
5. Evaluate the evolved stirred batch apparatus for possible industrial use in evaluation of feedstocks relative to stability, foaming, yields and fouling.
6. Write final report with data, theories, correlations, and math models.

Once committees were formed and the actual work began, recommendations and modifications were made by the participants. The sequence in which these activities were conducted is shown in Figure 1.



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Final Report																																						X	X	X	X

Figure 1 - Gantt Chart Showing Actual Times for Experimental Tasks

6. Test Facilities

The coking test facilities included 3 reactors or cokers and eleven utilities. The operational micro-coker was supplied by the U.S. Department of Energy (U.S. DOE). The batch-coker reactor, also supplied by U.S. DOE, required construction of the heating, control, and product gathering systems. The operational pilot-coker was obtained from Fluid 1 in exchange for membership. The utilities include an on-line gas chromatograph and caustic scrubber from Equilon; house air and nitrogen; a University of Tulsa glycol chiller, purchased steam generator, hydrogen sulfide monitors and sample storage refrigerators; and donated vent hood and oven. The three cokers and associated utilities are described below.

A. MICRO-COKER

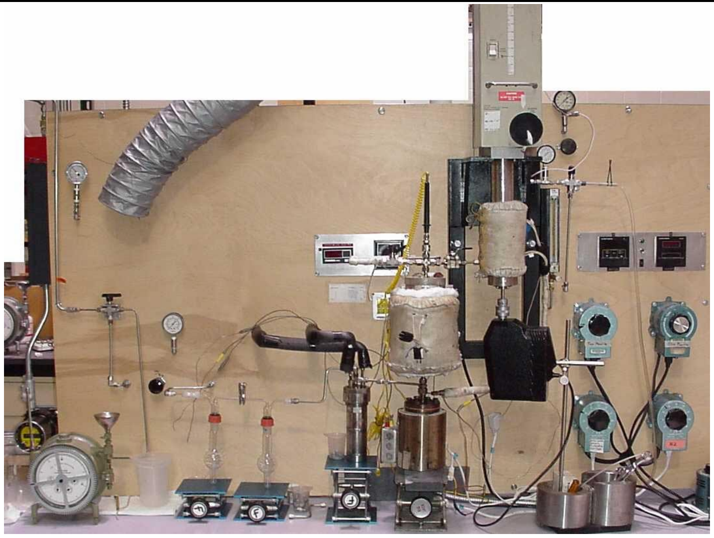


Figure 2 - Picture of Micro-Coker

The micro-coker is shown in Figure 2. 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 first cooled liquid trap is metal and the following two are glass. The first trap collects the majority of the liquid. Potential leaking between the glass joints limited the operating pressure of the micro-coker as described and shown. Higher pressure is desirable to match refinery-operating conditions. Also foaming occurred in the pilot-coker coke drum when processing Fluid 1 feed at the low pressure. For these two reasons and since the majority of the liquid was captured in the metal trap, a modified micro-coker set-up was developed and tested. In this modified set-up the glass traps were removed and replaced by a single piece of metal tubing.

The main objectives for utilizing this reactor are to:

1. Reproducibly mimic commercial operation for a very short time, producing small quantities of coke, liquids and gases for testing,
2. Investigate and correlate the effect of feedstock composition and to a lesser extent pressure, temperature and residence time on product rates and compositions and on coke morphology,
3. Develop and validate a model(s), and

4. Investigate scale-up issues.

B. STIRRED-BATCH REACTOR

The stirred batch reactor unit is shown in Figure 2. It consists of a stainless steel cylinder, 13 inches tall and 11 inches outside diameter, with flanged lid. An 8”x 9.5” stainless steel liner that holds the feed and the coke product is placed inside the reactor. In addition, an impeller, for mixing and better heat transfer, is mounted on an overhung shaft and is situated two inches from the bottom. The shaft is driven by a 3-phase motor, which is controlled by an AC inverter for variable speed. The reactor is heated from the outside by two Mica band heaters. Other, auxiliary equipment include: two gas-liquid separators, a blowdown tank, a cooler, a gas flowmeter, temperature controllers, and a back-pressure regulator.

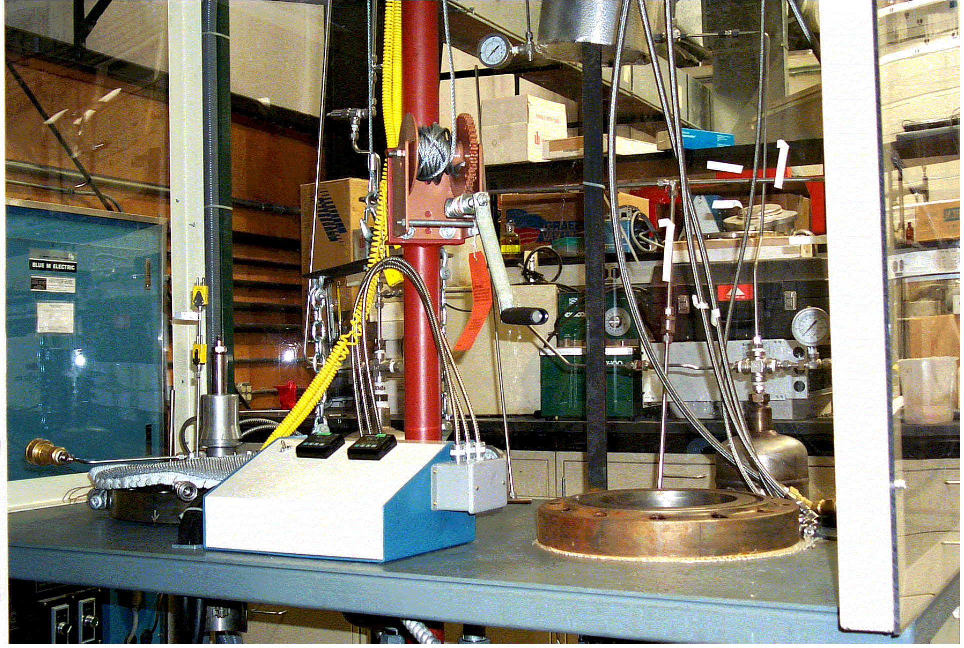


Figure 3 - Stirred Batch Reactor Unit

The main objectives for utilizing this reactor are to:

1. Identify the coke precursors,
2. Study heat rate effect on yields (simulate furnace tube), and
3. Study the kinetics of the thermal cracking reactions.

A hot resid sample is placed inside the liner. The band heaters heat this reactor and liner. To homogeneously heat the feed, the stirrer is rotated at a predetermined shaft speed. Unless there are two phases that cannot be mixed, the mixing effect also helps obtain a homogeneous composition of the contents of the reactor. The system is purged and pressurized with nitrogen to the desired test pressure. Also, the nitrogen displaces the vapor and gases remaining in the system at the end of the run.

During the test, processed resid samples are drawn from the reactor to identify the coke precursors. Since the samples are viscous or solid at room temperature or at a temperature lower than their sampling temperatures, they have to be set in the oven overnight and collected in a 20 ml sample jar. These samples then were analyzed using the high temperature gas chromatograph (HTGC) that can cover up to n-C_{100} – n-C_{110} (~1330 °F).

The vapor from the reactor flows to the gas-liquid separator that is wrapped with a steam coil. Approximately 80 # steam, 250 °F, is used to cool the hot vapor. Gas that is not condensed flows to a cooler, which uses 37 °F water as a coolant. Liquid from this cooling process is collected in a second gas-liquid separator. The liquid samples are collected using eight receivers (4 for the lights and 4 for the heavies) with quick disconnect fittings. Using the quick disconnect fittings there is no opening or closing of valves during the test. The receivers are connected and disconnected during the test to collect the different condensate batches. The gas trapped with the liquid is taken into account. The liquid and the gas are weighed in the receiver, then the liquid is weighed alone and the differences in weights, i.e. receiver, liquid, and gas, give the mass of the gas. This gas is assumed to have the same composition as the gas analyzed in the GC during the liquid collection period. This system is shown in Figure 4.

Figure 4 - Liquid Collection System with Hoke Cylinders and Quick Disconnect Valves

The remaining gas flows to a gas flowmeter and then to the online GC. A back-pressure regulator before the flowmeter maintains the system at the desired pressure.

C. PILOT-COKER

The pilot coker can be viewed as two main pieces: the process equipment and the control system. In the section below each piece is described.

1. Process Equipment Description

The pilot-coker obtained from Equilon Enterprises, LLC is shown in Figure 5. It consists of a feed tank and circulation system, and a furnace with both the preheater and the coke drum. The feed drum holds approximately 15 gallons and is mounted on a scale. Feed passes from the outlet of the drum, goes to a Zenith pump (see Figure 6) with some return flow back to the feed drum. All the lines are steam traced. From the pump, the resid can flow back to the feed tank, to a slop tank or to the furnace. Initially the flow is back to the feed tank to circulate feed and stabilize the temperature. Once the unit is lined out the feed can be switched to a slop tank to check the flow rate (based upon the loss of weight measured by the scale).

When the rate is correct, flow is sent to the furnace. In the furnace are first a preheater coil (mimicking the commercial furnace) followed by a coke drum. The coke drum, with dimensions of 3" x 40" and a volume of ~4,750 cc, is located in the furnace to prevent heat loss. Commercial coke drums are well insulated and have a high volume-to-surface area ratio, making them adiabatic. To simulate commercial steam injection water is injected upstream of the preheater coil. Operating variables include temperature, pressure, steam injection rate, and charge flow rate. The latter two variables affect residence time and Reynolds number.

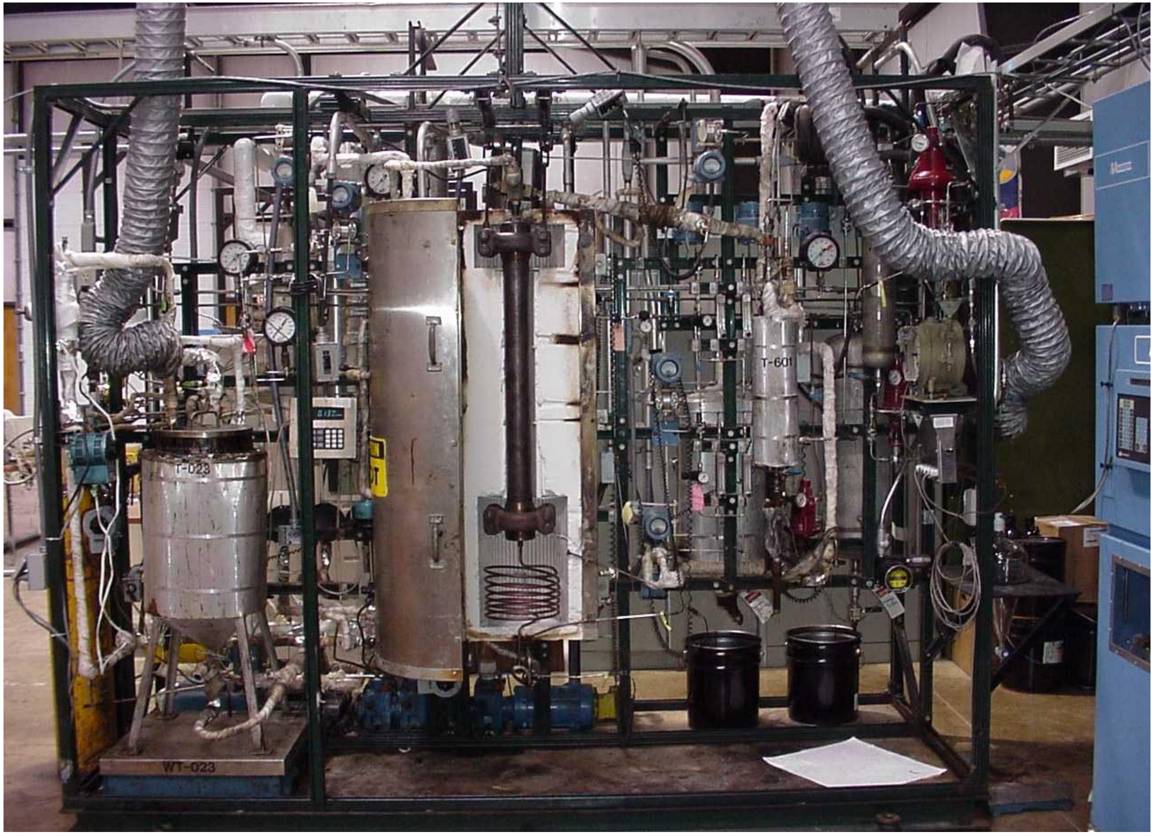


Figure 5 - Picture of Pilot-Coker Unit

The main objectives for utilizing this reactor are to:

1. Reproducibly mimic commercial operation producing sufficient quantities of coke, liquids and gases for testing,
2. Investigate and correlate the effect of feedstock composition and reactor conditions on product rates & compositions and coke morphology,
3. Maximize distillate product production and minimize coke and gas production,
4. Find ways to reduce tube fouling,
5. Develop and validate a model(s), and
6. Investigate scale-up issues.

This reactor was the workhorse in this Joint Industry Project (JIP) experimental investigation.

Figure 6 - Zenith Pump for Pilot-Coker

2. Control System Description

The control system included an electrical control box, a cabinet that houses the Foxboro field bus modules (FBM's), a Foxboro μ-IA controller, and Foxboro's Softpack 6.1 control software for NT installed on a 450 MHz Pentium 2 computer (see Figure 7). The control logic is built on top of the Softpack utilities. The University bought the μ-IA from Foxboro and Foxboro donated the Softpack 6.1 software.

(a) (b)

Figure 7 - Pictures of (a) Electrical Control box, (b) Foxboro Field Bus Module Cabinet and a Foxboro μ-IA Controller Mounted on the Bottom

D. FOAM DETECTING PILOT-COKER

As shown in Figure 8, the pilot unit was modified to study foaming by adding a larger furnace, a gamma densitometer and a lift. The gamma densitometer is used to measure the density of the gas, foam, liquid layer, and coke columns in the drum. The data, as a function of height is displayed on the control monitor for each scan. Time, drum location and the corresponding density are recorded in an Excel spreadsheet. A Macro was built that plots the data as height vs. density as a function of time and density as a function of time vs. height in the drum. This set up allows the researchers to establish and track, via the forklift, the interfaces and densities as a function of time. The system is automated with a Labview control system.

To obtain a continuous flow of steam, the pulsating pump used in the parametric study was replaced with the HPLC pump that injects continuously. The antifoam is injected using an Eldex Metering Piston pump.

Figure 8 - New Foaming Studies Apparatus

The objectives of this system are:

1. Quantify foam heights for model development,
2. Compare overhead injection of anti-foam versus injection with feed,
3. Determine how anti-foam partitions in the products,

4. Establish whether injection anti-foam in the feed alters the coke density, and
5. Longer coking runs (10 to 15 hours at feed rates used in the prior JIP).

E. UTILITIES

The utilities include an on-line gas chromatograph and caustic scrubber from Fluid 1, plus an ASTM distillation unit, a HP 5890, HP 6890 HTGC, house air and nitrogen; a University of Tulsa glycol chiller, purchased steam generator, hydrogen sulfide monitors, two freezer; and donated vent hood and oven.

7. Test Fluids

Prior to the first advisory board meeting in April 1999 each participant was asked to submit information on possible feedstocks for the coking tests. Potential feedstocks were to be well characterized analytically, have an operational history of the type of coke made and product yields, and the samples had to be available for the next three years. At the April 1999 advisory board meeting, a workshop was held in which the feedstocks to be used in the test program were selected. The samples selected covered a wide range of parameters that included API, metals, asphaltenes, CCR or MCR, source, structure, sulfur, sodium and coke type made. Each feedstock was to be provided in four 55-gallon drums

Feedstock samples were obtained from six companies. Two companies also provided recycle samples. All the resids were transferred from the 55-gallon drums they were shipped in to 5-gallon drums for easier handling in the coking tests. One gallon samples of the 6 feedstocks & 2 recycles were taken and sent for analysis. One drum of slurry decant oil was also sent for the tests with fluid 1.

Table 1 below is an overview table showing both the values provided by the companies and the values measured for the actual resid samples provided. Also included are values for the recycle samples. Table 2 gives measured micro-carbon residue, vapor phase osmometry molecular weight and elemental analysis for the resids, recycles and two other resids which were used in shakedown tests. Table 3 contains the feedstock analysis data provided by Baker-Petrolite. Table 4 and Table 5 show the raw and normalized acid/base/neutrals results, respectively.

Table 1 - Feedstock Properties Provided by the Companies Compared to those Measured

Property	Fluid 1		Fluid 2		Fluid 3		Fluid 4		Fluid 5		Fluid 6		Fluid 7	Fluid 8
	P	M	P	M	P	M	P	M	P	M	P	M	M	M
API	3	0.5	5.5	4.6	6.5	5.7	2.5	2.9	13	10.3	8.5	6.5	16.8	0.3
Asphaltenes wt %	20	39.2	18	34.2	6	17.6		25.2	5 to 7	12.1	8.4	24.3	0.2	8
CCR, Wt %	25	28.5	25	24.3	20	19	20	20.2	14	15.6	18	20.7	0.8	9
Source	Maya		Venezuela		San Juaquin		Canada		Mixed		Offshore		Fluid 5 Recycle	Fluid 4 Recycle
Structure	Intermediate		Naphthenic		Naphthenic		Aromatic		Paraffinic		Paraffinic?			
Metals, ppm														
Ni	110	142	80	110	40	193		125	30	38		63	2	3
V	530	739	600	703	120	148		330	12	57		69	0	8
Sulfur, Wt %	5	5.51	3.5	3.09	4	2.16	5	5.76	1.1	2.62	Low	1.45	2.46	5.45
Sodium, pp	<10	8	8	8	<10	8		30	<10	7		23	6	4
Coke Type	Shot		Shot		Shot		Sponge		Anode/Sponge		Anode			

P=Provided; M=measured

Table 2 - Carbon Number, Vapor Phase Osmometry Molecular Weight, and CHSN Weight Percentage Feed Analysis (TRW)

Sample ID	Carbon Residue wt%	Molecular Weight	Carbon wt %	Hydrogen wt %	Sulfur wt %	Nitrogen wt %	Total wt%	API
Fluid 2	24.30	1,386	85.04	9.91	3.09	0.53	98.57	4.6
Fluid 3	19.00	941	84.86	10.03	2.16	0.87	97.92	5.7
Fluid 1	28.50	1,849	83.54	9.41	5.51	0.57	99.03	0.5
Fluid 5	15.60	1,116	85.56	10.90	2.62	0.33	99.41	10.3
Fluid 5 Recycle	0.80	350	85.88	10.69	2.46	0.35	99.38	16.8
Fluid 6	20.70	1,397	86.46	10.41	1.05	0.61	98.53	6.5
Fluid 4	20.20	1,179	82.04	9.71	5.76	0.48	97.99	2.9
Fluid 4 Recycle	9.00	411	84.35	8.72	5.45	0.54	99.06	0.3
Midway Sunset	20.7		85.35	10.2	1.78	1.46	98.79	5.6
Hondo	22.4		80.69	9.92	6.39	1.05	98.05	3.0

Table 3 - API, SARA, Acid Number, NMR, and Chlorine Feed Analysis (Baker-Petrolite)

Sample ID	API	Asphaltenes	Asphaltic	Filterable	Acid #	NMR	Total
		%	Resins %	Solids (ppm)	mg KOH/g	% Sat/Arom	Chlorine mg/L
Fluid 2	4.6	34.2	54.7	128	0.2	1.9	26.6
Fluid 3	0.5	17.6	53.0	215	1.6	2.4	16.6
Fluid 1	5.7	39.2	41.6	801	1.1	2.3	28.3
Fluid 5	10.3	12.1	48.1	320	0.6	2.8	23.6
Fluid 5 Recycle	16.8	0.2	21.2	<10	<.1	2.0	16.2
Fluid 6	6.5	24.3	49.8	103	1.2	2.4	14.5
Fluid 4	2.7	25.2	51.3	10451	2.6	2.5	26.7
Fluid 4 recycle	0.3	8.0	87.6	1624	0.4	0.9	14.9

Table 4 - Acid/Base/Neutrals Tests (Raw Data)

Sample Name	Strong Acid	Weak Acid	Strong Base	Weak Base	Neutrals	Total Percentage
Fluid 5	11%	6%	10%	4%	72%	103%
Fluid 2	12%	8%	14%	6%	61%	101%
Fluid 4	15%	9%	13%	6%	61%	104%
Fluid 1	12%	9%	16%	9%	57%	103%
Fluid 6	12%	9%	16%	9%	56%	102%
Fluid 3	15%	12%	14%	8%	54%	103%
Midway Sunset	2%	14%	23%	14%	57%	110%
Midway Sunset	3%	13%	19%	15%	56%	105%
Hondo	4%	16%	25%	14%	49%	107%
Hondo	6%	11%	22%	9%	46%	94%

Table 5 - Acid/Base/Neutrals Tests (Normalized Data)

Sample Name	Strong Acid	Weak Acid	Strong Base	Weak Base	Neutrals	Total Percentage
Fluid 5	11%	6%	10%	4%	70%	100%
Fluid 2	12%	8%	14%	6%	60%	100%
Fluid 4	14%	9%	13%	6%	59%	100%
Fluid 1	12%	9%	16%	9%	55%	100%
Fluid 6	12%	9%	16%	9%	55%	100%
Fluid 3	15%	12%	14%	8%	52%	100%
Midway Sunset	2%	13%	21%	13%	52%	100%
Midway Sunset	3%	12%	18%	14%	53%	100%
Hondo	4%	15%	23%	13%	46%	100%
Hondo	6%	12%	23%	10%	49%	100%

At the May 2000 meeting, it was observed that the asphaltene numbers (see Table 1) were higher than expected. Upon discussion, it was concluded that the higher numbers are due to Baker-Petrolite using pentane to precipitate the asphaltenes rather than the expected heptane (Baker-Petrolite uses pentane in their analytical procedure because, for predicting fouling, they have found better correlation with pentane insolubles). After the meeting Chevron-Texaco offered to perform SARA analysis on our 6 feeds and 2 recycles. Chevron-Texaco's procedure is as follows:

1. Determination of insolubles (asphaltenes).: The test determines the content of "hot" (80°C) heptane insolubles (asphaltenes). It is a modification of the ASTM D3279-90 method. The test is applicable to samples containing 20 ppmw to 20 wt% of insolubles. No further separation of the soluble fraction is performed.
2. Determination of saturates, aromatics, polars (resins), and insolubles (asphaltenes).: Determined using one of the following two methods:

   a). ASTM D2007-93 method: which determines n-pentane insolubles (asphaltenes). The n-pentane soluble fraction is further separated by liquid chromatography on a clay-silica gel column into the following three fractions: - saturates, which are defined as "material that, on percolation in a n-pentane eluent, is not adsorbed on either the clay or silica gel"; - aromatics, which are defined as "material that, on percolation, passes through a column of adsorbent clay in a n-pentane eluent but adsorbs on silica gel under the conditions specified"; - polar compounds, which are defined as "material retained on adsorbent clay after percolation of the sample in n-pentane eluent under the conditions specified".

   b). In-house method (Test # 50310), uses n-hexane to determine n-hexane insolubles (asphaltenes) and further separates the n-hexane soluble fraction into saturates, aromatics, and polars by using liquid chromatography on a silica gel column.

The feedstock measurements made by Chevron-Texaco are summarized in Table 6. Boiling point distributions from the HTGC tests are reported in Table 7, while the corresponding boiling point curves are shown in Table 8.

Table 6 - Results from Fluid 3's Feedstock Analysis

	Fluid 6	**Fluid 1**	**Fluid 3**	**Fluid 2**	**Fluid 5**	**Fluid 4**	**Fluid 5 Recycle**	**Fluid 4 Recycle**
Test Analysis								
API gravity @ 60F	5.4	1.1	4.3	3.3	9.7	1.6	15.6	-0.1 to 0.4
MCRT (wt%)	21.77	29.40	20.25	25.74	16.25	21.15	1.18	12.42
Pour Point (C)	97	112	78	87	35	76	31	19
Viscosity @ 70C							17.13	541.8
@ 100C					661.3		7.058	70.22
@ 135C	1,764	7,117	703	1,561	120	829		
@ 150C	785	2,584	309	650		384		
C7 Asphaltenes (wt%)	8.56	24.60	8.75	15.27	2.35	12.97	0.15	2.18
Sodium (ppm)	11.1	6.11	4.13	1.91	2.8	23.6	< 0.5	0.65
Metals ICP								
Ni (ppm)	63.94	132.05	183.3	106.62	36.85	121.29	0.25	3.77
V (ppm)	68.17	>695.84	139.46	688.6	55.2	316.19	< 0.32	8.05
Sulfur (wt%)	0.924	4.939	1.843	3.049	2.11	5.385	1.752	5.021
Carlo Erba								
Carbon	88.395	83.51	85.287	85.357	85.811	82.965	86.045	84.764
Hydrogen	10.732	9.394	10.099	10.023	11.065	9.825	10.786	8.452
Nitrogen	1.143	1.474	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
CHNS total	101.2	99.3	98.2	99.4	100.0	97.0	99.6	99.2

Table 7 – Fluid 3's HTGC Analysis of Feedstocks

Fluid 5		Fluid 2		Fluid 1		Fluid 3		Fluid 4		Fluid 6	
% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)
1	725	1	782	1	757	1	766	1	694	1	792
2	802	2	835	2	824	2	803	2	739	2	855
3	838	3	868	3	863	3	826	3	767	3	891
4	867	4	892	4	890	4	845	4	788	4	916
5	888	5	911	5	911	5	862	5	805	5	935
6	906	6	927	6	928	6	876	6	820	6	950
7	920	7	941	7	942	7	888	7	834	7	963
8	932	8	953	8	954	8	899	8	846	8	975
9	943	9	964	9	965	9	908	9	858	9	986

Fluid 5		Fluid 2		Fluid 1		Fluid 3		Fluid 4		Fluid 6	
% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)
10	953	10	974	10	976	10	917	10	869	10	995
11	962	11	984	11	985	11	925	11	879	11	1005
12	970	12	993	12	994	12	932	12	889	12	1013
13	978	13	1001	13	1003	13	939	13	897	13	1022
14	985	14	1009	14	1011	14	946	14	906	14	1030
15	992	15	1017	15	1019	15	952	15	914	15	1037
16	998	16	1024	16	1027	16	959	16	922	16	1044
17	1005	17	1032	17	1034	17	965	17	930	17	1051
18	1011	18	1038	18	1041	18	971	18	937	18	1057
19	1017	19	1045	19	1047	19	976	19	944	19	1063
20	1023	20	1051	20	1054	20	982	20	951	20	1068
21	1029	21	1057	21	1060	21	987	21	958	21	1074
22	1034	22	1062	22	1065	22	992	22	965	22	1080
23	1039	23	1068	23	1071	23	997	23	971	23	1085
24	1044	24	1073	24	1077	24	1002	24	978	24	1090
25	1049	25	1078	25	1083	25	1008	25	984	25	1095
26	1054	26	1083	26	1088	26	1013	26	990	26	1100
27	1059	27	1088	27	1094	27	1018	27	997	27	1105
28	1063	28	1093	28	1099	28	1023	28	1003	28	1109
29	1068	29	1098	29	1104	29	1028	29	1009	29	1114
30	1072	30	1103	30	1110	30	1034	30	1016	30	1119
31	1077	31	1107	31	1115	31	1039	31	1022	31	1124
32	1081	32	1112	32	1121	32	1043	32	1029	32	1129
33	1085	33	1117	33	1126	33	1048	33	1036	33	1133
34	1090	34	1122	34	1132	34	1053	34	1042	34	1138
35	1094	35	1127	35	1137	35	1058	35	1048	35	1143
36	1098	36	1131	36	1143	36	1062	36	1054	36	1147
37	1102	37	1136	37	1149	37	1067	37	1061	37	1152
38	1106	38	1141	38	1154	38	1072	38	1067	38	1157
39	1110	39	1146	39	1160	39	1077	39	1073	39	1161
40	1115	40	1150	40	1165	40	1081	40	1079	40	1166
41	1119	41	1155	41	1171	41	1086	41	1085	41	1170
42	1123	42	1160	42	1176	42	1091	42	1092	42	1175
43	1127	43	1165	43	1182	43	1095	43	1098	43	1179
44	1132	44	1169	44	1188	44	1100	44	1104	44	1184
45	1136	45	1174	45	1194	45	1105	45	1110	45	1189
46	1140	46	1179	46	1199	46	1110	46	1117	46	1193
47	1144	47	1184	47	1205	47	1115	47	1123	47	1198
48	1149	48	1189	48	1211	48	1120	48	1130	48	1203
49	1153	49	1194	49	1216	49	1125	49	1136	49	1207
50	1157	50	1199	50	1223	50	1130	50	1143	50	1212
51	1162	51	1204	51	1230	51	1135	51	1150	51	1216
52	1166	52	1209	52	1237	52	1140	52	1157	52	1221
53	1170	53	1214	53	1243	53	1146	53	1163	53	1227

Fluid 5		Fluid 2		Fluid 1		Fluid 3		Fluid 4		Fluid 6	
% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)	% off	bp(F)
54	1174	54	1219	54	1250	54	1151	54	1170	54	1232
55	1179	55	1225	55	1258	55	1157	55	1176	55	1238
56	1183	56	1232	56	1265	56	1162	56	1183	56	1243
57	1188	57	1238	57	1272	57	1168	57	1190	57	1247
58	1193	58	1244	58	1278	58	1173	58	1197	58	1254
59	1197	59	1250	59	1284	59	1179	59	1204	59	1259
60	1202	60	1257	60	1292	60	1184	60	1210	60	1265
61	1207	61	1263	61	1298	61	1190	61	1216	61	1270
62	1211	62	1270	62	1305	62	1196	62	1224	62	1275
63	1215	63	1276	63	1313	63	1202	63	1232	63	1280
64	1221	64	1282	64	1320	64	1208	64	1240	64	1284
65	1226	65	1288	65	1328	65	1214	65	1247	65	1290
66	1232	66	1295	66	1334	66	1220	66	1256	66	1295
67	1238	67	1301	67	1341	67	1227	67	1264	67	1300
68	1243	68	1308	68	1348	68	1234	68	1272	68	1305
69	1249	69	1316	68.8	1355	69	1241	69	1279	69	1310
70	1255	70	1323			70	1248	70	1286	70	1316
71	1261	71	1330			71	1256	71	1294	71	1322
72	1267	72	1337			72	1264	72	1301	72	1327
73	1273	73	1344			73	1271	73	1309	73	1332
74	1278	74	1351			74	1278	74	1317	74	1337
75	1283	74.4	1355			75	1284	75	1325	75	1342
76	1290					76	1292	76	1333	76	1347
77	1296					77	1299	77	1340	77	1352
78	1301					78	1307	78	1347	77.5	1355
79	1307					79	1315	78.9	1355		
80	1314					80	1324				
81	1321					81	1332				
82	1327					82	1339				
83	1333					83	1347				
84	1339					83.8	1355				
85	1345										
86	1352										
86.5	1355										

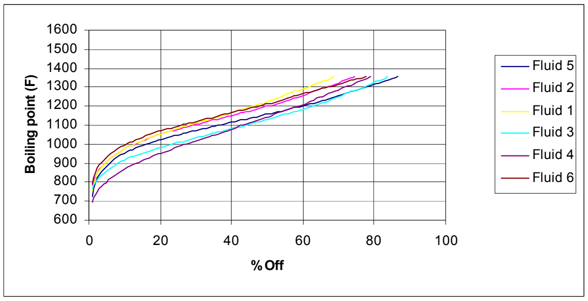


Figure 9 – Boiling Point Distribution Plot for Feedstocks from HTGC (Fluid 3's Data)

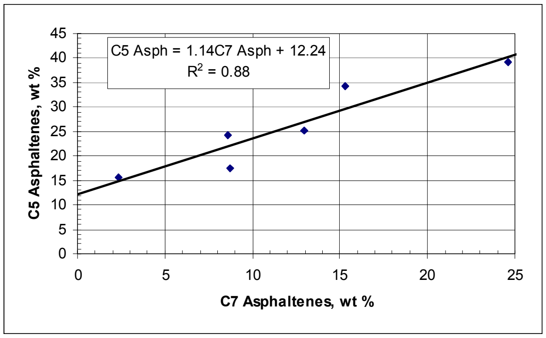


Figure 11 - Comparison of C7 Asphaltene Values Measured by Fluid 3 to C5 Asphaltene Values Measured by Baker-Petrolite

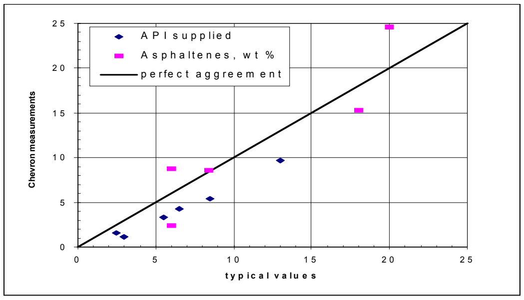


Figure 10 - Comparison of API & C7 Asphaltene Values Measured by Fluid 3 to those Originally Supplied by the Companies as Typical Values

The results are in good agreement with the values expected. For example, the measured API and heptane asphaltene numbers are graphed versus the typical values originally supplied by the companies, see Figure 9. The heptane asphaltene numbers from Fluid 3 are graphed with the pentane numbers from Baker-Petrolite in Figure 10. The pentane numbers are 12% higher.

HTGC results for the Fluid 5 resid were also run at Phillips. The results are shown in Table 8 as boiling point distribution data and in Table 9 as cut point data. These data are plotted in Figure 11 and Figure 12.

Table 8 - Boiling Point Distribution Data for Fluid 5 Resid (from HTGC)

Test #1		Test #2	
% off	bp(F)	% off	bp(F)
IBP	644.7	IBP	646.2
5	909.7	5	913.0
10	974.2	10	976.7
15	1012.5	15	1014.8
20	1042.9	20	1045.0
25	1066.7	25	1068.7
30	1088.3	30	1090.2
35	1107.7	35	1109.6
40	1126.6	40	1128.5
45	1144.7	45	1146.7
50	1162.5	50	1164.5
55	1179.3	55	1181.6
60	1197.2	60	1199.7
65	1214.4	65	1217.4
70	1236.7	70	1240.3
75	1259.8	75	1263.7
80	1281.4	80	1285.2
85	1303.3	85	1306.7
90	1327.3		

Table 9 - Cut Point Data for Fluid 5 Resid (from HTGC)

Test #1			**Test #2**		
Start (F)	End (F)	% off	Start (F)	End (F)	% off
0	650	0.56	0	650	0.65
650	1000	12.34	650	1000	12.65
1000	1100	19.61	1000	1100	19.78
1100	1200	27.64	1100	1200	27.87
1200	1327.9	29.32	1200	1327.9	29.3
Total % off		89.47	Total % off		90.25

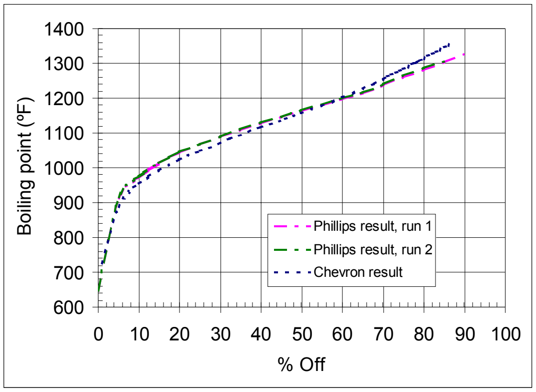


Figure 12 - Boiling Point Distribution Plot for Fluid 5 Resid (from HTGC)

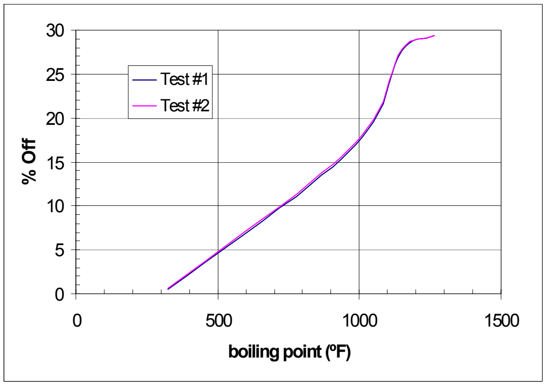


Figure 13 - Cut Point Plot for Fluid 5 Resid from HTGC (Phillips Results)

8. Facility Proving

A. CONFIRMATION OF OPERABILITY AND PROCEDURES

1. Micro-Coker

A series of shakedown tests were conducted using the Hondo and Midway Sunset feeds (provided by the Department of Energy). All of the shakedown tests were conducted at 930 °F reactor temperature and 6 psig pressure, with a feed rate of approximately 2 g/min. The shakedown tests resulted in several modifications to the equipment and procedures. Seven of these tests were successful enough for mass balance calculations, and showed good material balance closure. These runs familiarized the operator with the equipment and procedures.

2. Pilot Coker

Shakedown tests for the pilot unit began with a 90-weight oil. This test showed a small leak between the furnace pre-heater coil and the coke drum; otherwise the unit operated as designed. The second through fourth tests used the Fluid 1 feedstock. For the second and fourth test we made coke and liquid product; for the third we plugged the system early in the run. These runs showed that it was not possible to run the system at the low pressure of 6 psig (chosen for comparison to the micro-coker). Also plugging of the preheater tube coil with this high asphaltenic feed occurred.

All coke produced using the Fluid 1 resid in these early runs made shot coke. Visual evidence of the solid plugs that were removed from the overhead line indicate that foaming is going on in the coke drum. The Fluid 1 feed in the pilot-coker feed tank formed a crust due to a reaction with the oxygen. The feed tank was modified such that a nitrogen blanket is on the feed and an antifoaming agent was mixed with the feed.

3. Stirred-Batch Coker

Six shakedown tests were conducted with Fluid 5 and Fluid 6 resids. Several problems were identified in the first shakedown test that helped in modifying the system. Those problems are listed below with the modification made to improve the test.

Problems identified:

1. The flex hoses leaked when gas started to flow.
2. Water was vaporizing in the cooler.
3. Chiller was not able to provide cold water to the cooler.

Modification:

1. The flex hoses were replaced with stainless steel tubes.
2. A Gas-liquid separator was built, and installed for a first stage cooling.
3. Steam is used for first stage cooling to reduce the gas flowing to the cooler.

After modifying the system, no problems were observed other than some leaks at the tube fittings. One of the major leaks was observed at the top of one of the gas-liquid separators. The fitting was welded to the tank and this leak disappeared. After fixing this leak an increase of 2-4 psi in the back-pressure regulator was noticed. The back-pressure regulator is manipulated manually to reduce the pressure to the desired pressure.

B. VERIFICATION OF TEST PROCEDURES

1. Micro-Coker

After the shakedown tests, four benchmark tests were conducted using the Fluid 1 and Fluid 6 feeds. These runs were conducted at 930 °F and 6 psig, with a feed rate of approximately 2 g/min. These test showed excellent reproducibility of gas, liquid and coke yields as well as excellent material balance closure (see Table 10).

Table 10 - Summary of Micro-Coker Results

				Charge	Coke	Liquid	Gas*	Recovery
Feed	Test #	Date	Type	(g)	(g)	(g)	(g)	%
Fluid 1	#1MR-1-BT	9/9/99	Benchmark	132.4	45.5	70.1	17.9	100.9%
					34%	53%	14%	
Fluid 1	#1MR -2-BT	9/14/99	Benchmark	136.5	49.3	69.8	19.0	101.2%
					36%	51%	14%	
Fluid 1	#1MR -3-BT	9/16/99	Benchmark	140.0	48.7	72.4	19.6	100.5%
					35%	52%	14%	
Fluid 6	#6MR -1-BT	9/22/99	Benchmark	147.4	41.2	84.5	16.8	96.7%
					28%	57%	11%	

2. Pilot Coker

Following the shakedown tests, the feed was changed to the Fluid 5 resid (since this is the lest asphaltenic feedstock and therefore the least likely to plug the lines) and the pressure increased to 40 psig (closer to industrial coker operation – and achievable with the modified micro-coker). Benchmark tests with the Fluid 5 resid were conducted during the fourth quarter of 1999. These test were successful, and are summarized in Table 11. The first run was a successful shakedown run; the next 3 runs were the benchmark runs.

These benchmark tests (conducted at 930 °F and 40 psig) showed consistent gas, liquid and coke yields as well as good material balance closure. These yields were also compared with a correlation from Gary & Handwerk using the carbon residue value supplied by Fluid 5 participation, and the experimental values were found to bracket the correlation values.

Table 11 - Fluid 5 Pilot-Coker Results Summary

	T	P	coil	Charge	Coke		Liquid		Gas Meas.		Gas calc*		Recovery
Test #	ºF	psig	ft	(g)	(g)	%	(g)	%	(g)	%	(g)		(g)
#5PU-8-PT1	930	15	20	2,594	470	18%	1,944	75%	282	11%	180	7%	104%

	T	P	coil	Charge	Coke		Liquid		Gas Meas.		Gas calc*		Recovery
Test #	ºF	psig	ft	(g)	(g)	%	(g)	%	(g)	%	(g)		(g)
#5PU-9-BT1	930	40	20	5,840	1,440	25%	3,650	63%	450	8%	750	13%	95%
#5PU-10-BT2	930	40	20	6,020	1,680	28%	3,581	59%	399	7%	759	13%	94%
#5PU -11-BT3	930	40	20	5,940	1,725	29%	3,650	61%	272	5%	565	10%	95%

3. Stirred-Batch Coker

Benchmark tests for the stirred-batch coker were conducted using the fluids and fluids resids. Table 12 contains the condition and results of the three-benchmark tests. The maximum temperature or the ending temperature was 930 °F, which was not recorded because the sensors were insulated with coke and the exact liquid temperature was not displayed. Although there was a thermocouple in the vapor phase, the vapor phase temperature was always less than that of liquid phase, which could not be substituted for the true liquid temperature. The skin temperature and a fixed power output of the band heater were used to control the tests. Excellent agreement between the two Fluid 5 benchmark runs can be seen.

Table 12 - Stirred Batch Reactor Conditions & Results for the Benchmark Tests

Run ID	Date	T (°F)*	P (psig)	RPM	Feed (g)	Coke %	Liquid %	Gas %	Recovery
#5BR-3-BT	6/9/00	930	40	1200	3652.6	24.2	65.5	9.2	99.0
#5BR-4-BT	6/14/00	930	40	1200	3738.0	24.2	65.5	8.8	98.6
#6BR-6-BT	7/10/00	930	40	1200	3511.0	29.6	59.7	10.0	99.3

* 930 °F was not seen by the thermocouple placed inside the reactor. Rather, this temperature was estimated using the outside skin temperature.

C. ANALYTICAL ANALYSES

1. On-line GC

In 1999 much effort was involved on Laura Young's and Applied Automation personnel's part to get both this hardware and the associated software working properly. Hardware problems included: thermal conductivity detector (TCD) failure, control board failure, replacement of GC columns, and wet house air spraying on the control valves in the oven. There are two TCDs; the beads and thermistors on both had to be replaced. Software problems included the graphics on the main computer screen being garbled and difficulty accessing some of the Applied Automation utilities.

After much persistence and effort, the unit was calibrated and brought on line. Three calibration gas samples were ordered and received. The pure hydrogen sulfide and the hydrogen sulfide-free samples are more stable and less expensive and are used weekly. The smaller more expensive hydrogen sulfide-containing sample is used monthly.

Three new issues arose during the third quarter of 1999 that were resolved as discussed below. These issues were: splitting between the methane and nitrogen peaks; obtaining a composition sum of 100%; and pressure regulation to the GC. The previous set-up did not correctly split between the methane and nitrogen peaks, resulting in a negative mole percentage of nitrogen for some analyses. This was resolved with the help of Rick Campbell of Applied Automation. Secondly, the on-line GC uses a fixed-volume of sample. So if the inlet pressure is fixed, the sample moles are fixed. However, the calibration gas and the gas from the micro-coker were being delivered at different pressures and thus, for the micro-coker samples, the mole fraction summation was less than 100%. This was resolved by closing down on the needle valve when feeding the calibration gas so the flow rate measured by the rotameter matched the flow for the micro-coker sample. Unfortunately, the rotameter measurement of micro-coker sample flow was at the bottom of the rotameter range; so a new rotameter with a smaller range was installed. This need for a low flow to the GC, in order to consistently get the same small number of moles in the sample chamber, led to the third issue. The original piping between the GC and micro-coker had all the gas going through the GC and thus through this needle valve. However, for the first low-residence-time micro-coker run this restriction pressurized the experimental apparatus. The micro-coker gas piping was modified to bypass excess gas to the scrubber and maintain the pressure at the GC inlet at 4 psig.

Before the end of 1999, with the experience gained, it became possible to establish an appropriate calibration flow rate so all micro-coker and pilot-coker runs could be accomplished without re-calibrating the on-line gas chromatograph.

2. SimDis (HP 5880A)

Simulated distillation analyses using the HP 5880A were repeated on several occasions to confirm the results.

To check for possible losses of light ends, simulated distillation was repeated for each old liquid sample in storage. The results indicated that all of the micro-coker liquid samples had nearly identical SimDis results, while 10 out of 50 pilot unit runs that were retested should differences exceeding 5%. Pilot unit samples were rerun again in 2002. These results, showed that, for some of the runs (about two thirds) the results were very similar and for others the amount of gasoline decreased dramatically with a corresponding rise in both diesel and more so in gas oil. At this point the cause of the variation is unknown. Although some light-end losses may occur over time, especially if the samples are not properly sealed and refrigerated, the changes in composition were too large to be accounted for by light end losses. These results prompted us to rerun all SimDis samples. We concluded that the errors were due to some systematic problems with the HP 5880A over several weeks of operation in 2001.

3. HTGC, PFPD & DHA (HP6890)

An HP6890 a high temperature gas chromatograph, manufactured by Agilent Technologies (division of Hewlett-Packard), was purchased by the JIP in 2001. There initially were some sulfur detection problems. At the October, 2001 advisory board meeting, measurement of sulfur in the liquid cuts was an unresolved issue. Baker-Petrolite measures the sulfur in the total liquid samples by x-ray florescence (XRF). For 20 pilot-coker and 10 micro-coker liquid samples the sulfur content was measured by

Phillips Petroleum using the Carlo Ebra combustion method. TU measures the sulfur in the individual liquid cuts by a pulsed flame post detector (PFPD) then calculates the total by a weighted linear combination. Samples were also sent to Fluid 1 for XRF sulfur measurement of the 430-650ºF and 650ºF+ cuts.

The initial TU data showed a wide variation in the sulfur content for the different cuts (IBP-113ºF, 113-400ºF, 400-430ºF, 430-650ºF, and 650ºF+). However, after improving our analysis technique the variation became smaller. The improved measurements relate to the dilution of the samples. Calibration curves showed that the response is linear with a break at about 450 ppm sulfur and then the detector become saturated causing an inverse response past around 2% sulfur. The procedure was modified to dilute the samples so the individual peaks are less than 450 ppm sulfur. Dilutions from 8 to 3 are typical, with the higher dilution being used for the lower boiling cuts as they tend to have tall individual peeks. As a result, all the liquid samples were reanalyzed. This new data compared well with both the Baker-Petrolite total sulfur and the Fluid 1 high boiling cut data.

4. ASTM distillation

In order to do in-house distillation of liquid products to minimize the analytical costs for liquid product analysis, the JIP purchased a laboratory distillation apparatus from B/R Instruments, Inc. This equipment is a semi-automatic apparatus that will do a two-liter D-2892 distillation or a one-liter D-5236 distillation. The equipment was received in December 2000, set up in early January 2001, and underwent shakedown tests by B/R Instruments personnel and Laura Young.

D. MATERIAL BALANCE CLOSURE

1. Micro-Coker

Micro-coker material balances were modified to better account for the nitrogen in the product gases. The gas chromatograph uses nitrogen as a basis for the calibration gases; this means that when the GC is unable to obtain a sufficient volume for measurement (when gas production is low), it assumes that the missing mass consists of nitrogen. Examination of the material balance calculations for the micro-coker showed that the nitrogen calculated from the gas flow and GC measurements greatly exceeds the nitrogen which should be exiting based on the volume of nitrogen initially charged to the system. Therefore, the material balances were modified with the assumption that all the nitrogen initially present in the system comes out in the first 15 minutes and thus is included in the first GC measurement. While this is probably not exactly true, it should be a good approximation to physical reality.

In addition to these modifications, the material balances were further modified to include all the C5+ material from the gas phase as liquid phase products, to include all the low-boiling liquids (< 82 F) from the SimDis results as gas phase products, and to correct the coke and liquid yields to obtain 8 wt% volatile matter in the coke. Also, the material balances were normalized (in light of the error analysis on the micro-coker) by adjusting the gas yields to obtain 100% closure.

Out of a total of 48 micro-coker runs, the average percent closure was 101.9%, with a standard deviation of 2.9%.

2. Pilot Coker

The mass balances for the experiments conducted after the shakedown runs showed good closure. Percent recoveries range from 87% to 104%, with an average closure of 98%.

3. Stirred-Batch Coker

The material balances for the 29 tests conducted showed an average closure of 97.2 % with a standard deviation of 2.5%. The gas yields for all runs were adjusted to obtain 100 % closure.

9. Test Results

A. TEST MATRICES

Delayed coking is a process of thermal cracking of petroleum into three main products, coke, liquids, and gases. The process that is called delayed coking was developed in part with thermal cracking. Both processes produce coke, except that delayed coking takes the reactions to their final state. This is the only process in the refining process where the equipment is opened on a regular basis. Most refineries that employ the delayed coking process have a multi-drum unit. The process starts by heating the coke drum with steam. The feed is then introduced into the drum. The term delayed coking is aptly named because the intention is to delay the coking process until the fluid enters the drum, therefore delaying the coking process. Unlike the FCC unit, most of the reaction takes place in the drum instead of in the feed line. After the unit is filled to some predetermined height or weight of product, the feed is switched to a stand-by drum. The coke is then steam stripped to remove the remaining volatile material and to cool the drum uniformly. Next, the drum is quenched with liquid water. After draining the drum, the coke is removed by using high-pressure water drills. The coke is a by-product and depending on its quality is disposed of in different manners.

The feed to the coker is usually vacuum residua. However, there can be other feeds mixed with the main feed to influence the coker performance or to rid the refinery of certain feedstocks. When the residua is fed to the furnace, the temperature is raised to what is known as "coking temperature". It is at this temperature that chemical reactions take place within the residua. "From a chemical reaction viewpoint, coking can be considered as a severe thermal cracking process in which one of the end products is carbon" (Gary and Handwerk, 2001). These reactions involve cracking of the molecules to produce compounds with a lighter weight. Many different types of molecules are produced in these reactions.

The coker produces many different feedstocks for the plant. The main three products from the coker are gas, liquids, and coke. The gas is usually condensed and compressed to remove the valuable light liquids. The remaining gas is used for fuel for the plant. One of the most important streams is the coker naptha. This stream is usually upgraded and then used for gasoline blending. Sometimes this stream is split into light and heavy naptha. After the streams are hydrotreated for sulfur removal and olefin saturation, the light stream is isomerized or blended and the heavy stream is reformed. The gas oil fraction is divided into a light and heavy cut also. The light fraction is usually hydrotreated and fed to the FCC unit. The heavier fraction may be used as heavy fuel or sent to the vacuum unit (Gary and Handwerk, 2001).

There are several different operational variables that can affect the coking process. Commonly two operating parameters are controlled during the process. These are inlet temperature and operating pressure. These are the easiest and most controllable variables available. Other variables may also be used. For example, flowrate may affect the coke that is formed in the process. Other variables such as recycle or slop processing may also affect the coke.

It is commonly known that as the temperature of the inlet flow to the coke drum is increased, that the coke yield is decreased and the liquid and gas products are increased. This is due to the fact that as the temperature is raised so is the amount of cracking present in the drum. Also more of the heavy material in the feed is vaporized by raising the temperature of the feed. There is a maximum temperature that should not be exceeded due to the fact that the coke will become very hard and dense. This creates a large problem for the coke cutting process. For shot coke drums, the length of the cutting process should not take more than 2 hours for a normal drum of coke. However, if the coke is very dense, this time may be more like 5 to 10 hours. This obviously will cause a cutback in production in a normal 16 hour or 14 hour cycle unit. Another problem with temperature is when the temperature of the feed is very low. This leads to the drum being full of pitch. Pitch is unconverted feed that is costly to the unit because it contains a lot of volatile matter which would normally be recovered in the products (Woodard, 2002).

Pressure is also a well known parameter in the coking community. As pressure is increased, the coke yield also increases. This is due to the fact that less of the heavy molecules are vaporized at higher pressures. Therefore they remain in the drum to form coke. Operating pressure is not commonly a control for the coker unit. The limitation of the control of the operating pressure is the system pressure drop losses and vapor velocity in the coke drum. There is no true way on a coker to control the actual drum pressure. This pressure is controlled by the pressure loses that are incurred between the fractionator and the coke drum. The fractionator pressure is controlled which in turn sets the coke drum pressure. This is usually the set up for most cokers (Louie, Ogren, and Hamilton, 1998).

Obviously, feedstock is the most important factor in the coke, liquid, and gas properties. This is the primary source of data and analysis that is available for the refinery to predict the operation of their cokers. The most commonly used feedstock properties are asphaltene content and Conradson carbon values. There are many rules of thumb that each individual company relies upon to predict the coke properties from the feed properties. However, it is more common to have a range of values for the two properties, that if the feedstock lies within then it is considered good feed for the cokers. Depending upon what type of coke the unit is preferred to make, more properties such as metal content may be needed. Many refineries use a mix of feedstocks for the cokers, so there is some flexibility in the feed in that if one stream does not meet the specifications for the coker, then it may be mixed so that the feed will have the right properties for the unit.

The higher the asphaltene ratio and the higher the Conradson carbon percent, the higher the tendency to produce more coke. The reason for this is that the greater amount of heavy material in the feed, the more coke will be left in the drum after the process is over. Both of these measure the amount of heavy material in the feed. These two parameters are also used to predict what type of coke will form in the drum. The metal content of the coke, as well as the sulfur content, are important in that this also determines what the coke may be sold and used for. Cokes with very high sulfur content may not be suitable for fuel, and therefore may not have very much value as a product.

However, usually the coke is considered a byproduct and the liquid and gas products the important products.

Recycle is a term that is used to describe how the feed to the furnace is comprised. The actual recycle is heavy gas oil that is used to wash and quench the overhead vapors from the coke drum. This wash is used to knock out the heavier components of the coke drum products and to prevent coke from tilling the upper trays of the fractionator. Usually, the recycle rate is kept to a minimum. The higher the recycle rate, the more coke that is produced and the less liquid products are produced. Generally, it is the heavy gas oil specs that dictate the amount of heavy gas oil wash that is required (Louie, Ogren, and Hamilton, 1998). The refineries usually discuss the total throughput of the unit and not necessarily the recycle ratio. The throughput is actually the amount of furnace charge that is sent to the cokers. The throughput ratio is the ratio between the furnace charge and the fresh feed. Therefore a throughput ratio of 1.10 is actually a recycle ratio of 10%. The throughput ratio is just an easier way to discuss the recycle because of the way the recycle is setup in the refinery. Most refineries will try to have a recycle ratio of around 5% and below, just to maximize the liquid product yields.

The recycle ratio can be important to the coke in that the amount of lighter material introduced to the feed through the recycle can affect the type of coke formed in the drum. Jansen (1984) says that recycle is the most important operating variable that affects coke yield and also increases the operating costs and capital investment. It is known to make a harder, denser coke to add more recycle to the feed. The effects on the coke due to the recycle ratio are hard to document, however there is an effect. It is important to note the discussion in further sections about how the recycle added to the feed in the pilot unit affected the coke.

As with any pilot study, a great deal of thought goes into trying to relate the information to the full scale issues. "In the use of a pilot delayed coker, it is essential to develop knowledge on the precision of the unit and to know how the coker operation compares to commercial practice," (Hardin and Ellis, 1991, pg. 611). In this paper it discusses that a pilot coker that is producing precise, repeatable, data can be related to a commercial unit. The data presented may not be exactly what would be represented for a commercial unit, but it may be correlated to compare. This is extremely important because without some comparison to the commercial unit, the pilot coker data would be useless. Therefore, it is necessary not only to analyze the data for precision, but also for its ability to be related to the commercial data.

There are many safety concerns with regards to delayed cokers. Over the years there have been several improvements and also several major disasters. One of the main concerns is with the removal of the coke, but that is just one of the safety issues. Operating a commercial coker is a very labor intensive process and includes many opportunities for a disaster. It is the intent of this research to look at ways that operation of the unit may be improved so that these types of accidents may be minimized. As mentioned previously, the coker is unique in that it is a process that is intentionally, routinely opened to the atmosphere and exposed to operators.

A major accident can occur during the removal of the coke from the coke drum. A drum fallout is when the coke drum is deheaded and the coke simply falls out of the drum. This allows for the operator loading the coke to be buried in the resulting coke pile.

This is an increasingly looked at problem due to more cokers producing shot coke, which is more likely to fallout. Sometimes this type of accident is merely just a delay in the process, but it does have the possibility to become a very severe accident. Predicting coke that may have the tendency to produce these fallouts would be an important tool for industry. Adding resins to the feed may indeed reduce the tendency for cave ins (Malik, 2001).

Another safety issue during the coke removal is when the drum has a “hot-spot”. There are different severities of these hot spots. Some are nothing more than a spot in the coke that when the water cutting spray contacts the spot that a small pocket of vapor is released and potentially the coke may fall out at a higher rate than expected. However, these hot spots can cause a tremendously dangerous situation. If the hot spot causes a violent enough expansion, coke may erupt from the top of the drum. This is very dangerous for the operators cutting the coke. It is also very dangerous for any personnel near the unit due to large pieces of coke falling in the vicinity. Another potentially dangerous aspect of an eruption is the gases released may contain poisons, which may be inhaled by the operators. Improvements have been made in this area by physically protecting the personnel, but no true changes have been made to the process to improve with this potentially dangerous situation. Several operational things need to be examined, such as drain time, porosity, and permeability of the drum. Drums with a higher density and lower Hargrove Grindability Index have a greater possibility of producing these eruptions (Malik, 2001).

Safety is a major concern for any industrial operation. However, with eighteen workers killed in coker accidents from 1992-2000, it is a very important aspect of any coker unit (Malik, 2001). It is important to understand how to mechanically prevent accidents, but it is also important to look at what chemically may be causing some of these problems.

Keeping these variables in mind, the test matix shown in Figure 14 was developed to study the delayed coking process and grasp and better understands of these effects. This data would also be used to develop two types of models. The micro-coker data was used to develop a screening tool while the data from the pilot unit would be used to develop a more detailed predictive model because of the extensive experimental efforts conducted.

The kinetics of the coking reactions is important to know for several reasons. Feed is heated rapidly in the coker furnace, then fed to the coke drum where the majority of the reactions take place, hence the term “delayed coking”. It is important that the feed enter the drum at a sufficiently high temperature for the desired reactions to occur. However, the residence time in the furnace must be short enough that coking in the furnace is minimized, to prevent coking off of the furnace tubes. It is known that some cracking reactions take place in the furnace, resulting in production of vapor. The amount of this vapor production is currently very hard to predict, but has an important effect on the hydrodynamics of the drum due to it strong effect on fluid velocity entering the drum. This hydrodynamic effect can have a strong influence on coke morphology, e.g. shot coke formation can result from high vapor velocity with a very reactive feed. The kinetics of the coking reactions within the drum as a function of temperature and pressure are also important to know. High-boiling liquid material in the drum is cracked to form vapors. If this material overcracks, the result is excessive gas and coke production and a reduction in liquid recoveries. On the other hand, if the feed does not crack at a sufficient kinetic rate, the result will be coke with a high volatile matter; this reduces the recovery of valuable liquid products and produces coke of poor quality. The batch reactor test matrix (Figure 15) was developed to study the kinetics of the coking reaction as a function of heating rate and pressure for the various feedstocks.

Figure 14 - Pilot Unit & Micro Reactor Test Conducted

PILOT UNIT & MICRO REACTOR TEST CONDUCTED

	6 PSIG					15 PSIG				40 PSIG				50 PSIG			
Type of Test	890	900	910	930	950	900	910	930	950	900	910	930	950	900	910	930	950
Fluid 1																	
1. Micro Reactor			3	5	3			1				1					
2. Pilot Unit																	
• P&F-3/8" coil				3													
• P&F-1/4" coil						1		1	2	1		2	1				
• Slurry Oil						1				1			1				
• Foaming								3									1
• Fouling																	
Fluid 5																	
1. Micro Reactor				1		3		5	3			3					
2. Pilot Unit																	
• P&F-3/8" coil						2		3		6		8	3				
• P&F-1/4" coil						1		1	1	1		2	1				
• Recycle												2					
• Foaming																	
• Fouling																	
Fluid 6																	
1. Micro Reactor				1				1				1					
2. Pilot Unit																	
• P&F-3/8" coil						1		5		2		2					
• P&F-1/4" coil						1		1	1	2		2	1				
• Foaming																	
• Fouling																	
Fluid 3																	
1. Micro Reactor								1									
2. Pilot Unit																	
• P&F-3/8" coil						3		3		2		3					
• P&F-1/4" coil						1		1	1	1		2	1				
• Foaming						2		2		2		1					
• Fouling																	
Fluid 2																	
1. Micro Reactor								1									
2. Pilot Unit																	
• P&F-3/8" c	2					2		4	1	4		9					
• P&F-1/4" coil						1		1	1	2		2	1				
• Foaming						2		4		1		1					
• Fouling												17					
Fluid 4																	
1. Micro Reactor		3		7				3				1					
2. Pilot Unit																	
• P&F-3/8" coil																	
• P&F-1/4" coil						1		1	1	1		2	1				
• Recycle												2					
• Foaming				?		1		6		1		1					
• Fouling																	
Total	2	3	3	17	3	23	0	48	11	27	0	64	10	0	0	0	1

Figure 15 - Batch Reactor Test Conducted

BATCH REACTOR TESTS CONDUCTED

	15 PSIG			30 PSIG			40 PSIG			
Resid	Low	Medium	High	Low	Medium	High	Low	Medium	High	# Runs
Fluid 1	1						3	4		8
Fluid 5	1				1		1	9	1	13
Fluid 6							4	3		7
Fluid 3								3		3
Fluid 2								1		1
Fluid 4		1					1	3		5
Total	2	1	0	0	1	0	9	23	1	37

B. CONFIRMATION OF KNOWN EFFECTS

1. Effect of temperature and pressure on yields

Results from the micro-coker, pilot coker, and stirred-batch coker all confirm the expected trends of temperature and pressure on gas and liquid yields and liquid product distributions. As temperature in the coke drum is increased or pressure is decreased, more heavy gas oil material vaporizes and leaves the drum, whereas at lower temperature or higher pressure the heavy gas oils remain in the drum where they crack, producing more gases. Thus, there is an increase in liquid yields at lower temperatures and at higher pressures, and an increase in the gas oil subfraction at lower temperatures and at higher pressures. This trend was confirmed by our experimental data, as shown in
to Figure 18.

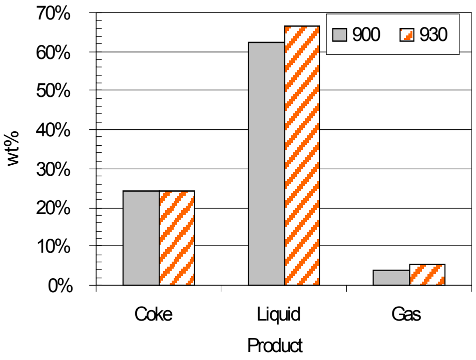


Figure 16 - Temperature Effect on Product Yields for Fluid 3 Resids at Medium Residence Time in the Pilot-Coker

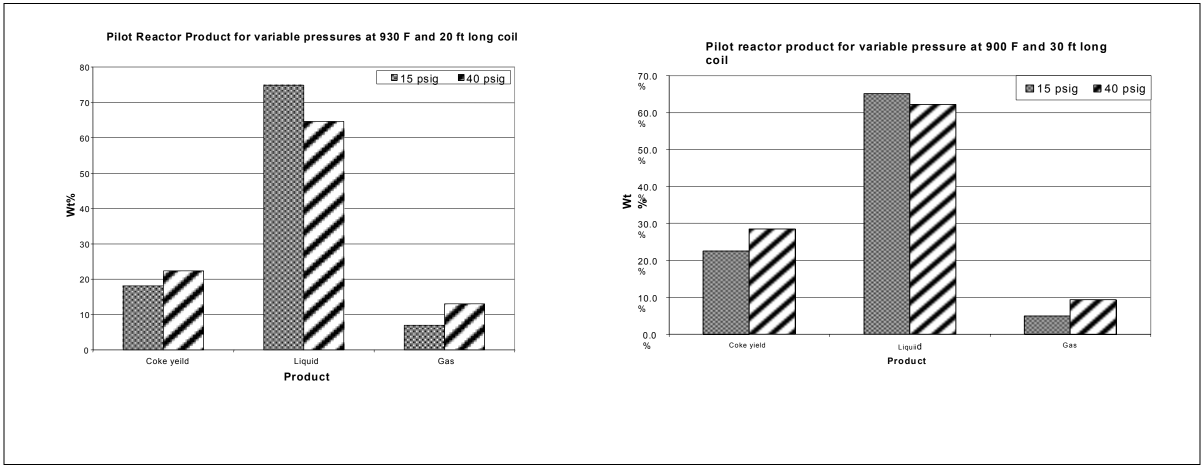


Figure 17 - Pressure Effect on Product Yields for Fluid 5 Resids at Medium and High Residence Time in the Pilot-Coker

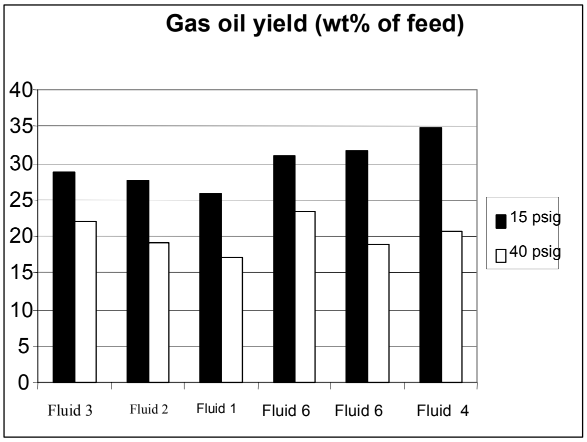


Figure 18 - Average Gas Oil Yields from Pilot Unit (as wt% of feed) vs. Pressure

2. Effect of MCR on coke yields

Higher microcarbon residue (MCR) feeds are expected to produce more coke, as the MCR test is an experimental measurement of the coking tendency of the feed. This trend was indeed observed, although the relationship between MCR and coke formation from delayed coking is not a simple direct relationship. Figure 19 illustrates the observed trend.

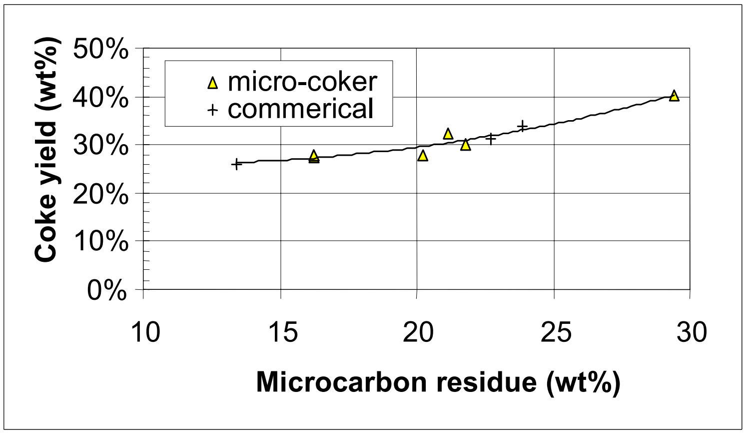


Figure 19 - Coke Yield vs. Micro Carbon Residue of Feedstock (commercial + micro-coker data)

3. Shot coke formation

Shot coke formation is a hydrodynamic phenomenon that is thought to occur when feed material enters the drum at high velocity, and the coking reaction occurs while resid droplets are still in a suspended state. Previous researchers have had difficulty duplicating shot coke formation on a pilot scale due to its high sensitivity to the hydrodynamics of the system. Our pilot unit studies were conducted at high enough feed velocities that the feedstocks that were expected to produce shot coke (Fluid #1, Fluid #2, and Fluid #3), based on refinery experience and asphaltene content, did indeed produce shot coke in the pilot unit.

4. Foaming

Foaming studies conducted in the pilot unit have confirmed the effect of antifoam in reducing foam height. These studies have also confirmed that foaming is more severe in under conditions of lower pressure and lower temperature. Lower pressure increases vapor velocity in the drum, resulting in more foam formation. Although higher temperature will also increase vapor velocity, this effect is more than offset by the reduction of liquid surface tension and viscosity, which aid in foam drainage and thus decrease foam height.

5. Fouling

Seventeen fouling tests were run with the pilot unit. Two different application techniques were used for the anti-coking agent; one where the coil was pre-treated and one where it was only added to the feed. The pre-treating agent passivated the metal surface inhibiting the lay down of coke precursors. This pre-treatment resulted in energy savings due to quicker warm-up as well as from only having to apply a 5^oF delta T rather than 10^oF for the test where the coil wasn't pre-treated. The additives also improved the heat transfer to the fluid and where the resistance to energy transfer analogy could be applied resulted in less fouling. An increase in temperature by as much as 20^oF was observed when a combination of anti-coking agent was used with a stabilizer. There were no distinguishable differences observed in the coke morphology produced from run to run. The coke morphology was described as a very small tightly aggregated shot. No BB shot was observed. The coke generated in the fouling studies was nearly identical to that described from the pilot unit runs that were called transitional.

Analysis of the coil fouling data from the parametric and feedstock tests run with the 3/8 inch coil and the ¼ inch coil indicated that more fouling occurred at higher temperatures and at lower velocities (larger coil).

6. Antifoam partitioning

Silicon-containing antifoamants are broken under the higher temperatures and long residence time conditions in the coke drum. Much of the silicon from these antifoamants ends up in the coke, but a measurable amount ends up in the hydrocarbon liquids and in the decant water. We were not able to do a material balance on this silicon, because the silicon content of the anitfoamant is proprietary information. We did, however, measure the silicon content of the hydrocarbon liquids and decant water. Data are shown below in Table 13. These results confirm that the silicon partitions largely to the hydrocarbon liquids rather than to the water.

Table 13 – Partitioning of Silicon between Water and Hydrocarbon Liquid

Run ID	g Si in water/g Si in hydrocarbon liquid
#3PU - 11	0.128
#3PU - 12	0.082
#3PU - 13	0.246
#3PU - 14	0.093
#5PU - 22	0.122
#5PU - 23	0.137
#5PU - 24	0.122
#5PU - 25	0.107
#5PU - 26	0.181
#5PU - 27	0.109
#5PU - 28	0.121
#6PU - 8	0.126
#6PU - 10	0.139
#6PU - 9	0.166
#6PU - 12	0.159
#6PU - 13	0.121

10. Discussion of Results

A. MICRO-COKER

1. Residence time effect

Figure 20 shows the effect of residence time on product yields in the micro-coker. It should be emphasized that residence time for the micro-coker does not have the same meaning as residence time in the pilot unit, since the feed never reaches coking temperature in the preheater even at the lowest residence time used. Rather, "residence time" here is really a measure of the feed rate to the coker, with a high residence time corresponding to a low feed rate. As can be seen from these figures, increasing residence time results in decreasing liquid yields and increasing gas yields; this is due to overcracking of the liquid product at the high reactor temperatures.

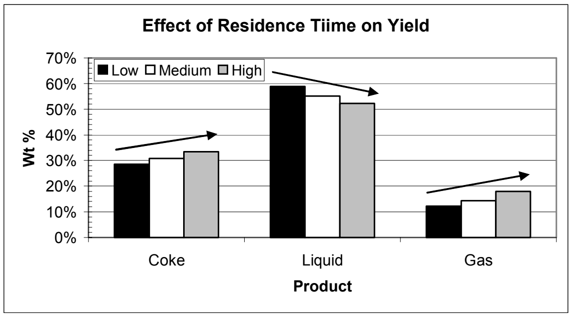


Figure 20 - Residence Time Effect on Product Yields.

2. Feedstock effect

The product yields for each feedstock, at 930 F, 15 psig and medium residence time, are shown in Figure 21. It can be seen that the highest liquid yields are obtained with the lowest API resid. Coke and gas yields approximately follow the reverse order from liquid yields.

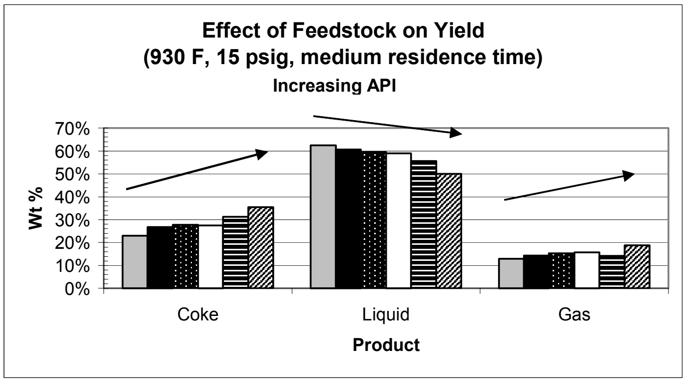


Figure 21 - Feedstock Effect on Product Yields at 930 F, 15 psig, Medium Residence Time in the Micro-Coker

The effect of feedstock on yield can also be shown as a function of feedstock API. For 930ºF, medium residence time at both 6 and 15 psig are shown in Figure 22 and Figure 23. As the feed API increases, the liquid yield increases and both the coke and gas yields decrease.

Similar graphs can be constructed as a function of feedstock micro-carbon residue. For 930ºF, medium residence time at both 6 and 15 psig are shown in Figure 24 and Figure 25. As the feed MCR increases, the liquid yield decreases and both the coke and gas yields increase.

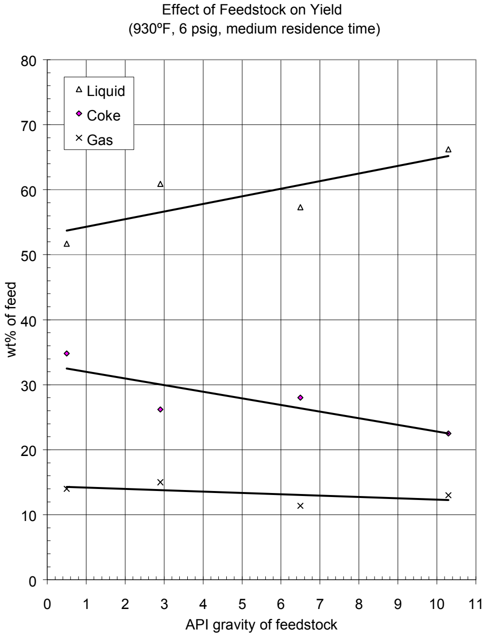


Figure 22 - API gravity effect on product yields at 930ºF, 6 psig and medium residence time for the micro-coker

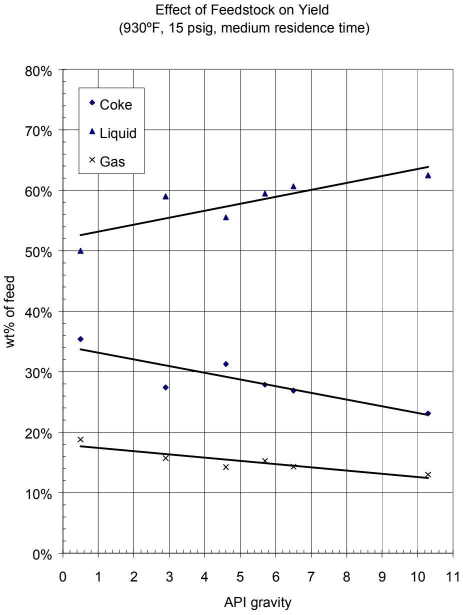
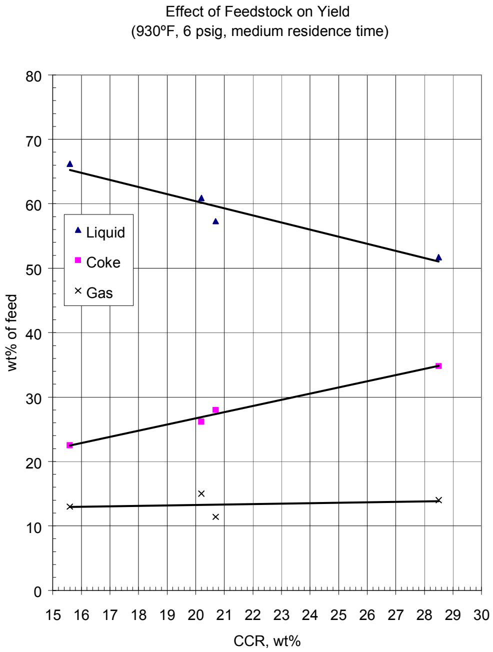


Figure 23 - API gravity effect on product yields at 930ºF, 15 psig and medium residence time for the micro-coker



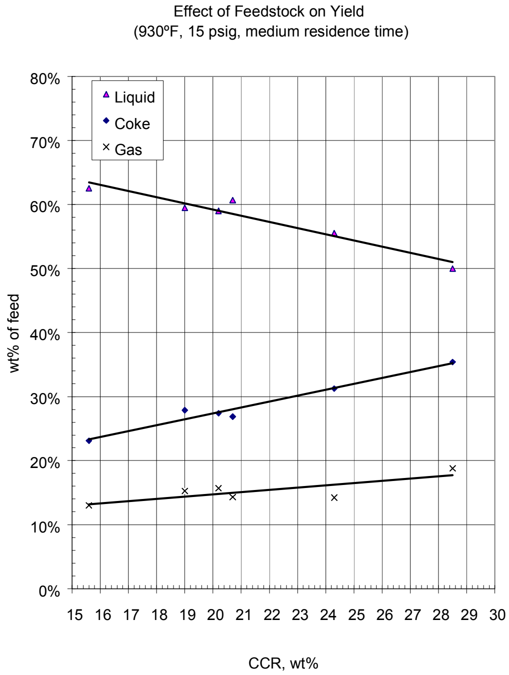


Figure 24 - Micro-Carbon Residue Effect on Product Yields at 930ºF, 6 psig and Medium Residence Time for the Micro-Coker

Figure 25 - Micro-Carbon Residue Effect on Product Yields at 930ºF, 15 psig and Medium Residence Time for the Micro-Coker

3. Liquid product distribution

Pressure seems to have the strongest effect on liquid product distribution in the micro-coker. At higher pressures, more gasoline is made and less gas oil.

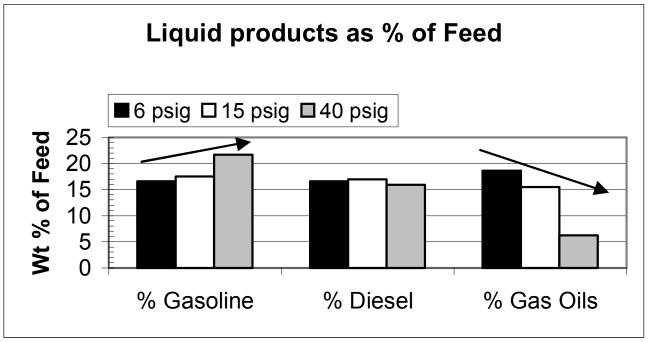


Figure 26 - Gasoline, Diesel and Gas Oils as Percentage of Feed vs. Pressure.

4. Gas analysis

For the micro-coker it was observed that toward the end of the run (i.e., after the feed is complete) the gas composition changes. In particular, the production of hydrogen tends to increase and the production of methane decreases (see Figure 27).

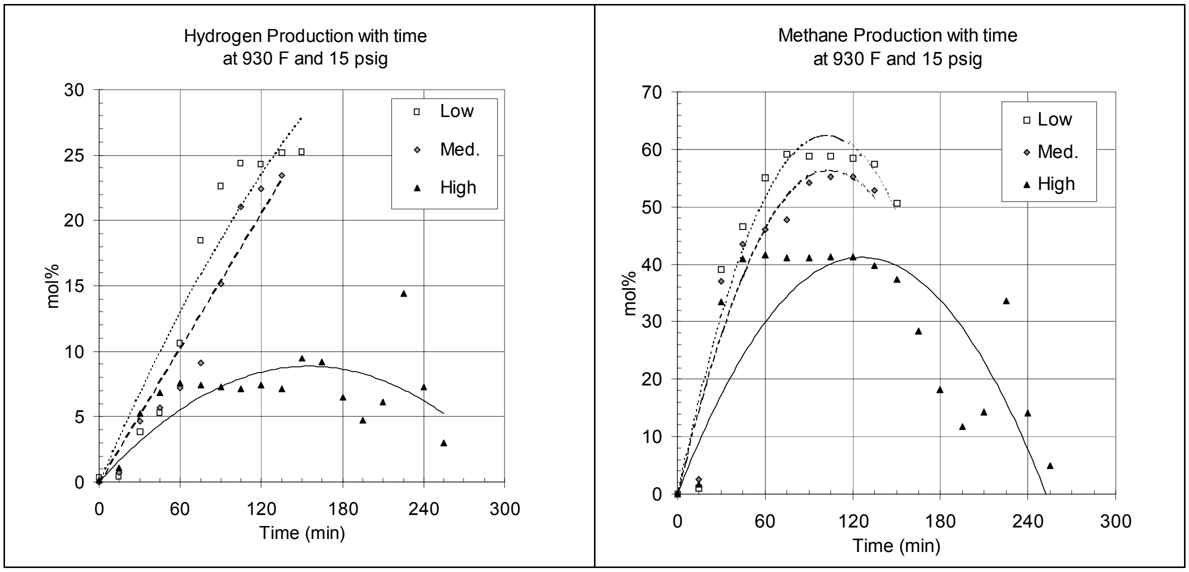


Figure 27 - Micro-Coker Hydrogen and Methane Production as a Function of Residence Time Versus Run Time for Fluid 5 Feed at 903 °F & 15 psig

B. BATCH REACTOR

1. Overall Material Balances Closure and Normalization

The material balances for the tests conducted are shown in Table 14. The gas yields were adjusted to obtain 100 % closure. Test #6-12 had a very high liquid yield and when normalized results in a very low gas yield. Test #6BR-13 and Test #5BR-14 had gas leaks and the liquids were collected using the old collection procedure that had venting and spillage problems. Subsequently, the normalization of these runs gave higher gas yields than other comparable runs.

Table 14 - Stirred-batch reactor test conditions

Run ID	Date	Heater Output	P (psig)	RPM	Comments
#5BR-3-BT	06/09/00	Medium	40	1200	
#5BR-4-BT	06/14/00	Medium	40	1200	
#6BR-6-BT	07/10/00	Medium	40	1200	
#5BR-7-SD	08/21/00	Medium	40	1200	No gas flow
#5BR-8-SD	08/28/00	Medium	40	1200	
#5BR-9-SD	09/27/00	Medium	40	1200	
#6BR-10-SD	09/29/00	Low	40	0	
#6BR-11-SD	10/31/00	Low	40	2400	Gas leak
#6BR-12-SD	11/18/00	Low	40	2400	Nitrogen flow and high stirring rate
#6BR-13-PM	12/07/00	Low	40	1200	Gas leak
#5BR-14-PM	12/18/00	Low	40	1200	Gas leak
#2BR-15-PM	01/09/01	Low	40	1200	Gas leak
#1BR-16-FS	02/08/01	Low	40	1200	
#4BR-17	02/12/01	---	40	1200	One of the heater burned and there was foaming
#3BR-18	02/21/01	Medium	40	1200	The vapor outlet plugged because of foaming
#4BR-19-FS	02/26/01	Medium	40	1200	
#4BR-20-FS	02/28/01	Medium	40	1200	
#1BR-21-PM	03/16/01	Medium	40	2400	
#1BR-22-PM	03/19/01	Medium	15	1200	
#3BR-23-PM	04/02/01	Medium	40	2400	
#6BR-24-PM	05/25/01	Medium	40	1200	Low N2 flow
#5BR-25-PM	06/11/01	Medium	40	1200	20% Recycle
#6BR-26-PM	06/20/01	Medium	40	1200	High N2 Flow, power failure at the end of the run
#4BR-27-PM	07/03/01	Medium	40	1200	20% Recycle
#5BR-28-PM	07/14/01	Low	15	1200	Heaters did not give enough output
#5BR-29-PM	08/06/01	High	40	1200	
#5BR-30-PM	08/17/01	Medium	30	1200	
#5BR-31-PM	09/04/01	Low	40	1200	
#4BR-32-PM	09/08/01	Low	40	1200	
#4BR-33-PM	09/24/01	Medium	15	1200	
#1BR-34A	10/04/01	Low	40	1200	Power failure
#1BR-34B	10/06/01	Low	40	1200	Water leaked from the stirrer assembly
#1BR-34-PM	10/29/01	Low	40	1200	
#1BR-35A	11/09/01	Medium	40	1200	Failed due to the heaters
#1BR-35-PM	11/19/01	Medium	40	1200	20% Slurry Oil

Table 15 - Stirred-batch reactor raw material balance

Run ID	Feed (g)	Coke %	Liquid %	Gas %	Gas % by difference	Liquid Sampled %	Recovery
#5BR-3-BT	3652.6	24.2	65.5	8.5	10.2	0.0	98.3
#5BR-4-BT	3738.0	24.2	65.5	8.2	10.2	0.0	97.9
#6BR-6-BT	3511.0	29.6	59.7	8.8	10.7	0.0	98.1
#5BR-7-SD	3932.5	24.1	66.0	0.7	9.9	0.6	90.7
#5BR-8-SD	3408.1	24.5	64.0	9.0	11.5	4.4	97.5

#5BR-9-SD	3570.1	24.4	64.8	9.1	10.8	3.0	98.3
#6BR-10-SD	3299.5	29.2	58.4	10.5	12.4	0.0	98.1
#6BR-11-SD	4702.4	29.7	60.0	5.2	10.3	0.0	94.9
#6BR-12-SD	3588.0	29.2	67.2	5.7	3.6	0.0	102.1
#6BR-13-FS	4033.6	28.8	57.6	5.2	13.6	3.3	91.6
#5BR-14-FS	3620.5	24.4	60.3	6.2	15.3	0.0	90.9
#2BR-15-FS	4161.7	32.7	55.2	7.2	12.1	2.1	95.1
#1BR-16-FS	4153.9	41.1	48.0	8.5	11.0	1.5	97.6
#4BR-19-FS	4280.1	30.1	57.6	11.5	12.3	2.3	99.2
#3BR-20-FS	4585.1	30.7	59.4	8.6	9.9	2.1	98.7
#1BR-21-PM	4576.1	38.8	50.8	9.8	10.5	2.3	99.3
#1BR-22-PM	4303.0	36.4	50.3	10.1	13.3	2.2	96.8
#3BR-23-PM	4110.1	30.7	57.4	9.5	12.0	2.6	97.5
#6BR-24-PM	4120.6	30.4	59.2	9.7	10.4	2.6	99.2
#5BR-25-PM	4493.8	28.9	60.9	10.2	10.3	2.2	99.9
#6BR-26-PM	3875.3	30.6	58.8	7.4	10.6	0.0	96.7
#4BR-27-PM	4112.7	34.6	52.8	9.7	12.6	2.5	97.1
#5BR-28-PM	4452.4	21.6	67.6	8.7	10.8	2.4	97.9
#5BR-29-PM	3990.2	23.1	67.8	6.4	9.1	2.5	97.3
#5BR-30-PM	3560.4	24.5	64.4	8.4	11.1	2.9	97.3
#5BR-31-PM	3850.3	24.3	65.3	7.3	10.4	2.7	96.9
#4BR-32-PM	4025.3	29.8	58.6	9.8	11.6	2.7	98.2
#4BR-33-PM	4218.7	28.1	60.4	7.9	11.5	2.5	96.4
#1BR-34-PM	4351.0	40.7	48.6	9.2	10.7	2.1	98.5
#1BR-35-PM	4324.0	33	54.6	---	12.5	2.1	---

*The GC was not working properly in #1BR-35

Before each test, one gram of an antifoaming additive mixed 3 grams of kerosene are added to each 1000 gram of feed. The weight of this mixture is added to the Resid weight. To calculate the yields, the resid drawn during the test is subtracted from the original feed weight. Calculating the yield in this manner is not exact but the error is very small compared to the large weight of the feed.

2. Heating Rate

As an important variable, heating rate should be reproducible to give meaningful comparisons and interpretations of the stirred batch reactor data. Since temperature is a key variable for the kinetic studies, it is also important to know the temperature profile.

Figure 28 shows the temperature profile of all runs of the stirred batch reactor conducted. There are two curves in

Figure 28. One curve is for the medium heating rate and the other for the low heating rate. Only test #6-12 falls below the low heating rate curve. Although test #5BR-20 and test#1BR-21 were run at 1200 rpm and test #1BR-22 and test #5BR-23 were run at 2400 rpm, they lie on the same temperature curve. This can be seen from Figure 29. This means that the stirring speed does not affect the heating rate.

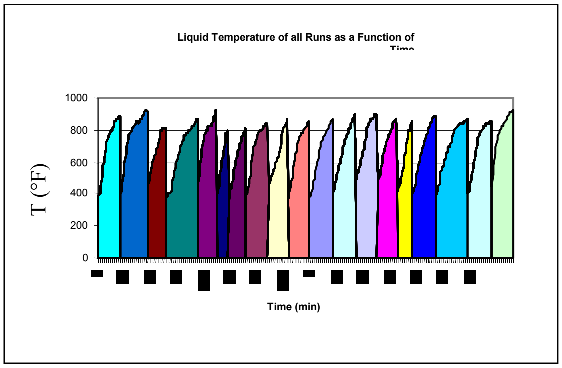


Figure 28 - Stirred batch reactor temperature profile for all runs

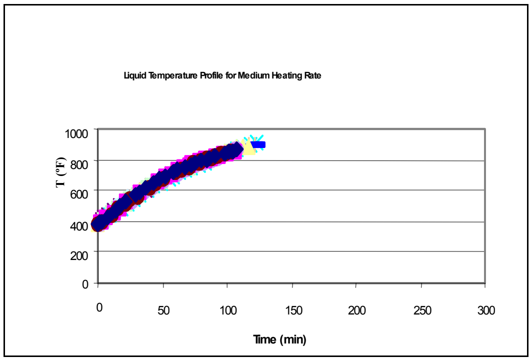


Figure 29 - Stirred batch reactor temperature profile with alike heating rate runs

3. Heating Rate Effect on Yields

Fluid 5 and Fluid 4 were tested with both low and medium heating rates. The low heating rate corresponds to 70% controller output while the medium is 85%. When the solid-state relay used by the controller fails the circuit closes and the output goes to 100%. Test #5BR-29-PM is an example of such a run. Fortunately, this run can be used to compare it with other fluid 5 runs.

Tests with the fluid 4 resid resulted in lower liquid and higher gas volumes with the medium-heating rate compared to the low-heating rate. A little more coke was produced using the medium-heating rate but it is not clear whether his is a parametric effect or an experimental error. Fluid 5 on the other hand did not respond to the low-heating rate. SimDis results for the low-heating rate runs are not available yet to see if there is an effect on the liquid fractions. However, with a high heating rate, fluid 5 gave lower coke and gas and higher liquid yield than both the low and the medium-heating rates. Fluid 1, in the same manner, produced less coke for the medium-heating rate, thus preferring higher temperature to yield higher liquid.

Table 16 summarizes the data for the heating-rate runs for both fluid 5 and fluid 4.

Table 16 – Heating rate effect on product yields

Run	Heating Rate	Coke	Liquid	Gas
#5BR-31	Low	24.3	65.3	10.4
#5BT	Medium	24.3	65.2	10.5
#5BR-29	High	23.1	67.8	9.1
#4BR-32	Low	29.8	58.6	11.6
#4BR-19	Medium	30.1	57.6	12.3
#1BR-34	Low	40.7	48.6	10.7
#1BR-21	Medium	38.8	50.8	10.5

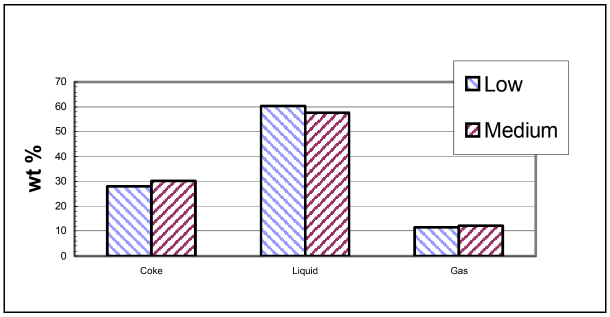


Figure 30 - Heating rate effect on Fluid 4 product yields

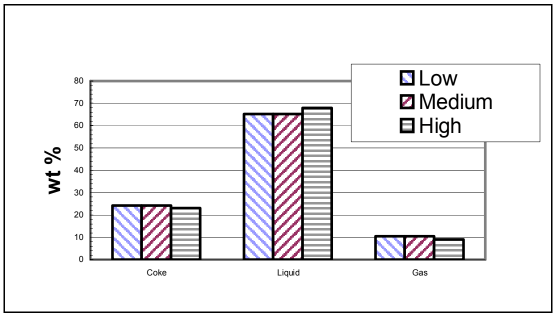


Figure 31 - Heating rate effect on Fluid 5 product yields

4. Pressure Effect on Yields

Figure 30 and Figure 31 shows the pressure effect on fluid 1, fluid 5 and fluid 4, respectively. With the lower pressure runs, all feedstock tested produced less coke. Furthermore, the liquid yields were higher for fluid 5 and fluid 4 at the lower pressure while fluid 1 had a slightly lower liquid. The gas did not have an obvious trend.

Fluid 1 not only produced less liquid with decreasing pressure, it also produced less gasoline and Diesel as shown in Figure 32. As depicted from the HTGC results in Figure 33, the liquid product for Fluid 1 in the lower-pressure run is heavier than that of the higher-pressure run.

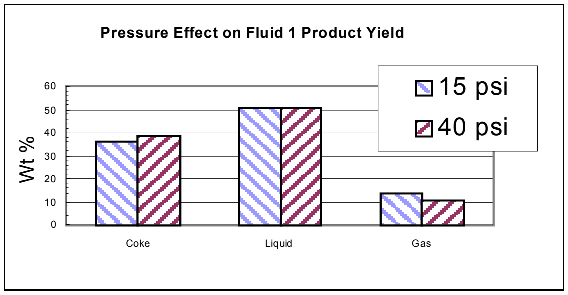


Figure 32 - Pressure effect on Fluid 1 product yields

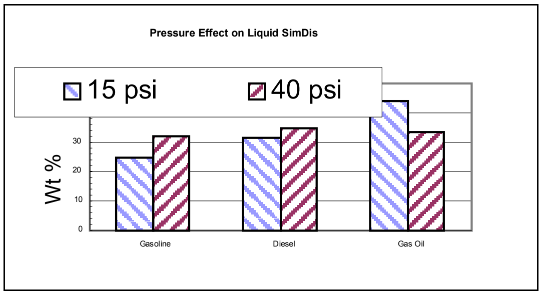


Figure 33 - Pressure effect on liquid yields Fluid 1

5. Recycle Effect on Product Yields

The recycle experiments were done for using the resids from fluids 4 & 5. A 20% recycle by weight was added to each resid. The calculation of the product yield did not include a subtraction of the recycle from the resid and adding it to the liquid as suggested by one company in the Advisory Board Meeting held in May 2001. The recycle and the resid were considered as the original feed. Using a recycle, coke yields increase and liquid yields decrease while gas yields do not change. The recycle has lower hydrogen content than the original feed. In the absence of hydrogen, carbon-carbon reaction will be more frequent. This explains why we have more coke and less liquid is made added to the recycle to the original feed. However, gasoline and diesel cuts increased in both recycle runs and the gas oil cut decreased. From the HTGC analyses lighter liquid are produced at the end of the run when recycles are used.

6. Nitrogen Effect

Nitrogen did not have any effect on the heating rate. In addition, nitrogen did not have any effect on the product yields. It was thought that a high flow of nitrogen might prevent internal reflux and help reduce cracking of the liquid. Higher liquid and lower gas was seen in one of the runs using fluid #6. However, the material balance for this run was above 100%, which is unusual for the stirred-batch reactor.

7. Coke Analysis

a) Volatile Matter Recovery

The average volatile matter for the six resids are shown in table 18 matter of Fluid 6 coke is 8.1%. Fluid 1 coke had an average volatile matter of 17.4 %. Fluid 2 coke has only 8% volatile matter while Fluid 4 and Fluid 3 cokes averaged at 14.8% and 16.4% respectively.

Table 17 – Fluid and Volitile Matter %

Fluid	VM%
1	17.4
2	8.0
3	16.4
4	14.8
5	8.1
6	8.1

Table 18 - Vanadium and Nickel Recoveries in the Batch-Coker

Run ID	Vanadium % recovery	Nickel % recovery
#5BR-3	98	102
#5BR-4	86	105
#6BR-6	124	129
#5BR-8	95	85
#5BR-9	88	107
#6BR-10	134	138
#6BR-12	123	128
#2BR-15	79	75
#1BR-16	64	59
#4BR-19	58	51
#3BR-20	113	112
#1BR-21	57	53
#1BR-22	70	73
#3BR-23	120	117
#6BR-24	124	143
#5BR-25	133	200
#6BR-26	108	108
#4BR-27	62	55
#5BR-28	103	97

8. Gas Yield

Methane is largest amount produced followed by ethane and Hydrogen. The average mole percent of methane is about 48. Ethane and hydrogen averaged at 14 % and 11 %, respectively. It is worth noting that fluids 5,6, 3, and 2 gave approximately 50 % of the gas in methane while the heavier feedstocks, namely fluids 1 and 4, gave around 40 %. This is an indication of feed behavior that may be related to feed properties.

9. Thermogravimetric analysis

Thermogravimetric runs were conducted on the resids. The runs are shown in Table 19 along with their conditions. We set the heating rates to be 5°C/min, 10°C/min, and 20°C/min. The weight of the sample is kept around 10 mg to avoid noises produced by the instrument. Furthermore, the weight was kept below 15 mg so that the heat load and mass transfer effects can be neglected. The thermogravimetric analysis (TGA) was then used to derive kinetic parameters for these samples under controlled conditions.

Table 19 - Thermogravimetric Analysis

Sample ID	Residue	°C/min	Wi (mg)	Max T (°C)	He P (psi)	time (min)	Time at Max T (min)
S-5-2	Fluid 3	5	10.221	499.7	40	32.5	10
S-5-3	Fluid 1	5	10.4792	499.0	40	32.5	10
S-5-4	Fluid 4	5	13.7709	500.1	40	32.5	10
S-5-5	Fluid 2	5	10.6763	500.8	40	32.5	10
S-5-6	Fluid 6	5	9.1396	499.5	40	32.5	10
S-10-2	Fluid 3	10	13.6237	499.9	40	55.0	10
S-10-3	Fluid 1	10	10.6958	499.1	40	55.0	10
S-10-4	Fluid 4	10	12.2989	500.1	40	55.0	10
S-10-5	Fluid 2	10	10.6855	502.1	40	55.0	10
S-10-6	Fluid 6	10	10.9024	499.6	40	55.0	10
S-20-2	Fluid 3	20	11.0117	499.9	40	100.0	10
S-20-3	Fluid 1	20	12.8633	500.0	40	100.0	10
S-20-4	Fluid 4	20	13.0795	501.1	40	100.0	10
S-20-5	Fluid 2	20	10.3023	499.8	40	100.0	10
S-20-6	Fluid 6	20	11.036	501.1	40	100.0	10

Figure 34 and Figure 35 shows an example of the data obtained from TGA, Figure 34 shows the sample is heated from 50°c to 500°F at a constant rate in 22.5 minutes. The temperature is then held constant for 10 minutes before shutting down the test.

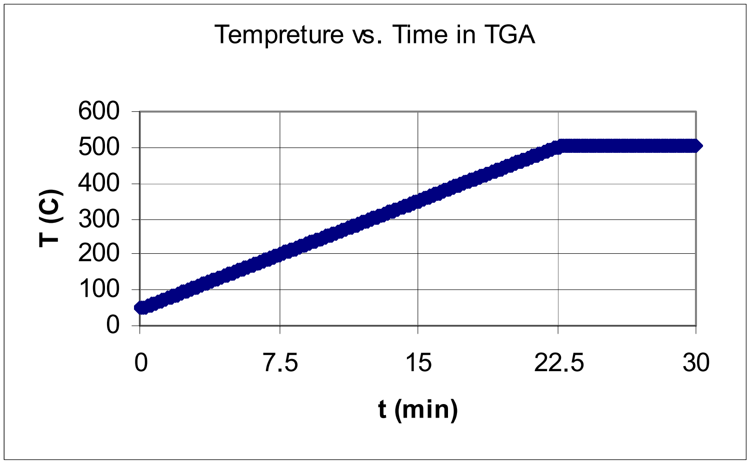


Figure 34 - Constant Heating Rate in TGA

In Figure 35 shows a typical graph of the weight reduction as a function of time. From this graph, one finds the temperature at which the reaction starts and ends. Other valuable information that can be depicted form the graph is the temperature at which the maximum reaction rate occurs. This data can be used to build a simple model that can be facilitated into the stirred batch reactor.

Figure 35 shows a typical graph of the weight reduction as a function of time. From this graph, one finds the temperature at which the reaction starts and ends. This data also shows the temperature at which the maximum reaction rate occurs. This data can be used to build a simple model that can be then be compared to the stirred batch reactor data.

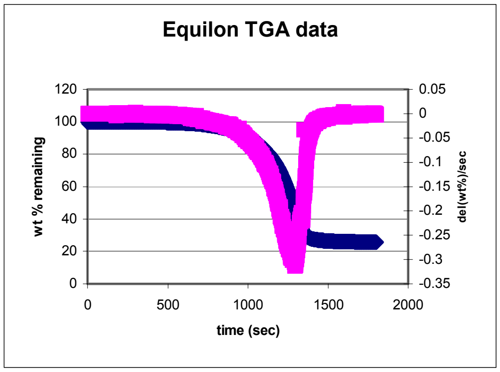


Figure 35 - Graphical Representative for TGA

Figure 36, Figure 37 and Figure 38 show the behavior of each feedstock at 5C/min, 10C/min, and 20C/min, respectively. Fluid 1, Fluid 2, and Fluid 6 seem to behave the same kinetically. Similarly, both Fluid 3 and Fluid 4 behave the same. However, Fluid 4 starts the reaction earlier but crosses the line of Fluid 3 at some point later in the reaction. Correspondingly, this would indicate that there are lighter components and heavier components than that of Fluid 3. In the same way, Fluid 6 and Fluid 1 seem to have the same light components but Fluid 1 has heavier components than that of Fluid 6. This is clear from the three graphs mentioned above. The two curves almost coincide at the beginning and then the conversion of Fluid 1 slows down while Fluid 6 is still reacting. Fluid 2 has the same curve Fluid 6 and Fluid 1; however, it seems to have lighter components and heavier components than Fluid 6 but still lighter than Fluid 1.

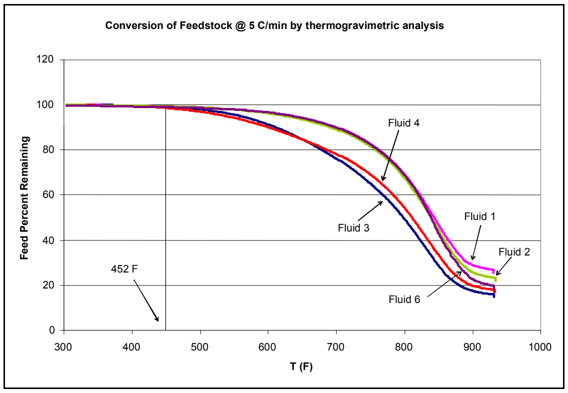


Figure 36 - Conversion of Feedstock at 5 C/min by TGA

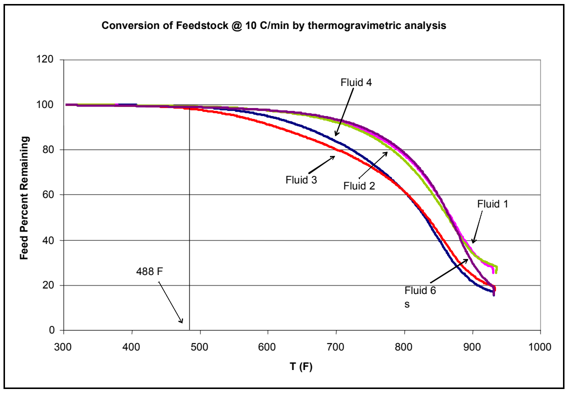


Figure 37 - Conversion of Feedstock at 10 C/min by TGA

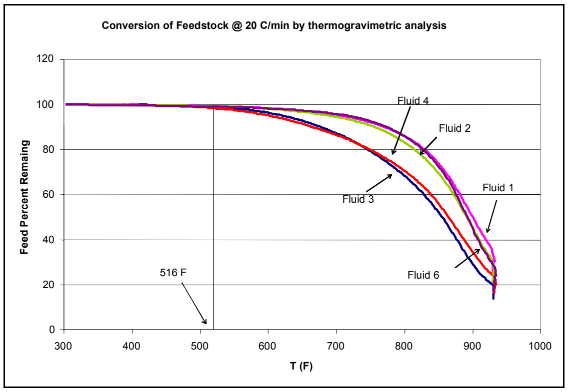


Figure 38 - Conversion of Feedstock at 20 C/min by TGA

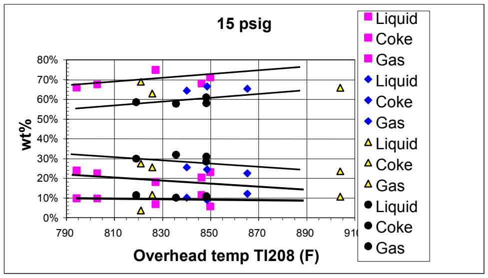
Another noteworthy point is the temperature where the reaction appears to start. Every time the heating rate increases, the cracking reactions delay for several degrees. At 5°C/min, the reactions start at an average temperature of approximately 452°F. When we double the heating rate the reactions starting point delays for about 36°F. Another observation that can be depicted from these figures is that at the slower heating rate there is not much to react at the end of the run when isothermal condition are reached. At the higher heating rate, in contrast, the reactions are still going when we reach the isothermal condition.

The higher heating rate starts the reaction at a higher temperature and it doesn't stop at the end of the nonisothermal reaction. This would suggests that increasing the heating rate (short residence time in the furnace) will delay the coking reactions.

C. PILOT UNIT

1. *Feedstock and Parametric Studies*

a) <u>Product yields</u>



All the 15-psig pilot-coker runs' product yields are shown in Figure 39, with the 40-psig data shown in Figure 40. One can see the liquid yields increase with an increase in temperature and are higher for the low-pressure runs. The coke and gas yields decrease with an increase in temperature and are higher for high-pressure runs. These trends are expected, as both favor boiling more of the liquid off the coke product. For the four resids plotted at 40 psig, yields vary over a range of 8%. While at 15 psig the liquid range is approximately 12%. This can be attributed to the feedstock properties.

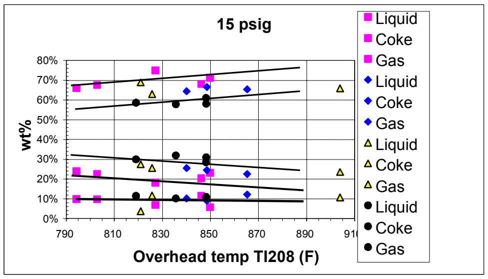


Figure 39 - All 15 psig pilot-coker normalized product yields versus overhead temperature (normalized by changing gas yield)

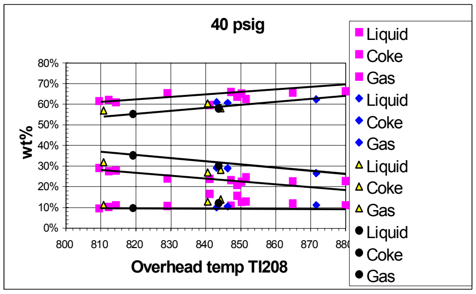


Figure 40 - All 40 psig pilot-coker normalized product yields versus overhead temperature (normalized by changing gas yield)

b) Coil fouling, volatile matter, & coke density

In the section below coil fouling, volatile matter, and coke density are correlated to coke-drum overhead temperature. Overhead temperature was selected for the coke properties, as it should reflect what is occurring in the coke drum.

(1) Coil fouling

The coil fouling, on a gram/foot basis, versus the maximum coke drum overhead temperature is graphed in Figure 41. However, we also cut the coils into sections and examined the fouling as it changed from the inlet to the outlet of the tube. One coil was dissected into portions of approximately one-foot lengths and weights obtained to allocate the weight on a gm/foot basis. Upon inspection, it was noticed that most of the coke did indeed occur within the last one and a half foot of the coil. This is the case for most of the runs in these coils in that the majority of the coke deposited around the 120º bend at the coil top, where the tube turns from the furnace wall toward the center.

Based on the theory that the sharp turns in the coil are contributing to the high fouling rates, we attempted to make a 20 foot coil with more gradual turns. Our first attempt failed with the tube being kinked. Because of the difficulties in making the coil, another approach was tried, that is, to increase the velocity by using a smaller diameter tube. This test was then repeated with a ¼” coil and run successfully for 5 hours. The higher velocities eliminated the fouling in the last 1 to 1-½ foot of the coil, and formed shot coke in the center of the drum, similar to what is made at the refinery using this resid.

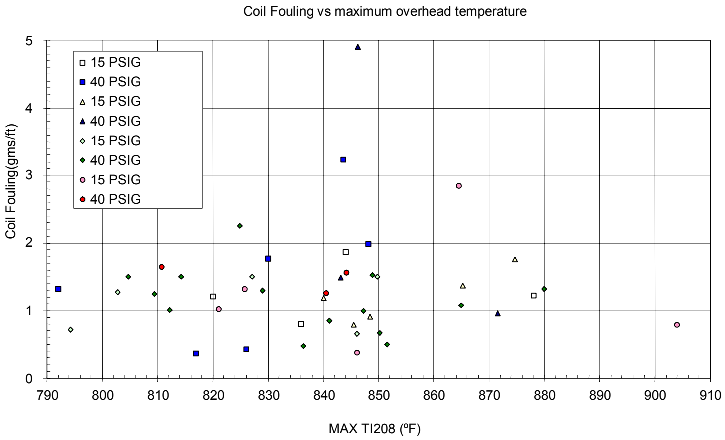


Figure 41 - Coil fouling for pilot-coker runs versus maximum coke drum overhead temperature

(2) Coke volatile matter

Coke volatile matter ranges between 8 and 20 wt%. As can been seen in Figure 42 it decreases with the maximum overhead drum temperature. In part this can be attributed to the higher temperature driving off more volatile matter. Also, some of the higher numbers are from earlier runs where there were more problems with large drops in the furnace temperatures which would result in less cracking and less volatiles being driven off. With time we experienced smaller and shorter temperature transients when the feed is introduced. So care must be taken in analyzing the coke volatile matter data, as the operating conditions of the furnace have not been constant in spite of our best efforts.

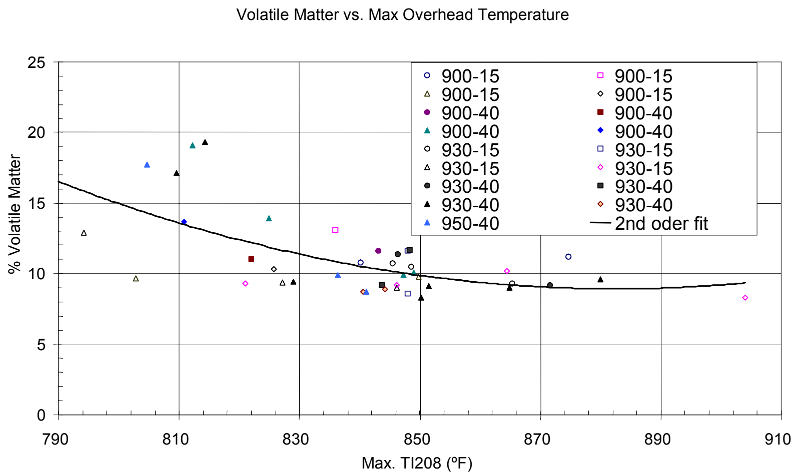


Figure 42 - Coke volatile matter versus maximum overhead temperature for pilot-coker runs grouped by temperature and pressure

(3) Coke density

During the parametric and feedstock studies, the coke density was measured based upon the measured total weight of coke divided by the total volume. The coke weight is the weight of the drum plus coke minus the initial drum weight. The volume is based upon measuring an average distance from the coke drum top to the top of the coke. Both measurements, but the volume in particular, are subject to error. An alternative method was to drill plugs and have the porosity determined and the density calculated.

Based upon the overall coke density calculation the data was graphed versus maximum overhead drum temperature for all the runs in Figure 43, for the low pressure runs in Figure 44, and for the high pressure runs in Figure 45. The downward trend with overhead temperature is clearer in the high-pressure data.

It has been suggested that the density goes through a minimum at some temperature as shown by the second order fit shown for high-pressure data in Figure 45. This could be explained by that at the lower temperatures the high volatile matter is contributing to higher density.

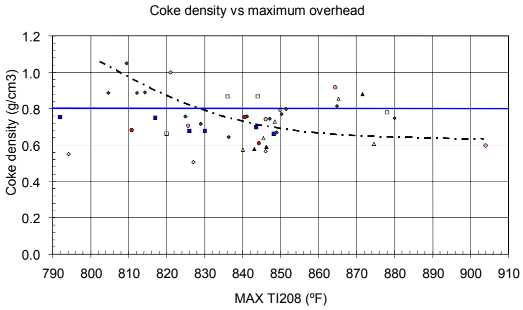


Figure 43 - Coke Density for Pilot-Coker Runs versus Maximum Coke Drum Overhead Temperature

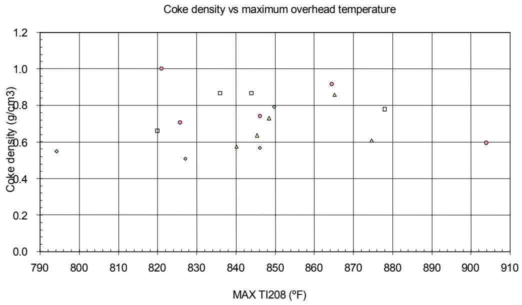


Figure 44 - Coke Density for 15 psig Pilot-Coker Runs versus Maximum Coke Drum Overhead Temperature

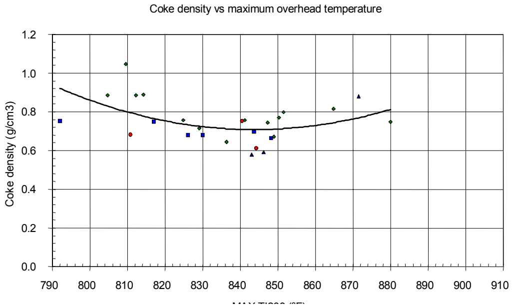


Figure 45 - Coke Density for 40 psig Pilot-Coker Runs versus Maximum Coke Drum Overhead Temperature

(4) Coke morphology

Coke morphology was studied by sizing the coke to determine the percentage shot. The procedure used for sizing the coke is as follows:

SHOT COKE DETERMINATION

1. Take the sample as prepared according to the Shot Coke Sample Preparation.
2. Take the +4 mesh fraction and separate into shot coke and sponge coke fractions. The visual guidelines for separation are described as follows:

   Shot Coke includes small ball-shaped particles about 2-5 mm. diameter; individual round particles which may be bird-egg shape; lumps of bonded or agglomerated shot particles; and lumps which are of high density with shot particles or circular domains surrounded with coke.

3. Take the –4/+10 mesh fraction and riffle it down with the small counter-top riffler in the lab to obtain ~10-15 grams of sample. Divide the total 4/10M fraction weight by the riffled sample weight to obtain a riffle factor (R).
4. Inspect the 4/10M fraction and separate into shot and sponge coke fractions as described in step 3.
5. Due to the difficulty in identification, it is not necessary to inspect the –10M fraction for the presence of individual shot particles. In our calculation, the % shot content of the –10M fraction is assumed to be equal to that of the cumulative +10M fraction.
6. The percent shot content is calculated as follows:

$$\%\ \text{Shot Content} = \frac{+4\text{M shot weight} + R^{*}\ (4/10\text{M shot weight})}{\text{Cumulative} + 10\text{M sample weight}} * 100$$

$$R = \frac{4/10\text{M total sieved fraction weight}}{\text{Riffled } 4/10\text{M sample weight}}$$

Table 20 lists the coke sizings that were done. In this table, "% Shot" is the total amount of shot coke obtained, which is subdivided into Aggregate shot (i.e., agglomerated pieces of shot coke) and BB shot (i.e., loose shot). There are trends that as temperature and pressure increase, the amount of shot coke is decreased. Figure 46 illustrates the trend associated with pressure.

Table 20 - Coke Sizing Results

Sample #	% Agg	% BB	% Shot	Temp	Pressure
Sample 1	60.9	3.6	64.5	900	15
Sample 2	29.7	0.1	29.7	950	40
Sample 3	2.4	0.5	2.8		
Sample 4	74.4	1.2	75.6	890	15
Sample 5	3	0.8	3.9	930	40

Sample 6	95.9	1.4	97.3	900	15
Sample 7	94.9	5.1	100	930	15
Sample 8	74.4	1.2	75.6	900	15
Sample 9	85.88	1.58	87.45	930	15
Sample 10	75.14	0.27	75.41	950	15
Sample 11	24.63	3.95	28.58	900	40
Sample 12	3	0.8	3.9	930	40
Sample 13	95.9	1.4	97.3	900	15
Sample 14	98	1	99	930	15
Sample 15	91.51	0.16	91.67	950	15
Sample 16	85.54	2.56	88.1	900	40
Sample 17	66.77	0.85	67.62	930	40

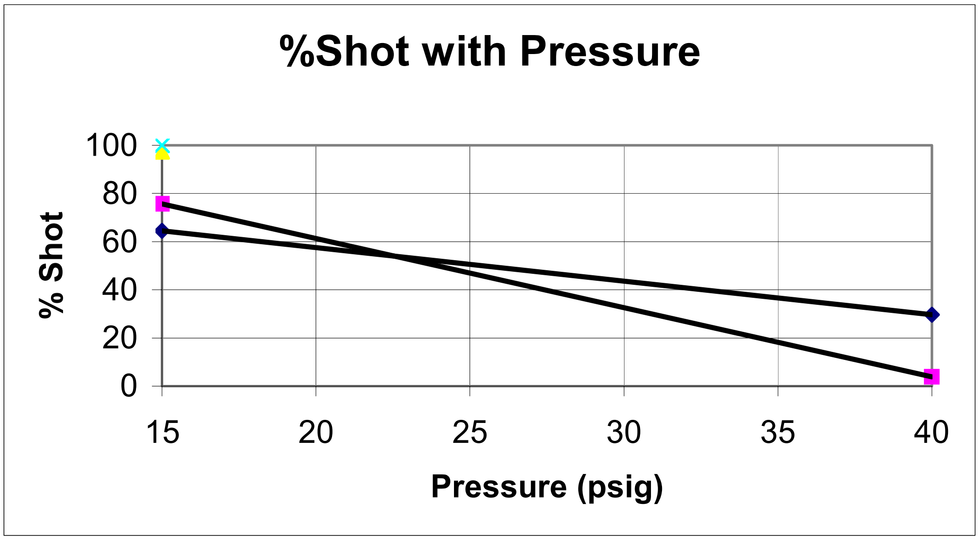


Figure 46 - Coke Sizing Relationship between Pressure and Shot Content.

Permeability and porosity data were attained for several runs. The samples were drilled from portions of the coke that were large enough to provide a plug suitable for the analysis. The plugs were drilled in a manner that the length of the plug was parallel to the length of the coke drum. This orientation was selected because the drain time is related to the permeability of the coke bed in the vertical direction. Being able to increase the permeability of the coke bed would allow for a shorter turn around time for the drum cycle, which in turn would allow for an increase in flow rate. The reason for the analysis was the fact that a faster drain time would lead to an economic advantage.

Table 21 contains the data from the permeability and porosity tests. It is interesting to note that the grain density was not significantly different from run to run. The grain density is a calculated value where the porosity is used to calculate the density. Essentially, it is the density of the coke without taking into consideration of the void space. The grain density is more likely to be related to the CHN properties of the coke than the operating conditions.

Table 21 - Permeability and Porosity Results

Sample #	Kair (mD)	Por (%)	Density (g/cc)
Sample 1	>50,000	44.84	1.385
Sample 2	300	21.7	1.43
Sample 3	94.6	26.41	1.412
Sample 4	10,900	33.22	1.402
Sample 5	8,380	33.25	1.399
Sample 6	6,620	36.04	1.405
Sample 7	14,400	27.51	1.423
Sample 8	>50,000	48.41	1.392
Sample 9	511	41.29	1.428
Sample 10	>50,000	36.42	1.406
Sample 11	>50,000	56.87	1.402
Sample 12	>50,000	45.51	1.41

There were no observable trends with the permeability or porosity and feedstock properties or operating conditions. This is primarily related to the fact that the permeability and porosity of the coke bed is not uniform. Therefore by drilling a plug from the coke bed, a representative sample was not taken. However, there is a general trend of higher porosity being associated with greater permeability. This is an area that needs further investigation to help discern the differences between permeability and porosity. This is a potentially important area to investigate due to the fact that it affects both safety and economics.

Another area that was exploited is the use of CT scans to see "inside" the coke drum. Many samples were taken for CT scan imaging. It was planned for two longitudinal scans and three horizontal slice scans to be taken of each sample. Coke samples from nine different runs were selected for CT scanning. Figure 47 is a a longitudinal scan sample image from the CT scan. It is evident that there is an abrupt change in coke morphology in the middle of the drum. Some of the scans show the tree type structure caused by the flow channels (Ellis and Hardin, 1993). Some of the samples had to be pieced together, so the scans will show the cracks. These cracks are also evident in Figure 48. The CT scans could possibly be linked to the permeability, porosity, and density.

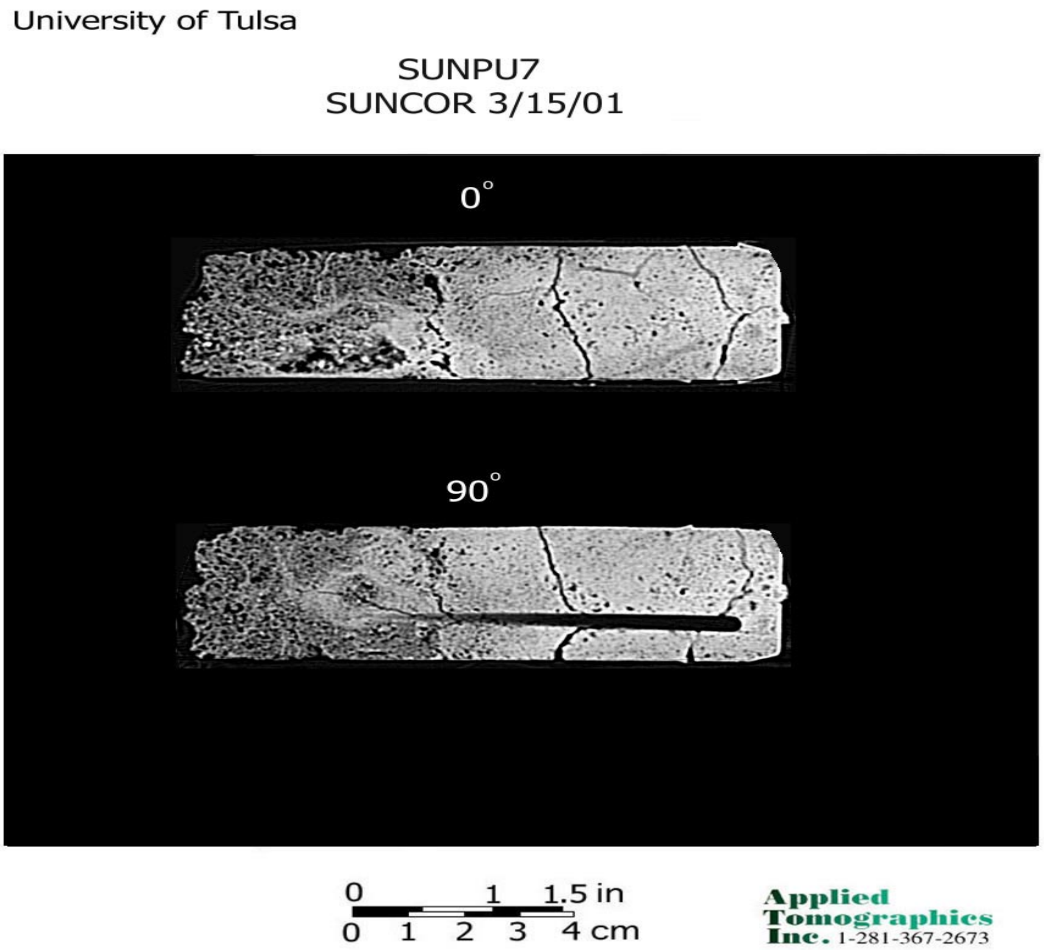


Figure 47 - Longitudinal CT Scan

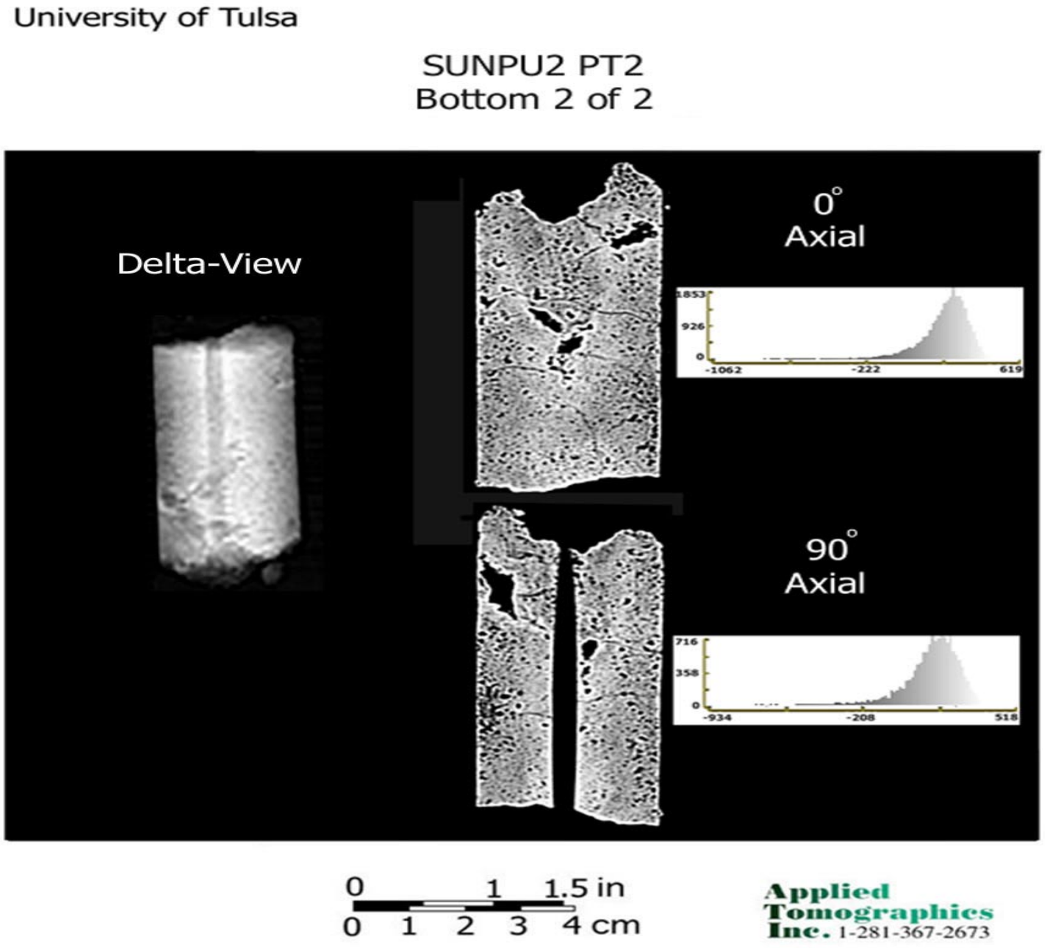


Figure 48 - Longitudinal Scan

The CT scans allowed for a better knowledge of what was going on in the coke drum and during the coking process. It is evident the “tree structure” of the coke bed is formed in the pilot coker. Figure 47 shows the flow channel of the resid fairly clearly. This is important because it gives an insight into how the hot spots and vapor pockets can be formed during the coking process. In Figure 48, the bar graphs represent the variation in the density. It is also interesting to note the large pockets of void space in the coke. These pockets provide evidence related to the analysis of the permeability and porosity. If the sample was taken and it contained one of these large pockets, the porosity value could be quite high and the permeability could be quite low. The detection of these pockets is also important because there is no true science in how the coke bed structure forms.

c) Gas Analysis

The effect of the different operational variables on the elemental composition of the gas product and its average molecular weight was investigated for Fluid 5 feeds in the pilot unit. Also, the relationship between the total gas production and the operational conditions will be studied in both reactors. Although these results give us a good idea about the effects of temperature, pressure and residence time on the elemental composition and average molecular weight of the gas, a thorough analysis considering all the different feeds and reactors is necessary before reaching any conclusions.

Before analyzing any effect of a specific operational variable on the elemental composition of the gas, a benchmark test was used to check the reproducibility of the results. The results (see Figure 49) show almost perfect agreement, as the content of carbon, hydrogen, and sulfur remain the same throughout the run for three different tests at 930°F, 40 psig and medium residence time.

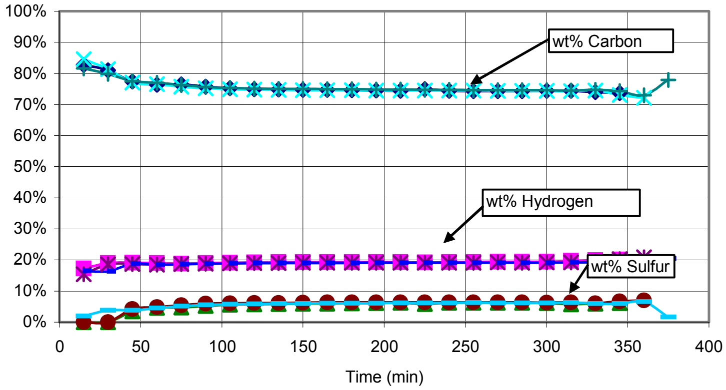


Figure 49 - Elemental Composition of Gas from Pilot Unit Run. (9A,10,11A).

Apparently, the operational conditions have little effect on the elemental composition of the gas. Regardless the conditions of temperature, pressure or residence time, the content of carbon is always around 75 wt% and the content of hydrogen is slightly below 20 wt% at any conditions of temperature, pressure and residence time. Sulfur content varies between 5-7 wt% (see Figure 50, Figure 51, and Figure 52). A common behavior was observed in the beginning of every run (first hour), where the content of carbon appears higher than at any point of the run, and consequently, hydrogen sulfur contents are lowest during this period.

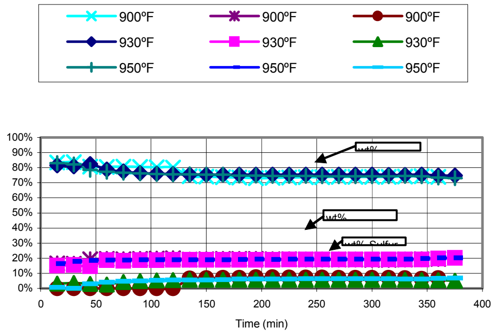


Figure 50 - Effect of Temperature on Elemental Composition of Gas from Pilot Unit.

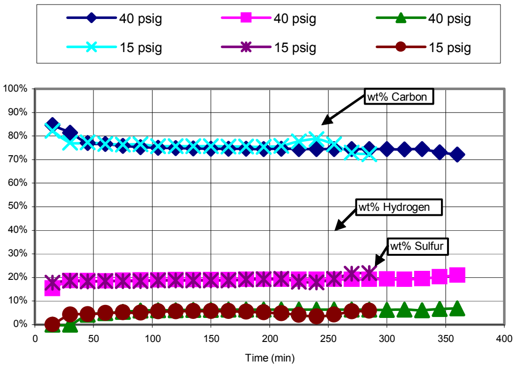


Figure 51 - Effect of Pressure on Elemental Composition of Gas from Pilot Unit.

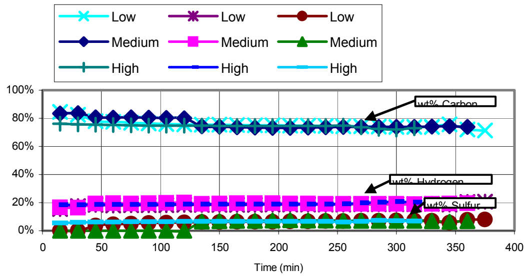


Figure 52 - Effect of Residence Time on Elemental Composition of Gas from Pilot Unit.

3. Fouling studies

Analysis of the coil fouling data from the parametric and feedstock tests run with the 3/8 inch coil and the ¼ inch coil indicated that more fouling occurred at higher temperatures and at lower velocities (larger coil). The test matrix for these tests are provided in Table 22. A total of 17 tests were conducted: seven were benchmarks (BM), three were with anti-coking additives (A1) added, two with stabilizers (S1) added, two with dispersants (D1 and D2) added, and three were a mixture of anti-coking agent with either a stabilizer (A1+S1), dispersant (A1+D1) and a dispersant and a stabilizer (D1+S1). For the tests where additives were used, the concentration was 200 ppm. The 3/8" coils from the baseline and the additive tests were sent to Baker Petrolite for SEM work. The results from the seventeen test conducted were reported in the January 2002 Quarterly Report.

Table 22 - Fouling Test Matrix

Fouling Test Matrix

Test	Temp (ºF)	Press (psig)	Residence Time (sec)	Additive			Treatment ppm	Date
				Anticoke	Dispersant	Stabilizer		
#2 1FT	930	40	20'-3/8 coil				0	07/25/01
#2 2FT	930	40	20'-3/8 coil				0	08/02/01
#2 3FT	930	40	20'-3/8 coil				0	08/08/01
#2 4FT	930	40	20'-3/8 coil				0	08/16/01
#2 5FT	930	40	20'-3/8 coil				0	08/22/01
#2 9FT	930	40	20'-3/8 coil				0	09/14/01
#2 10FT	930	40	20'-3/8 coil				0	09/20/01
#2 6FT	930	40	20'-3/8 coil	A1			200	08/27/01
#2 11FT	930	40	20'-3/8 coil	A1(PT)			200	09/26/01
#2 13FT	930	40	20'-3/8 coil	A3(PT)			200	10/05/01
#2 12FT	930	40	20'-3/8 coil			S1	200	10/02/01
#2 7FT	930	40	20'-3/8 coil			S1	200	08/29/01
#2 8FT	930	40	20'-3/8 coil		D1		200	09/05/01
#2 14FT	930	40	20'-3/8 coil		D2		200	10/10/01
#2 15FT	930	40	20'-3/8 coil	A1		S1	100/100	10/13/10
#2 16FT	930	40	20'-3/8 coil	A1	D1		100/100	10/17/01

The objective of these tests specifically designed to study fouling was to gain insight as to how the following three different classes of inhibitors work:

1. Anti-coking Agents: The anti-coking agents act to passivate the metal surfaces, inhibiting the initial lay down of coke precursors. They adhere to the metal surface of the unit and act to effectively block reactions sites that would exist otherwise; thereby preventing reactive species in the fluid stream from interacting with the metal surface. Anti-coking agents will inhibit destabilized colloidal particles from precipitating out of solution and acting as nucleation sites for further buildup of fouled material.

2. Dispersants: Dispersants react with metals and organometallic compounds preventing them from catalyzing free radical or condensation polymerization reactions. They will also interact with and prevent coke precursors from agglomerating and precipitating on hot metal surfaces by keeping them finely dispersed in the stream.

3. Stabilizers: Stabilizers interact with asphaltic material preventing interaction with reactive sites and the metal surface inhibiting these sites ability to react with material in the fluid which could lead to fouling and coke buildup.

Shack Hawkins described the coke samples for these tests. There were no distinguishable differences observed in the coke morphology produced from run to run. The coke morphology was described as a very small tightly aggregated shot. No BB shot was observed. It was very close to the coke described in the pilot unit runs that were called transitional. The only reason for not calling it transitional in these tests is because it usually was a lot grayer in color, whereas this coke is a lot darker (black). The major difference in the samples produced in the fouling tests is that it appears that there is more volatile matter with this coke but until we receive the analysis from GLC we won't be able to quantify the amounts. It is noted that many of these runs were of shorter duration (2 to 3 hours in length), and difficulties were encountered with the steam stripping.

It was also noted during breakout that the coke in the drum was easily removed as a cylindrical piece when the coil and coke drum were pretreated with 1000 ppm of anti-coking additive A-1. This treatment is under consideration for use in the fouling studies.

d) Evaluation Criteria for Fouling

Three techniques to evaluate the performance improvement when additives are used could be utilized: 1) weight loss in the coil, 2) pressure drop, and 3) comparison of skin and fluid temperatures. The direct approach would be to use weight difference. However, the experimental error could be large because the weight difference being measured is small (+/- several grams) and an excessive amount of fouling was observed in the coil prior to the inlet of the drum. Pressure drop can also be used as an indicator. A sudden drop in pressure would be an indicator of stripping. However, having the coke drum connected to the coil clouds this interpretation because a similar effect could occur as a result of opening another tree structure in the coke drum. The third approach, and the one used here, is to compare temperatures from the benchmark test to the temperatures of the additive test. The difference between the skin temperature at the outlet of the coil and the fluid temperature at this point is the resistance to energy transfer. A larger difference indicates more fouling. Since the fluid temperature is being controlled at 930ºF, rather than comparing the temperature difference between the benchmark tests and the additive test under consideration, one can just compare the skin temperatures. A lower skin temperature for an additive test versus the benchmark probably indicates the additive has reduced the fouling. Quicker energy transfer to the fluid is also an indicator of less fouling. One could argue that the fluid temperature would recover more quickly if the viscosity of the mixture of the fluid was reduced as a result of the addition of 200 ppm of additive. However, previous experiments have been run specifically designed to evaluate a dispersants ability to reduce the viscosity of a crude oil. A viscosity reduction was observed when ≥1000 ppms of certain dispersants were added. For additive levels below this amount viscosity measurements were indistinguishable.

e) Discussion of Results

Comparisons to the benchmark were made for each individual additive (A1, D1, and S1) and for three combinations of additives (A1+S1, A1+D1, and D1+S1). Data from the eight good tests are summarized in Table 23. Each of the tests will be discussed individually below.

Table 23 - Test Run Comparison Data

Test Name	Pretreatment (ppm)	Additive (ppm)	RunTime (hours)	Coke Density
1 BM	None	None	4.1	0.847

5 BM	None	None	4.0	0.886
11 A1	1000 A1	200 A1	3.23	0.931
12 S1	None	200 S1	3.2	0.761
8 D1	None	200 D1	3.2	0.953
15 A1+S1	1000 A1	100A1&S1	2.03	0.863
16 A1+D1	1000 A1	100A1&D1	2.62	0.839
17 D1+S1	None	100D1&S1	2.30	0.910

(1) <u>Benchmark Tests</u>

As shown in Figure 53, the data obtained for benchmark 1 and 5 are very similar. For these tests, approximately 30 grams of coke deposited in the coils. The comparisons in this report were made to the results from benchmark 1. A plot of the temperature and pressure data for this test is shown in Figure 54 below.

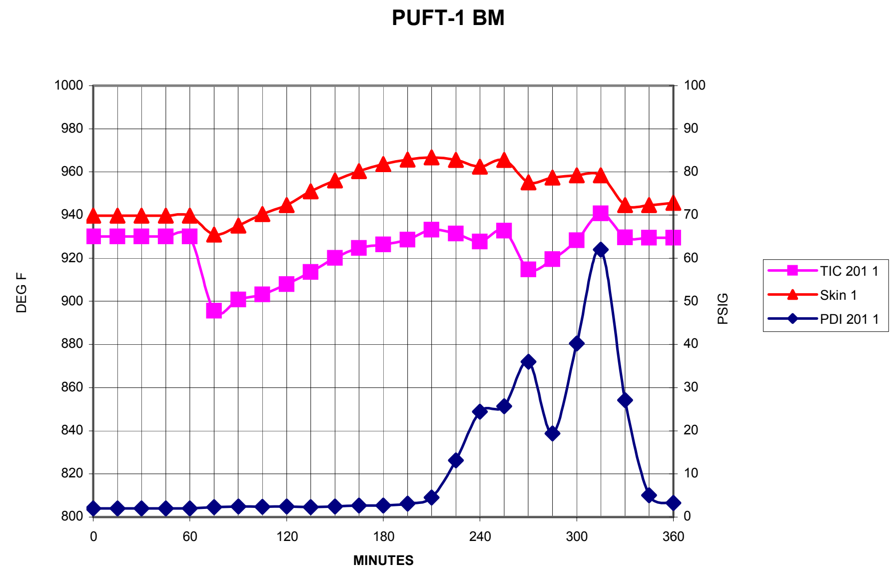


Figure 53 - Benchmark Test Data

This 4-hour test began after 60 minutes when the fluid was cut to the furnace coil. At 300 minutes, steam stripping begins.

(2) <u>Anti Coking, Dispersing, and Stabilizing Additive Tests</u>

Figure 54 shows the effect of the anti-coking additive on fouling using two different application techniques. In test PUFT 6 the anti-coking agent is added to the feed only and in test PUFT 11 the anti-coking agent is used to pre-treat the furnace coil before the feed is sent to the furnace. This allows the anti-coking agent to passivate the metal surfaces, inhibiting the initial lay down of coke precursors. Based on this data, pre-treating would be the preferred application method because of the associated advantages in energy savings due to the quicker warm-up as well as the energy savings as a result of only having to apply a 5°F delta T rather than the 10°F required for test 6.

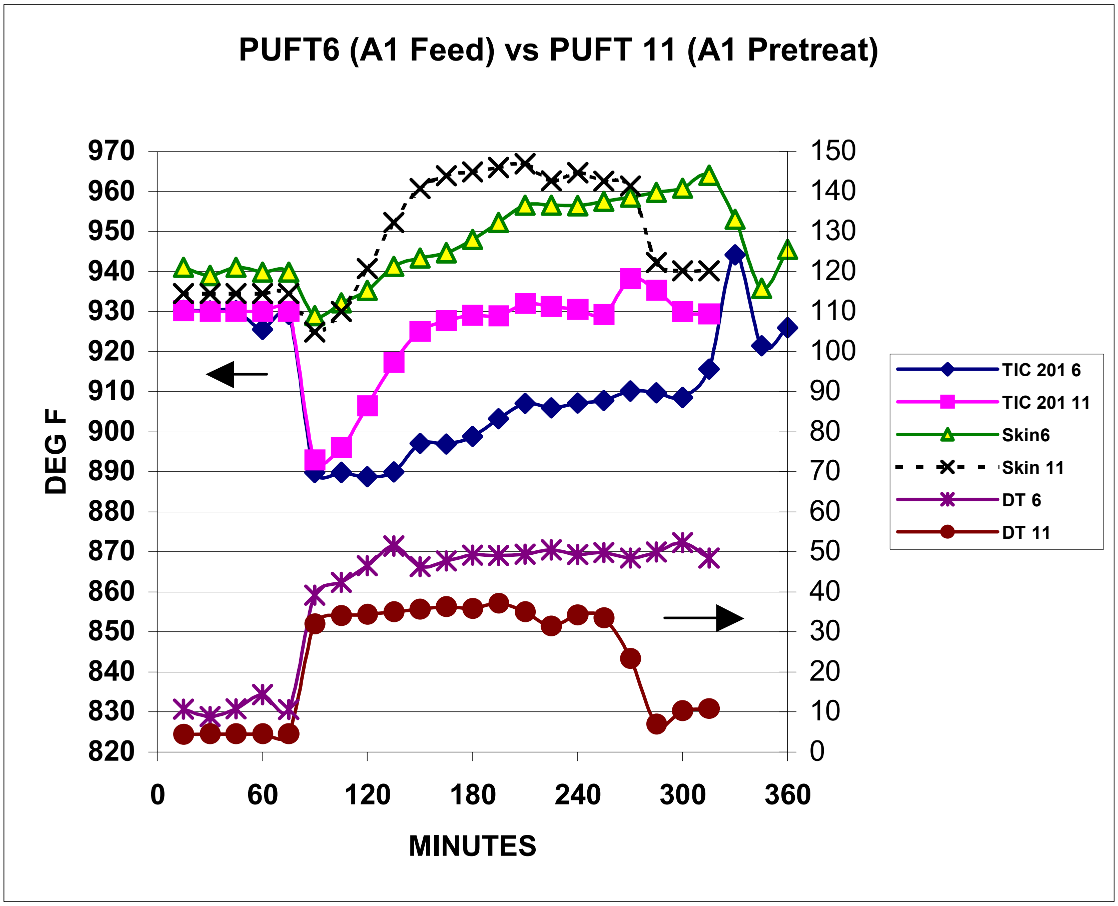


Figure 54 - Impact of Anti-Coking Agent Application Technique

The lower part of Figure 54 shows the difference between the skin temperature at the outlet of the coil and the fluid temperature at this point. As discussed in the evaluation criteria section, this temperature difference is the resistance to energy transfer. A larger difference indicates more fouling. Note that the test without the pre-treat has a larger difference indicating more fouling.

The results from test 11 were also used here for comparison of fouling with and without anti-coking agents. The coil was pre-treated with a 1000 ppm A-1 solution prior to cutting in the resid to the furnace tube. 200 ppm of A-1 was also added to the resid in the feed tank.

A similar effect as seen in Figure 54 was observed because skin temperature of the benchmark are less than the skin temperature when the additive was used and that the fluid temperature recovered more quickly when the additive was used indicating that less fouling is occurring as a result of the better heat transfer. However, using the temperature difference as the resistance to energy transfer analogy as discussed above is not possible because the benchmark coils were not pre-treated with the anti-fouling agent, as was the one using the additive

For dispersants and stabilizers one again saw, in general, that the skin temperature of the benchmark was less than the skin temperature when the additive was used and that the fluid temperature recovered more quickly when the additive was used indicating that less fouling is occurring as a result of the better heat transfer. In general, better performance was seen with the stabilizer.

(3) Mixture Additive Tests

Three different tests were run. Test 15 showed the impact of utilizing a stabilizer with the anti-coking agent while Test 16 showed the impact of utilizing a dispersant with an anti-coking agent.

The best fluid response of all the tests conducted was observed using the combination of 100 ppm A1 and 100 ppm of S1 with a 1000 ppm pre-treat of the coil prior to cutting the resid into the furnace tube. In examining the data, one saw, in general, that the skin temperature of the benchmark is less than the skin temperature when the additive combination is used and that the fluid temperature recovers more quickly when the additive combination is used indicating that less fouling is occurring as a result of the better heat transfer. However, using the temperature difference as the resistance to energy transfer analogy as discussed above is not possible because the benchmark coils were not pre-treated with the anti-fouling agent as was the one using the additive mixtures.

(4) Comparison of All Tests

All the test results are compared in Figure 55. It can be seen that the additives improve the heat transfer to the fluid and where the resistance to energy transfer analogy could be applied resulted in less fouling. An increase in temperature by as much as 20 ^{o}F was observed when a combination of anti-coking agent was used with a stabilizer.

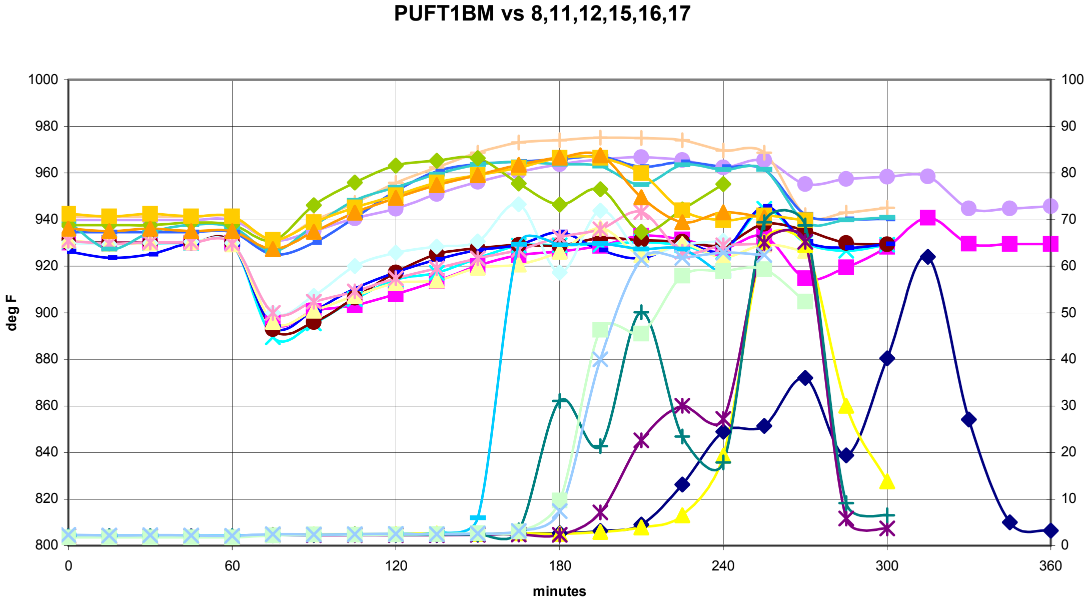


Figure 55 - Comparisons of All Test Runs

2. Foaming Studies

a) Discussion of Test Matrix

The pilot unit was modified in the fall of 2001 and then utilized to study foaming. The objectives of the study are:

- To quantify foam heights for model development,
- To quantify the effects of operating variables, such as, pressure, temperature, feed rate, steam velocity for different feedstocks, etc.,
- To compare overhead injection of anti-foam versus injection with the feed,
- To determine how the anti-foam partitions in products, and
- To establish whether injecting anti-foam in the feed alters the coke density.

A new furnace was purchased that holds a six-foot long, three-inch diameter coke drum. This allows for:

- Longer coking runs (10 to 15 hours at a feed rate of 1200 gms/hr),
- The ability to increase the feed rate by a factor of four to 4800 gms/hr, and
- Additional volume to minimize foam over (prior runs in the 3 foot drum without anti-foam foamed over, plugging the overhead line and terminating the run).

The Coker Facility and Operations committee discussed the potential variables to be studied in the foaming tests at the May 2001 Advisory Board Meeting and a vote was taken on the most important variables to study. The results are shown in Table 24.

Table 24 - Advisory Board Input on Foaming Studies

Variable	Vote
Temperature	8
Pressure, pressure reduction	5
Feed rate	1
Velocity steam/nitrogen	3
Recycle	0
Feedstocks	8
Drum diameter/superficial vapor velocity	3
Injection point (feed vs. drum)	3
Antifoams	4
Carrier	0
Viscosity	1
Dilution	0
Contaminants	0
Continuous vs. intermittent injection	0

Based on these results, it was decided to go with a test matrix consisting of two temperatures (900 and 930° F), two pressures (15 and 40 psig), and four resids (Fluid 2, Fluid 1, Fluid 4, and Fluid 3) using five-hour fill times. One run will be conducted with no antifoam. Antifoam will be added to the feed for one run, and to the drum for all other runs. One run will be made using 600,000 cSt antifoam, and the rest with 100,000 cSt antifoam. The antifoam will be diluted with light coker gas oil (1 part antifoam to 3 parts LGO). The feed rate will be 2400 gms/hr with a N_2 flow rate of 1.0 scfh and a steam velocity of 40 cc/hr. The gamma densitometer will be used for foam measurement with ~1 in/sec scans. An attempt will be made to sample the foam. The preliminary test matrix developed is provided in Table 25 and the test conditions are listed on Table 26.

Table 25 - Foaming Test Matrix

TEST NO.	RESID	T	P	ANTIFOAM	POINT OF INJECTION	DATE
1*	FLUID 2	930	15	NONE	N/A	NOV
2	FLUID 2	930	15	100,000	FEED	NOV
3	FLUID 2	930	15	100,000	OVHD	NOV
4	FLUID 2	900	15	100,000	OVHD	NOV
5	FLUID 2	930	40	100,000	OVHD	NOV
6	FLUID 2	900	40	100,000	OVHD	NOV
7	FLUID 2	930	15	600,000	OVHD	DEC
8	FLUID 3	930	15	NONE	NA	DEC
9	FLUID 3	930	15	100,000	FEED	DEC
10	FLUID 3	930	15	100,000	OVHD	DEC
11	FLUID 3	900	15	100,000	OVHD	DEC

TEST NO.	RESID	T	P	ANTIFOAM	POINT OF INJECTION	DATE
12	FLUID 3	930	40	100,000	OVHD	DEC
13	FLUID 3	900	40	100,000	OVHD	JAN 02
14	FLUID 3	930	15	100,000	OVHD	JAN 02
15	FLUID 1	930	15	NONE	NA	JAN 02
16	FLUID 1	930	15	100,000	OVHD	JAN 02
17	FLUID 1	900	15	100,000	OVHD	JAN 02
18	FLUID 1	930	40	100,000	OVHD	JAN 02
19	FLUID 1	900	40	100,000	OVHD	FEB 02
20	FLUID 4	930	15	NONE	NA	FEB 02
21	FLUID 4	930	15	100,000	OVHD	FEB 02
22	FLUID 4	900	15	100,000	OVHD	FEB 02
23	FLUID 4	930	40	100,000	OVHD	FEB 02
24	FLUID 4	900	40	100,000	OVHD	FEB 02

* Duplicate one run

Table 26 - Test Conditions

Feed rate	2400 gms/hr
Steam	40 cc/hr
Antifoam	100,000 cSt
	600,000 cSt
Injection Rate	At commercial rates
Carrier	Sun Diesel
Dilution rate	1 part anti-foam, 3 part LGO
Run length	5 hrs

b) Logic for Foaming Tests

The purpose of this section is to give the reader insight as to why the tests were conduced in the sequence listed in the table. A detailed discussion of the data collected from these tests will be provided later in this section.

The first set of foaming tests were conducted to learn how to operate the facility, establish what a foaming density was and then inject antifoam to knock the foam height back. These tests revealed that the temperature fluctuations were much larger (± 20^{o}F) than encountered in the parametric runs conducted utilizing the 3'drum. This difference appears to be due to the higher flow rates used, which may alter the two-phase flow pattern in the furnace coil. It was determined that the best way to control the unit was to monitor the fluid temperature while adjusting the heat input using the skin temperatures recorded prior to entering the drum.

The second set of foaming tests were conducted to show that reproducible data could be generated.

The third set of foaming tests were conducted to gather initial data for the two untested resids to provide an understanding of how each of the four resids behaves for a given set of operating conditions. This data would be used to classify the resids from the worst foamer to the one that foams the least.

The fourth set of foaming tests were conducted to get an understanding of the effect of superficial vapor velocity and steam velocity on foaming. These tests would also help verify the drum velocity calculations that show the major component of the drum velocity is due to the hydrocarbon vapors. One test would also be conducted with the antifoam injected with the feed to compare it with one in which the antifoam was injected overhead. This test would also determine if injection with the feed alters the coke density.

The objective of the last set of foaming tests is to determine the effects of operating conditions, mainly pressure and temperature, on foaming.

In the sections below, the results from all the studies will be discussed. In interpreting the results, one must keep in mind that during the first hour of coking, a fairly large drop in fluid temperature is experienced before it recovers and achieves steady state. As a result, comparisons will only be made during the steady state portion of the run. Once the controls are totally automated, the early time data (first hour) will be processed and analyzed.

c) Comparison of Facilities (6' vs. 3' drum)

In this section, results from the coking studies in the new (6') drum are compared with the results previously obtained in the pilot unit (3' drum). Comparisons are made between the product yields (liquid, coke, and gas), the liquid product distributions (SimDis), the temperature profiles, and coke morphology.

Product yield data for comparable runs for the two drums are shown in Figure 56 through Figure 60. The agreement is seen to be excellent.

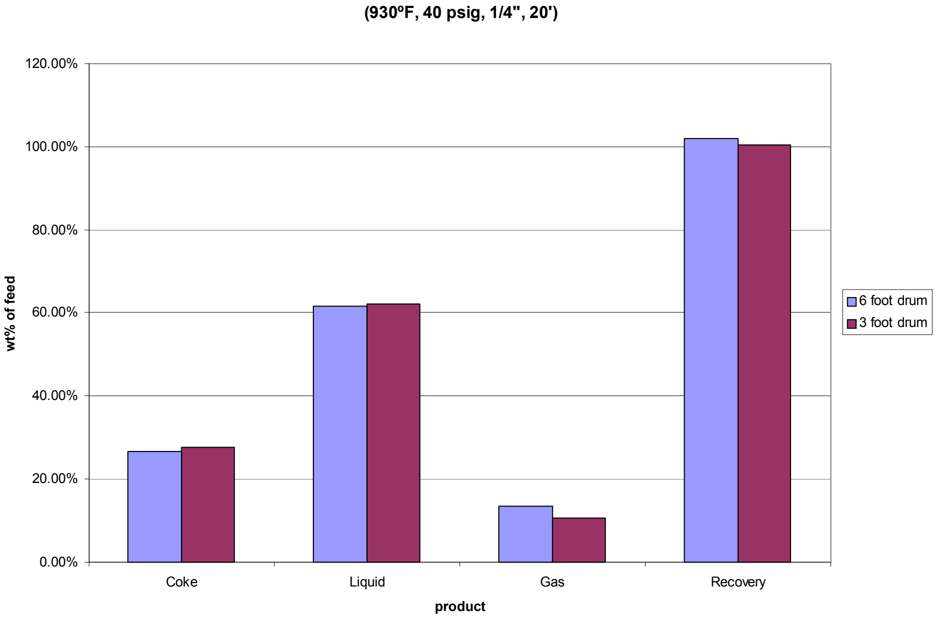


Figure 56 - Comparison of Yields from 3' and 6' Drums for Fluid 3 40 psig Runs

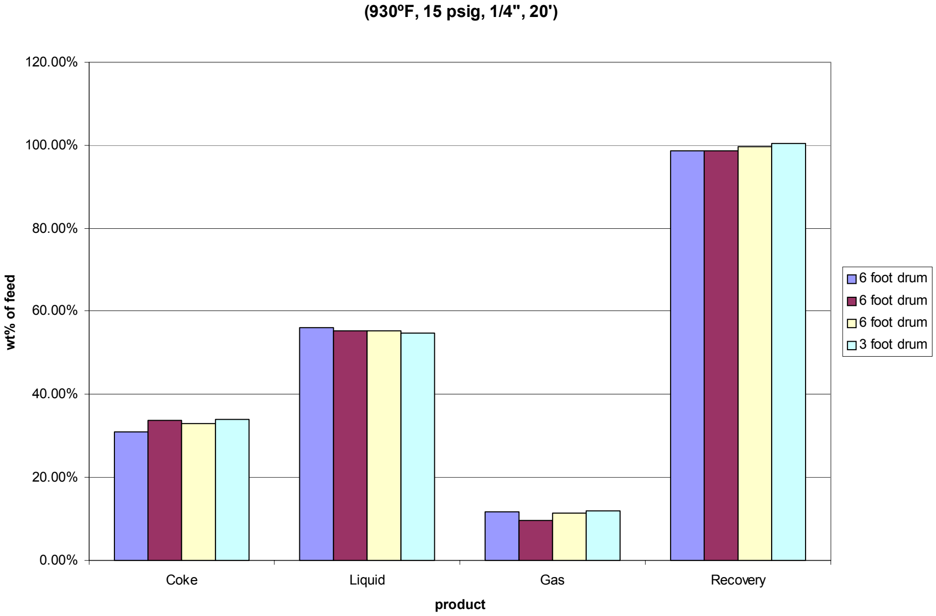


Figure 57 - Comparison of Yields from 3' and 6' Drums for Fluid 1 15 psig Runs

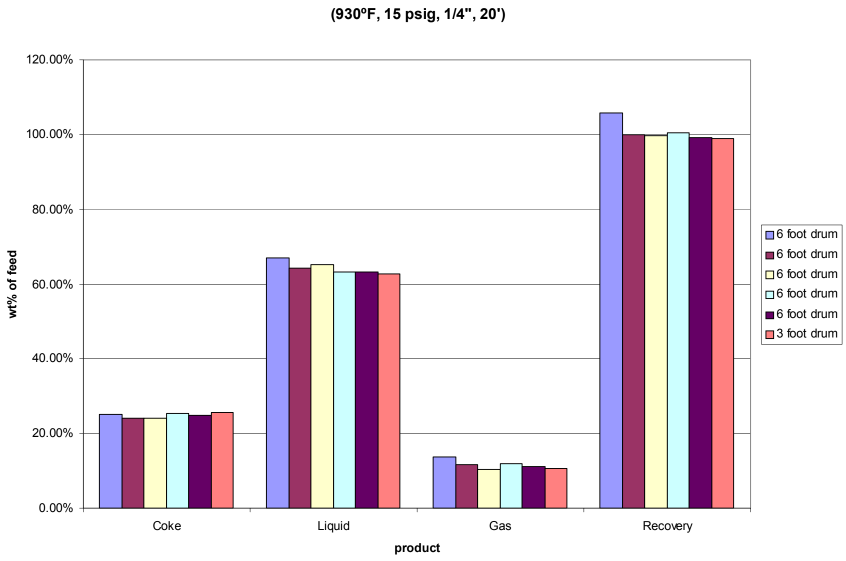


Figure 58 - Comparison of Yields from 3’ and 6’ Drums for Fluid 4 15 psig Runs

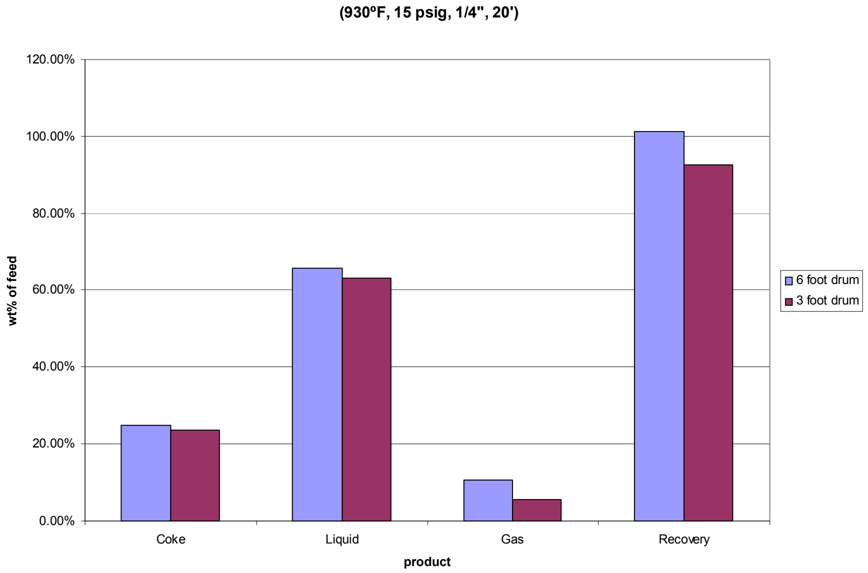


Figure 59 - Comparison of Yields from 3’ and 6’ Drums for Fluid 3 15 psig Runs

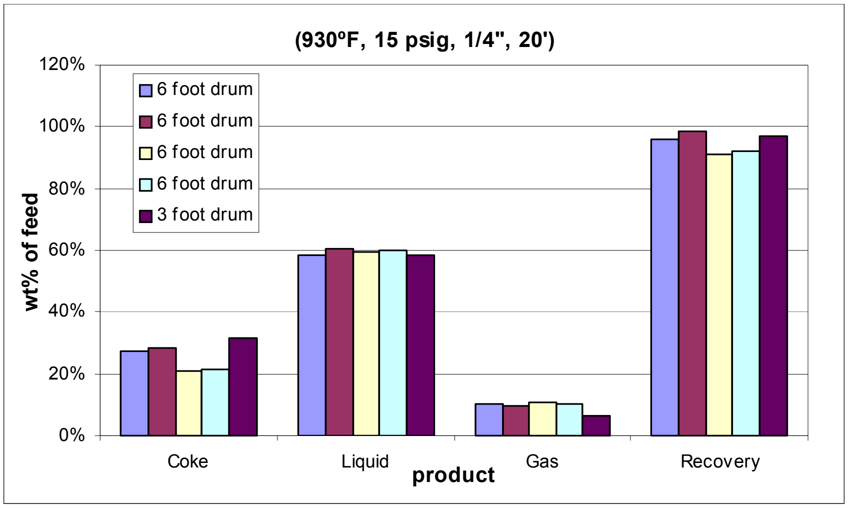


Figure 60 - Comparison of Yields from 3' and 6' Drums for Fluid 2 15 psig Runs

Simulated Distillation data for the 6' drum are presented in the Figure 61. These values compare favorably with the retested SimDis data from the 3' drum, shown graphically in Figure 61 and Figure 62.

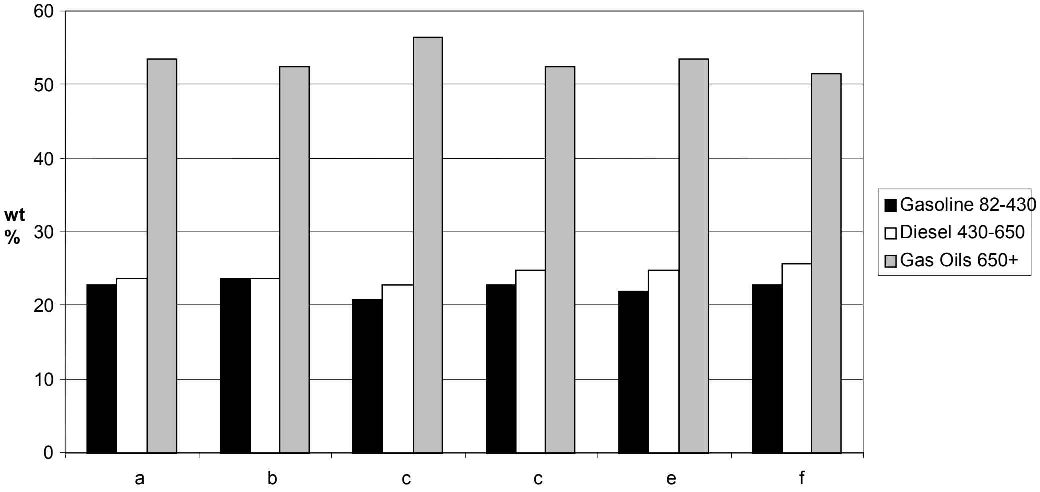


Figure 61 - SimDis Comparison for 6' Drum vs. 3' Drum

Drum temperature profiles also compare favorably for the two drums. Figure 62 shows the drum temperature profiles for one of the fluid 3 runs in the 3' drum. These may be compared to Figure 67 through Figure 89, shown later in this section, for the 6' drum. When scaled for height, the results look comparable.

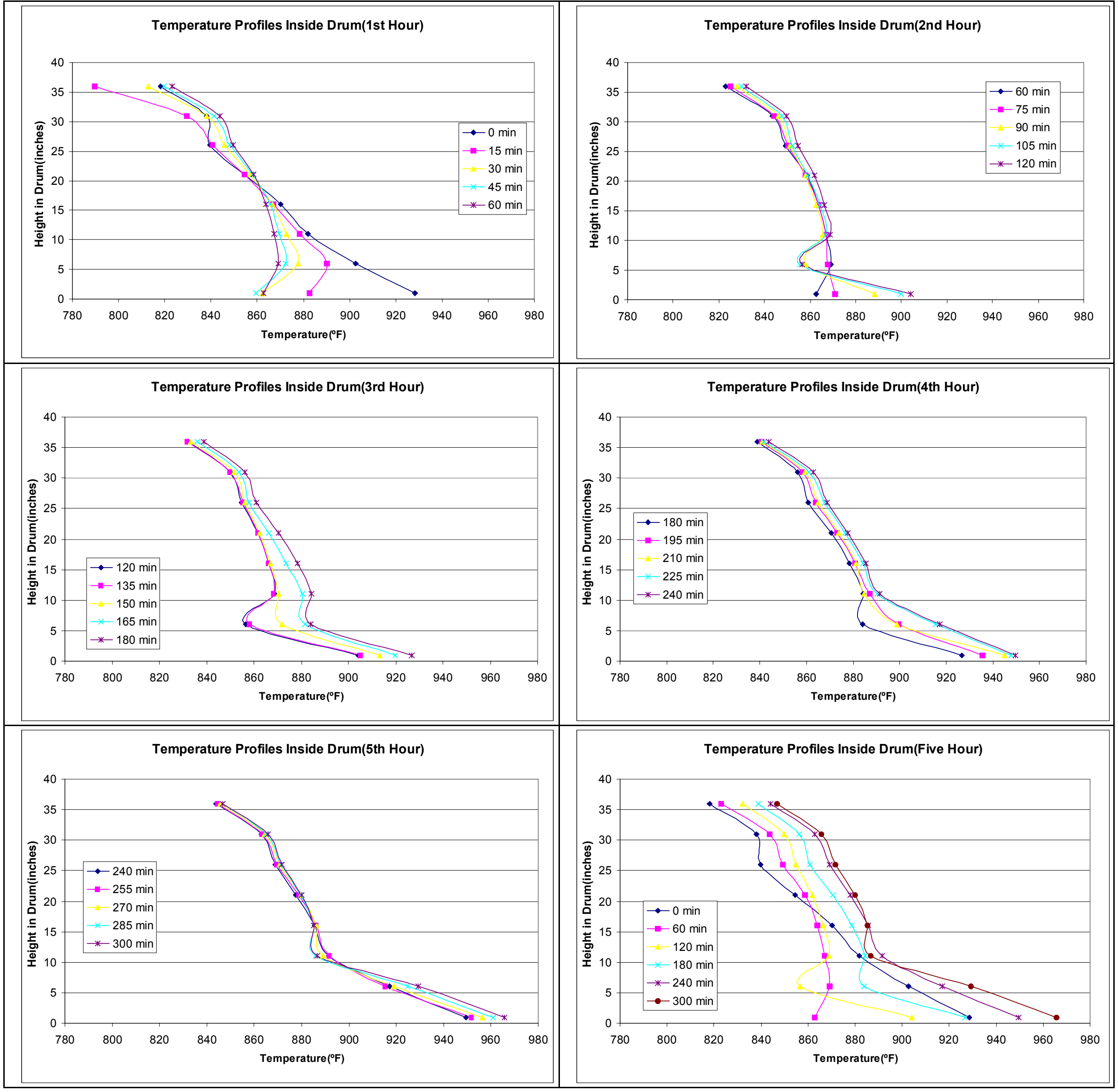

Temperature Profiles Inside Drum(1st Hour)
Temperature Profiles Inside Drum(2nd Hour)
Temperature Profiles Inside Drum(3rd Hour)
Temperature Profiles Inside Drum(4th Hour)
Temperature Profiles Inside Drum(5th Hour)
Temperature Profiles Inside Drum(Five Hour)

Figure 62 - Drum Temperature Profiles

Coke morphologies do show some differences between the 3' drum and the 6' drum, due to differences in the fluid velocities that were used. The higher feed and steam rates in the foaming runs for the 6' drum lead to a stronger tendency toward shot coke formation, and appear to lead to more variation in coke morphology with axial position in the drum.

d) Shakedown Tests using Fluid 2 Resid

The shakedown tests for the new foaming apparatus were conducted with Fluid 2. Four runs were made. As shown in Figure 64, these runs were controlled using fluid temperature, as was done in the pilot unit parametric studies. For the first run, temperature fluctuations (± 20°F) were seen. The second run was controlled better; however, for the third run it was decided to monitor the fluid temperature while adjusting the heat input using the skin temperatures recorded prior to entering the drum because they did not vacillate as much as the fluid temperatures. These runs provided an understanding as to the best way to control the tests. As a result of these tests, it was decided to control the tests using skin temperature trying to achieve steady state conditions (fluid temperature) after a one-hour period. Future efforts will include work to automate the control.

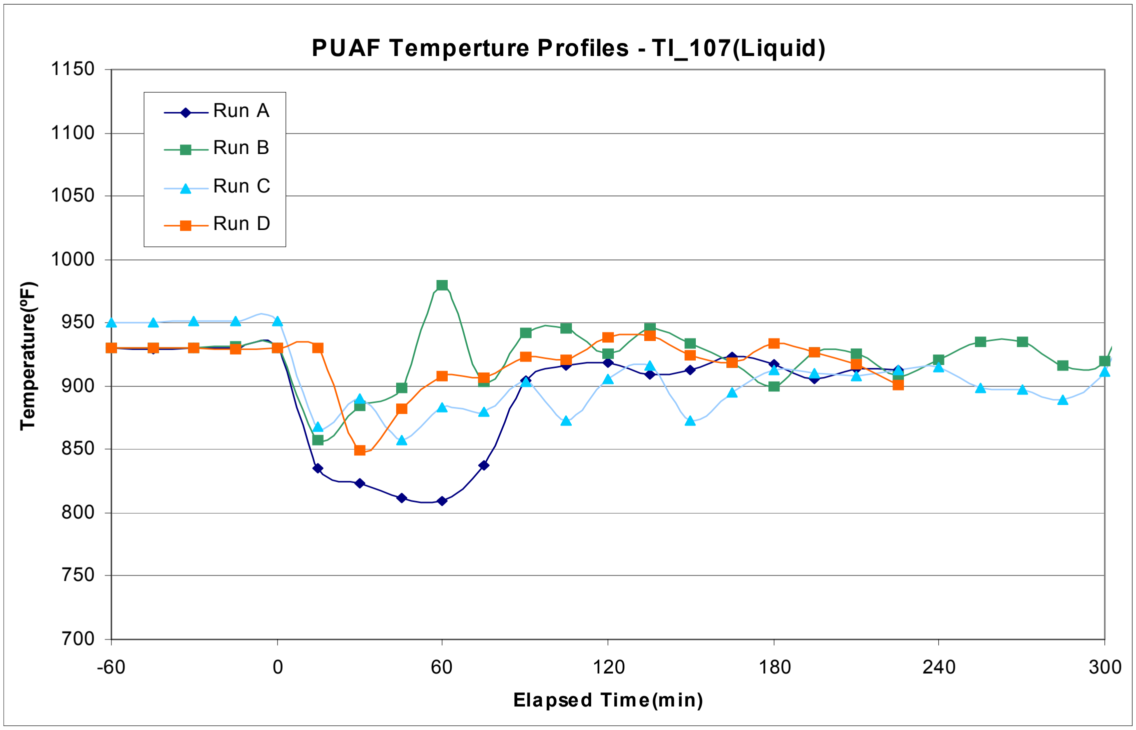


Figure 63 - Fluid 2 Anti-Foaming Runs – Liquid Temperature Profiles

These tests were also used to determine the best way to illustrate the data and to gain some insight as to what the value is for foam density. As shown in Figure 64 and Figure 65 for the Fluid 2 1 run, the data is plotted as density in the drum versus height at a given time increment and as density vs. time for a given height in the drum.

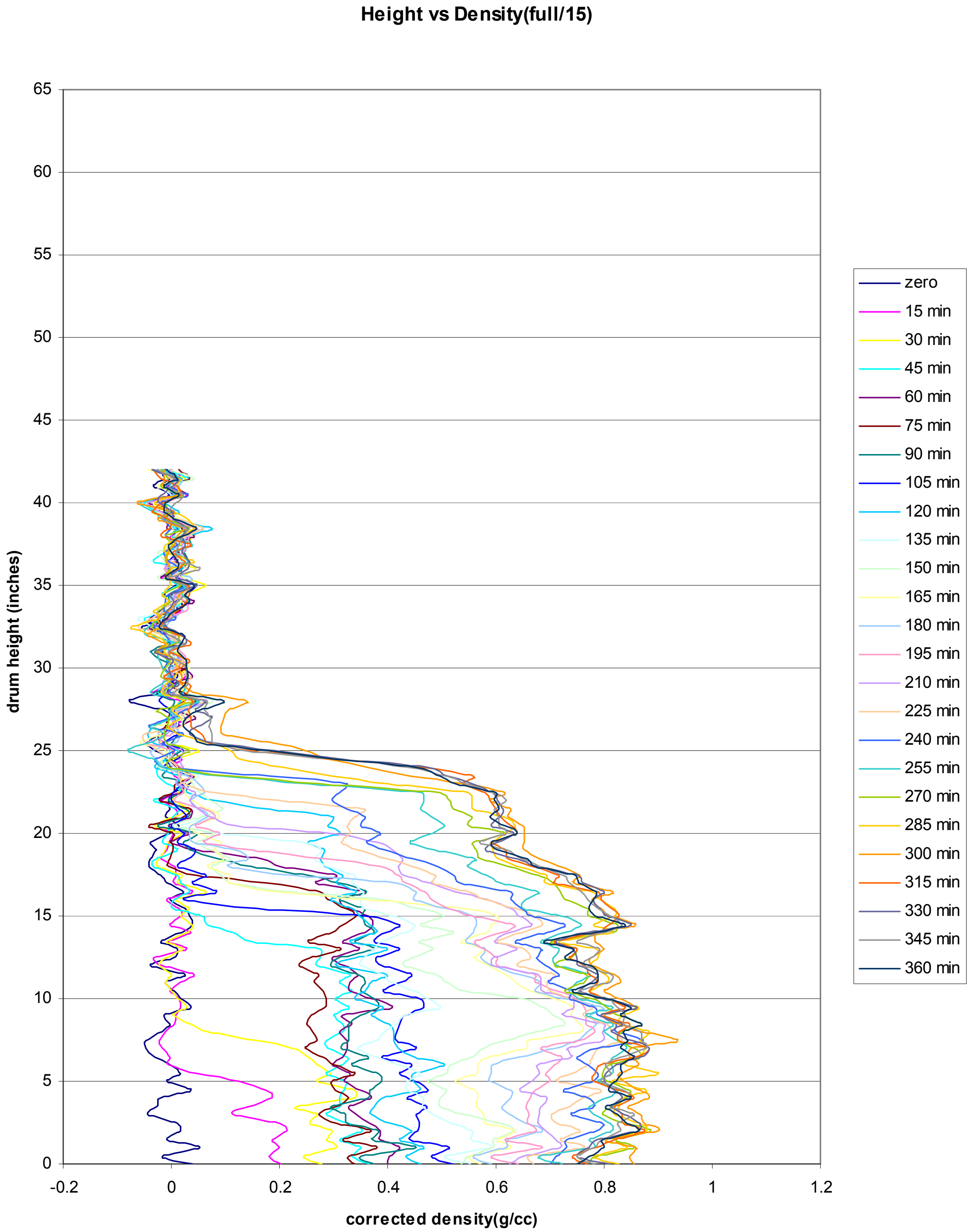


Figure 64 - Height vs. Density at various times for Fluid 2

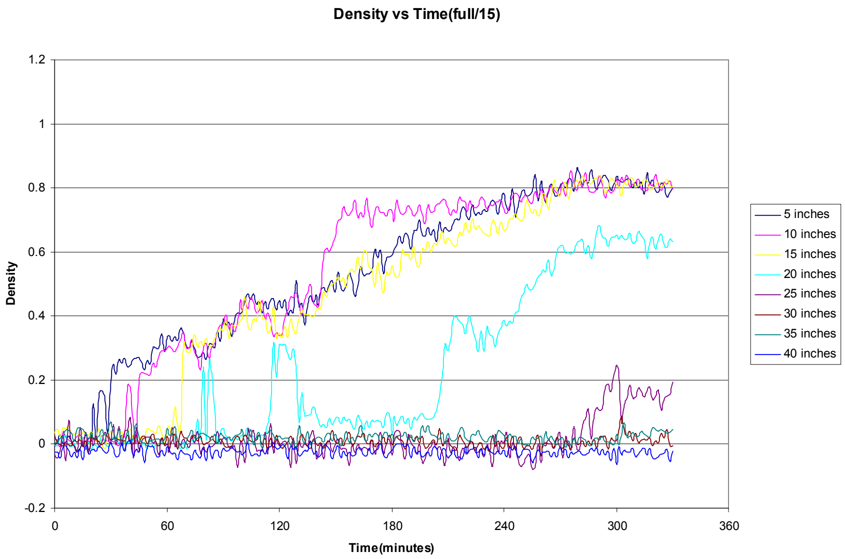


Figure 65 - Density vs. Time for a Given Height for Fluid 1

Figure 65 can also be used to illustrate foam collapses and foam suppressions that were observed during the run. Examination of the density profile for a point in the drum 20 inches from the bottom shows that at approximately 70 minutes into the run a foam column with a density of 0.2 gm/cc was observed. After about 20 minutes, this column collapsed on its own. After 20 minutes it appeared again with a density of approximately 0.3 gm/cc. After 30 minutes, this column collapsed for another 35 minutes before growing again. After this collapse, the density of this column continued to increase until the end of the test. To determine whether a foam column could be collapsed with the 100,000 cSt antifoam, a large dose of antifoam (9 cc) was injected 244 minutes into the run. Note that the density at the 25 inch level in the drum was suppressed to 0.2 gm/cc while the density at the 30 inch level was suppressed to 0 gm/cc. Other examples of this phenomenon were observed in tests conducted later where as much as 24 inches of foam column was collapsed. It was decided that in future tests, antifoam would be injected continuously at a rate of 0.1 ml/min when the foam level reached the 52-inch mark in the drum (two-thirds full). The antifoam injection would continue until the foam was suppressed.

e) Reproducibility of Data using Foaming Test Apparatus

To show that reproducible results could be generated with the new facility, two runs were made using Fluid 3. These tests were conducted at a feed rate of 2400 gms/hr, and steam/nitrogen velocities of 40 cc and 0.25 scfh, respectively. As shown in Figure 66, a steady state temperature of 930^{o}F was achieved after one hour. Also note (see Figure 67 through Figure 88) the similarities in the temperatures recorded at 8 different locations in the drum as a function of time. These temperatures were recorded with an internal thermocouple that took readings approximately 11 inches apart starting with TI-215 at the bottom of the drum and ending with TI-208 at the top of the drum. Good agreement can also be seen when the same data is used to plot the temperature profiles in the drum (see

Figure 67 through Figure 86) for both runs. The pressure profiles, drum and delta p, are shown in Figure 87 to Figure 88.

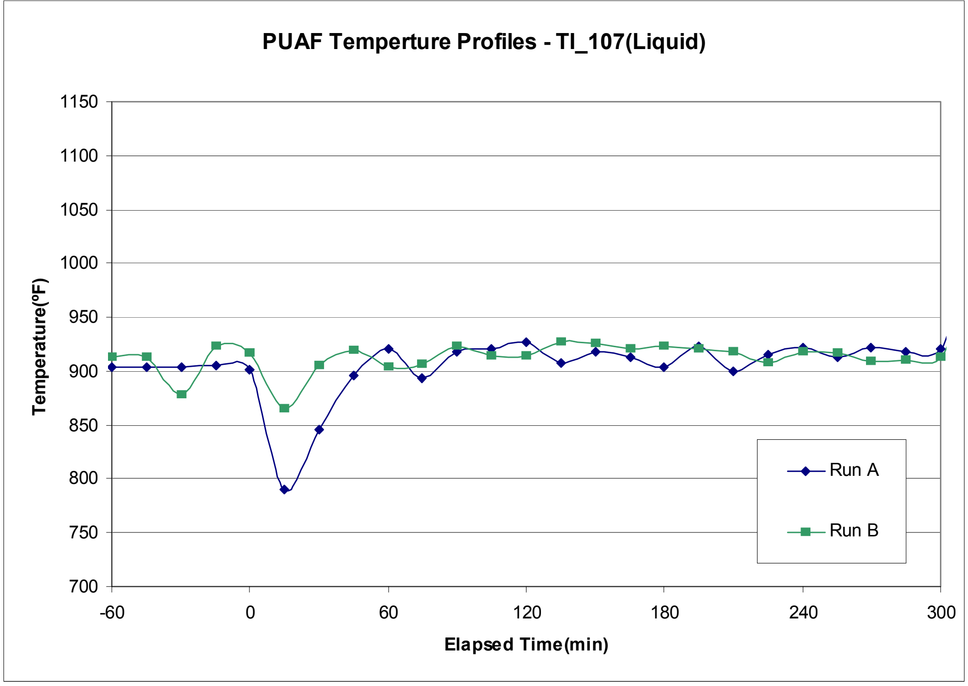


Figure 66 - Fluid 3 Anti-Foaming Runs - Liquid Temperature Profiles

The yield data and SimDis comparison for these runs was excellent. These results also compared very well with those generated using the 3' drum for the parametric runs

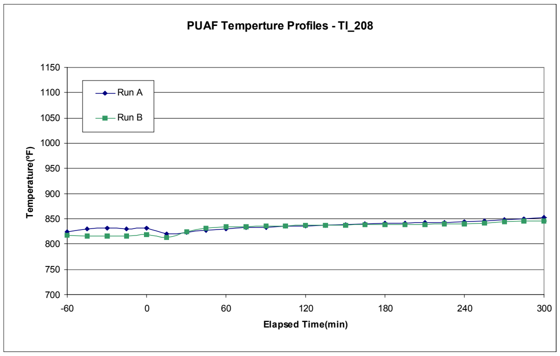


Figure 67 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

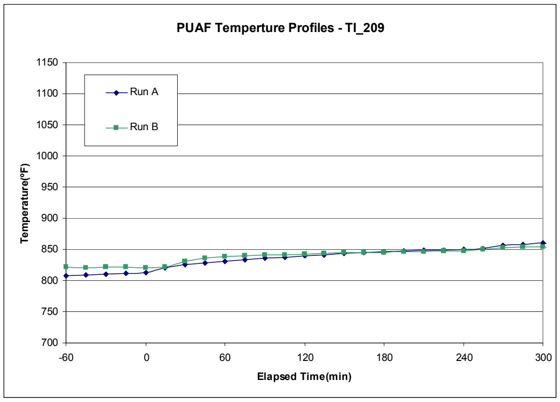


Figure 68 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

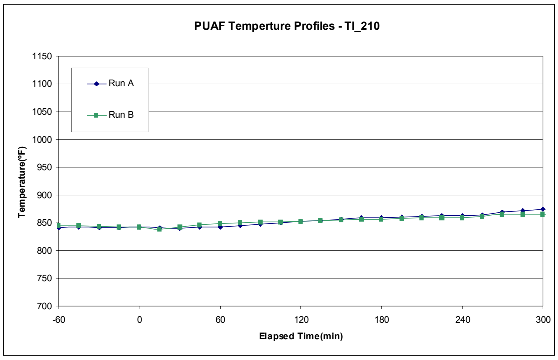


Figure 69 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

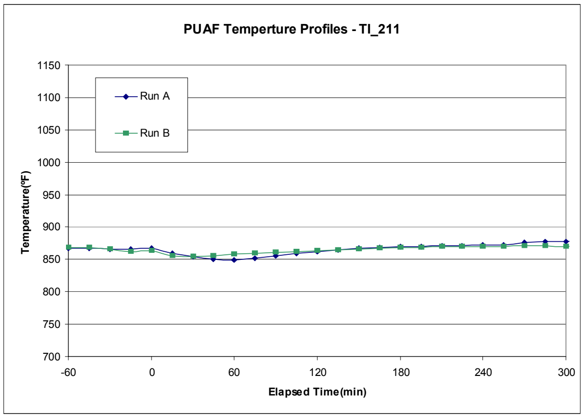


Figure 70 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

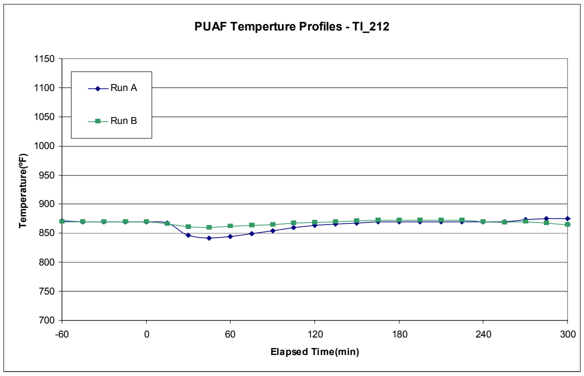


Figure 71 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

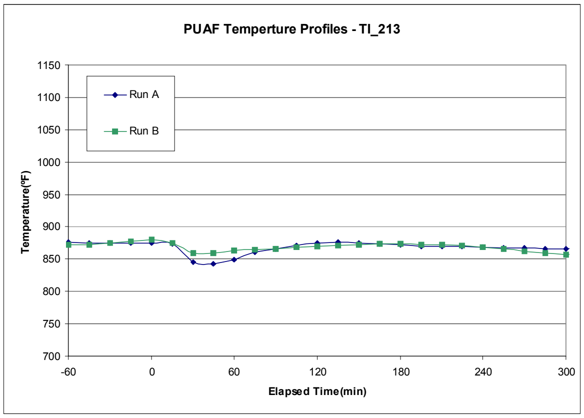


Figure 72 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

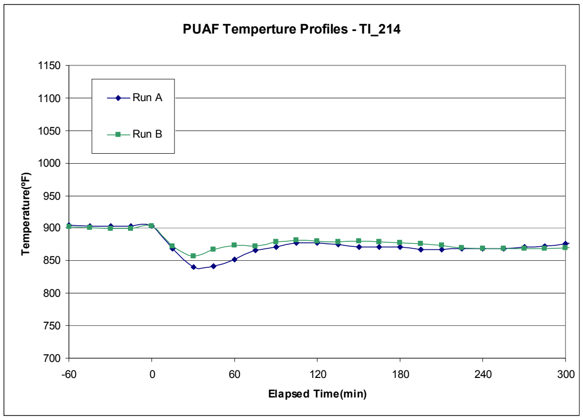


Figure 73 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

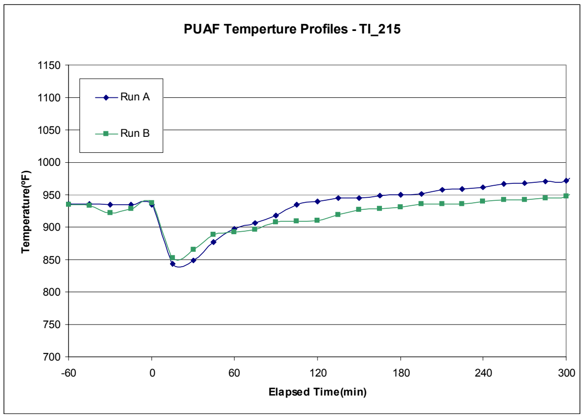


Figure 74 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

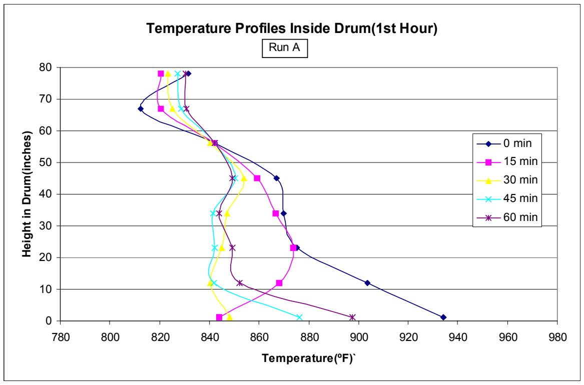


Figure 75 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

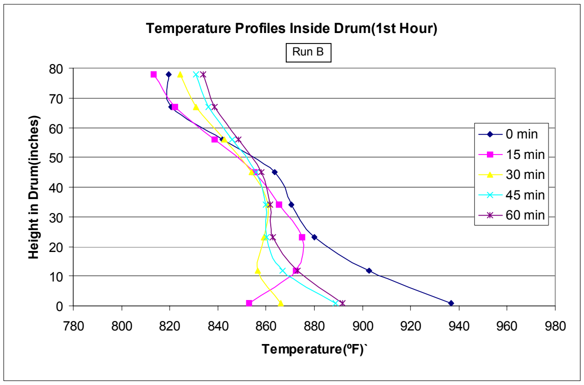


Figure 76 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

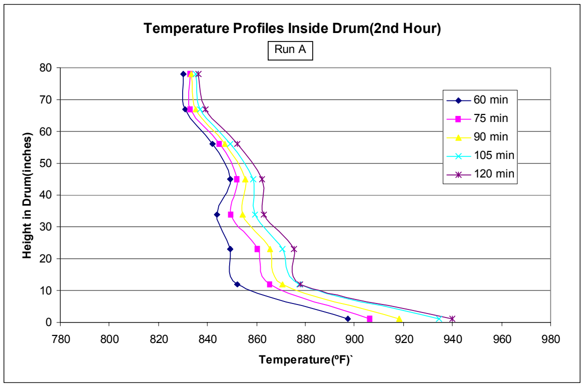


Figure 77 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

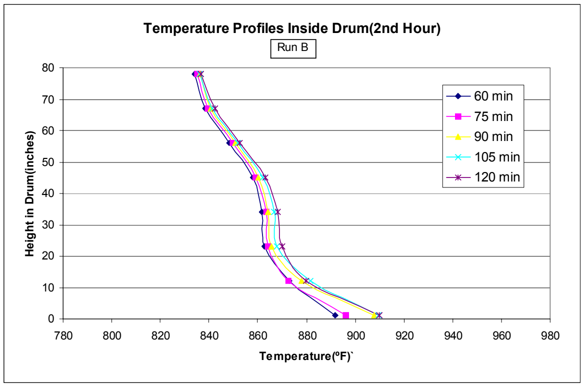


Figure 78 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

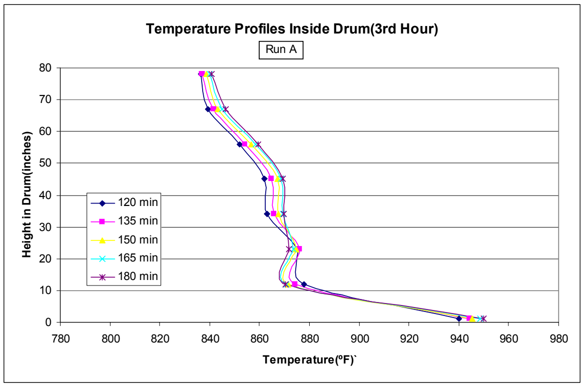


Figure 79 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

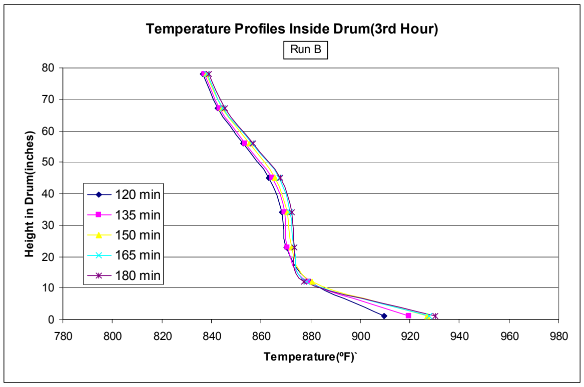


Figure 80 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

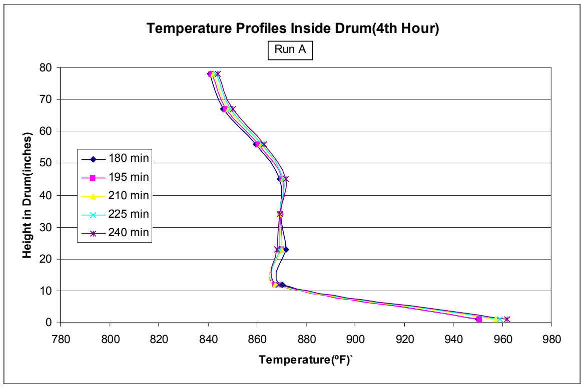


Figure 81 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

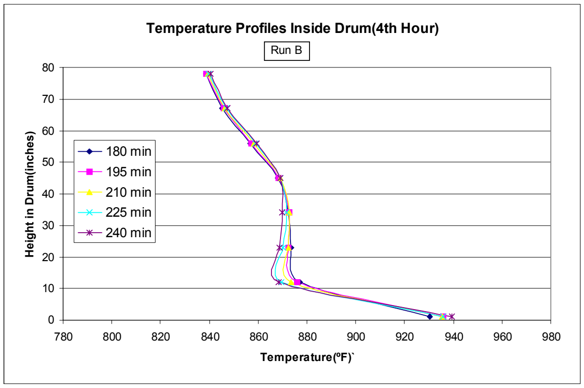


Figure 82 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

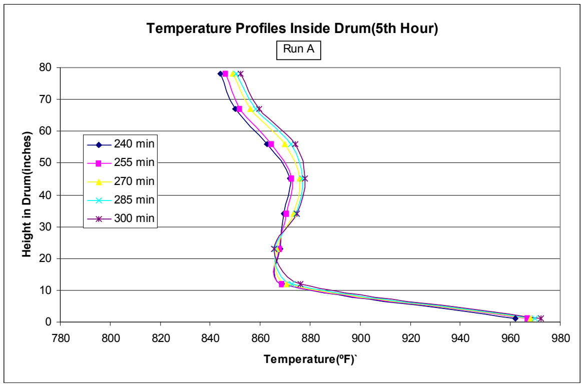


Figure 83 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

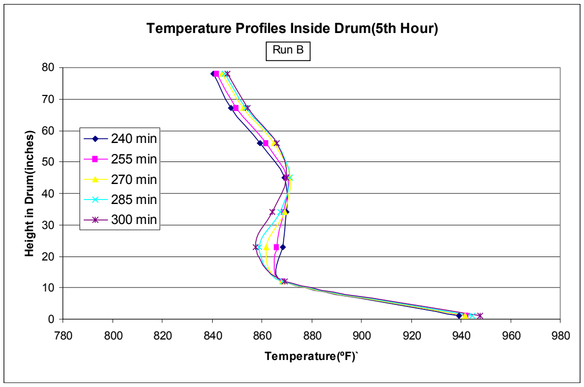


Figure 84 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

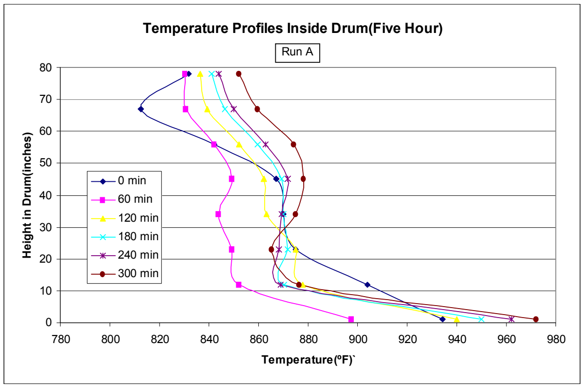


Figure 85 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

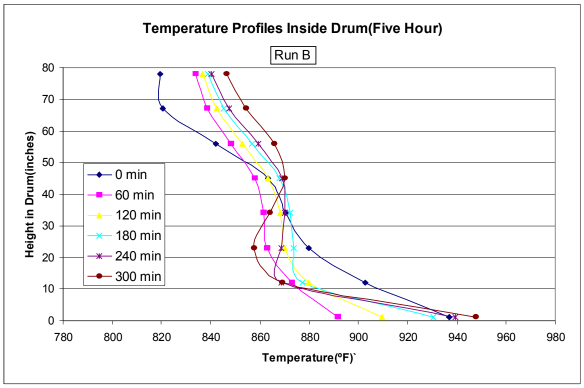


Figure 86 - Fluid 3 Anti-Foaming Runs – Drum Temperature Profiles

As shown in Figure 89, the gas volume trends for the produced gas were nearly identical. The total volumes produced during the Fluid 3 runs a and b were 10.71 and 10.23 scf, respectively.

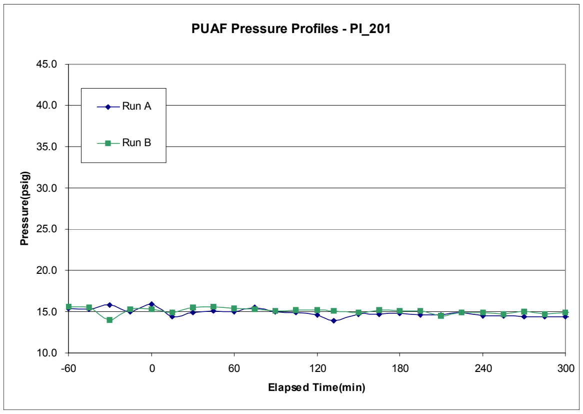


Figure 87 - Fluid 3 Anti-Foaming Runs – Drum Pressure Profiles

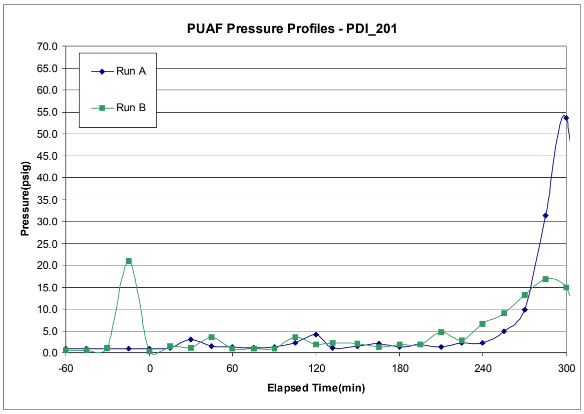


Figure 88 - Fluid 3 Anti-Foaming Runs – Drum Pressure Profiles

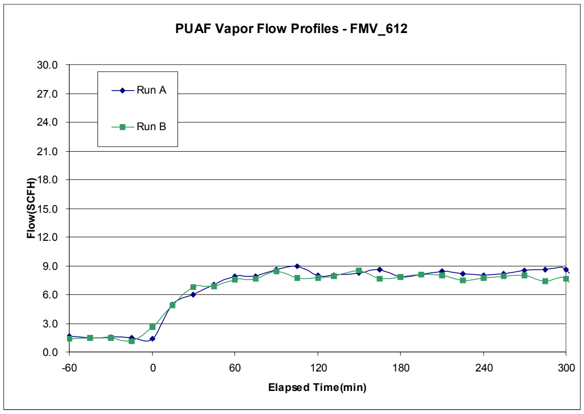


Figure 89 - Fluid 3 Anti-Foaming Runs – Drum Vapor Flow Profiles

The coke morphology was compared for both runs. In both runs, there was shot at the bottom. The coke at the top was a denser conglomerated shot. Again, good agreement was obtained. Plots of density vs. elapsed time at 5-inch increments were made and are shown in Figure 94 and Figure 95 for the runs a and b respectively. The trends are similar; however, antifoam was injected at 38 minutes and at 88 minutes during the Fluid 3 run. These injections suppressed the foam column and could have impacted the density traces. Another run should be made without injecting any antifoam for comparison.

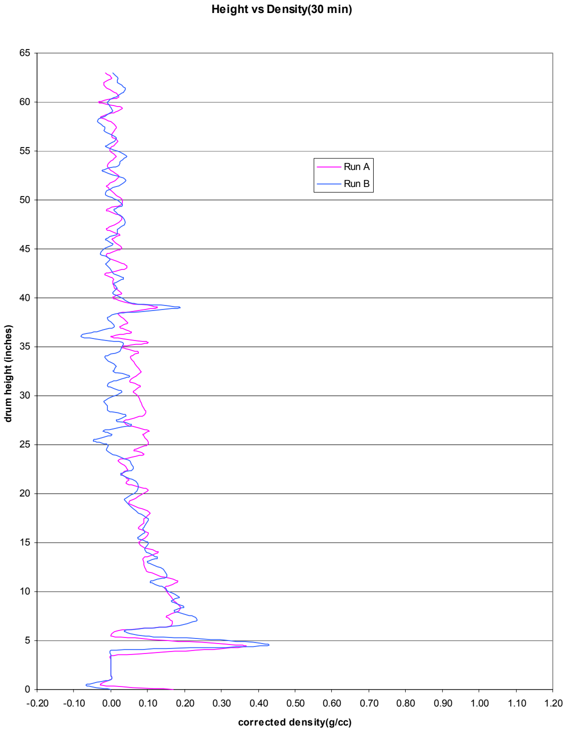


Figure 90 - Fluid 3 Anti-Foaming Runs – Height vs. Density (30 min)

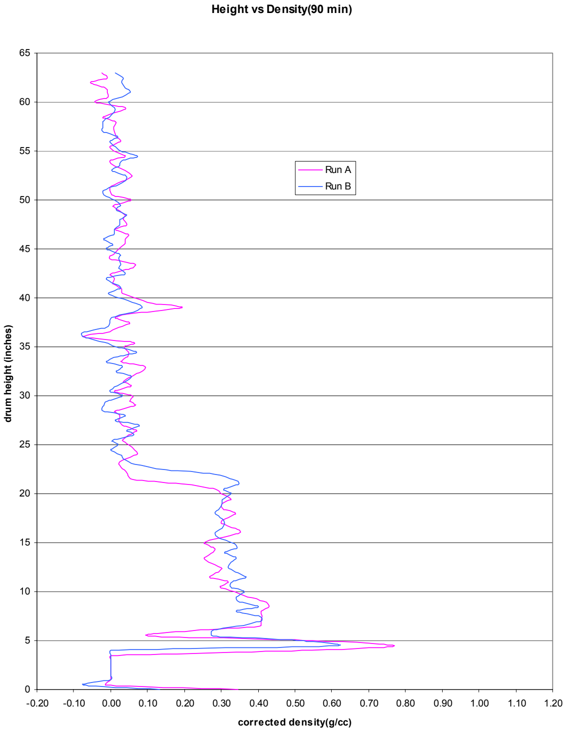


Figure 91 - Fluid 3 Anti-Foaming Runs – Height vs. Density (90 min)

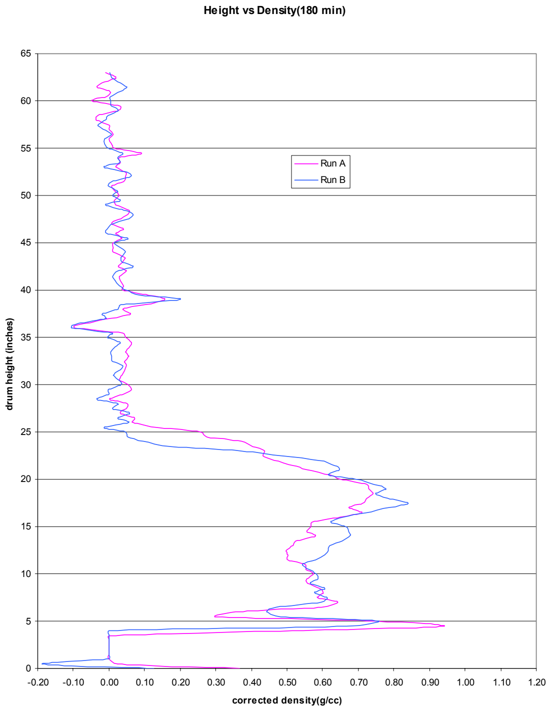


Figure 92 - Fluid 3 Anti-Foaming Runs – Height vs. Density (180 min)

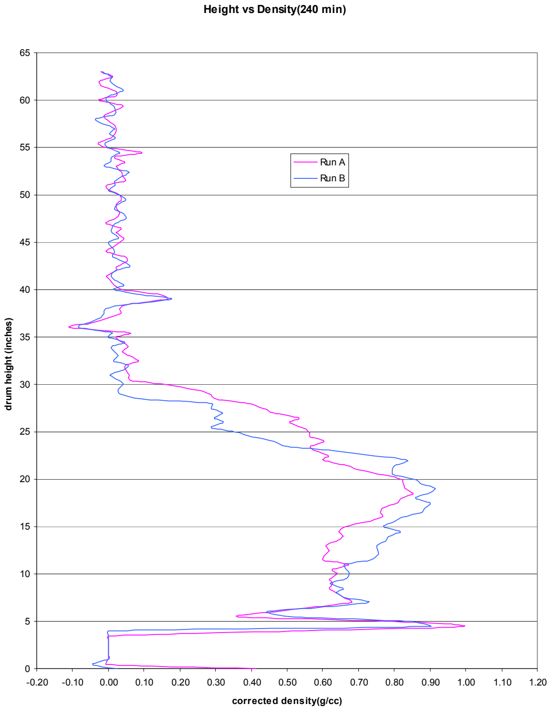


Figure 93 - Fluid 3 Anti-Foaming Runs – Height vs. Density (240 min)

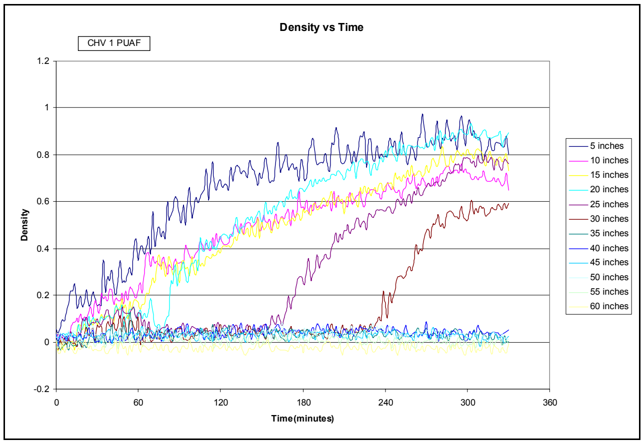


Figure 94 - Fluid 3 Anti-Foaming Runs – Density vs. Time (5 inch increments)

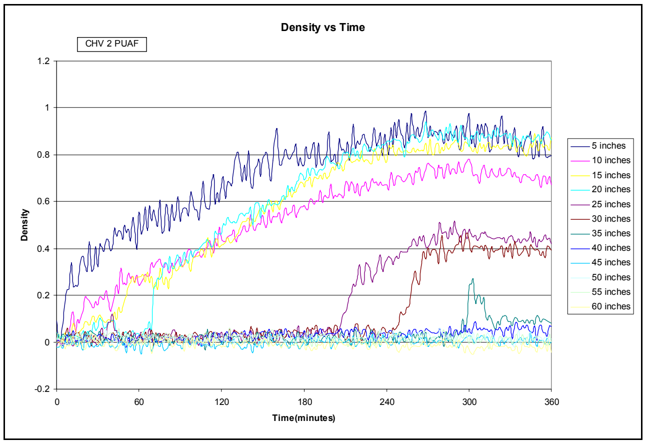


Figure 95 - Fluid 3 Anti-Foaming Runs – Density vs. Time (5 inch increments)

f) Effects of Operating Conditions on Foaming

This section will discuss the effects of operating conditions on foaming. The impact of pressure and temperature will be discussed first. Comparisons will be made for the four runs made using Fluid 3, at two temperatures for pressures of two pressures. Feed rate variations will be discussed next, for tests where feed rates of 2400 and 3600 gm/hr were used. For the Fluid 1 resid, two tests were conducted at 2400 gm/hr and one at 3600 gm/hr while for the Fluid 4 resid, one test was conducted at a rate of 2400 gm/hr and four were conducted at a rate of 3600 gm/hr. In one of the Fluid 4 runs the antifoam was injected in the feed. It will be compared to another Fluid 4 run where the antifoam was injected overhead. For one of the Fluid 1 runs, steam and Nitrogen velocity were varied. These results will be discussed as well.

3. Effect of Temperature and Pressure on Foaming

Four runs were made using the Fluid 3. Two runs were made at a high temperature and at low and high pressures, while runs were made at a low temperature and at a low and high pressure. The control for these runs was very good.

One of these runs was used to establish a value for the foam density for this resid. As shown in Figure 96, a foam column 54 inches in height with a density of approximately 0.1 gm/cm existed after one hour. Since the height continued to grow, antifoam was injected continuously after 71 minutes of coking and wasn't stopped until the 121 minute mark. As shown in Figure 97, by 90 minutes the foam height was suppressed 14 inches. A total of 1.4 cc of antifoam had been injected. After another 44 minutes of antifoam injection (2.5 additional cc's) the foam height was suppressed an additional 10 inches for a total suppression of 24 inches, as shown in Figure 98. This suppression can also be seen on the density versus elapsed time plot shown in Figure 100 through Figure 105. For these runs, based on what was being collapsed, a good number for foam density is less than 0.1 gm/cc to 0.2 gm/cc.

The effects of pressure and temperature can be seen by examining the four runs presented in Figure 99 after 60 minutes of coking. Both temperature runs at the high pressure behaved similarly. Very little foaming was observed. However, the 15 psig runs had a foam column of approximately 0.1 gm/cc that filled two-thirds of the drum. Until additional runs are made, one can only conclusively conclude that more foaming occurred at lower pressures. These tests also showed that more foaming occurred at lower temperatures. Further testing is planned on the next phase of the study.

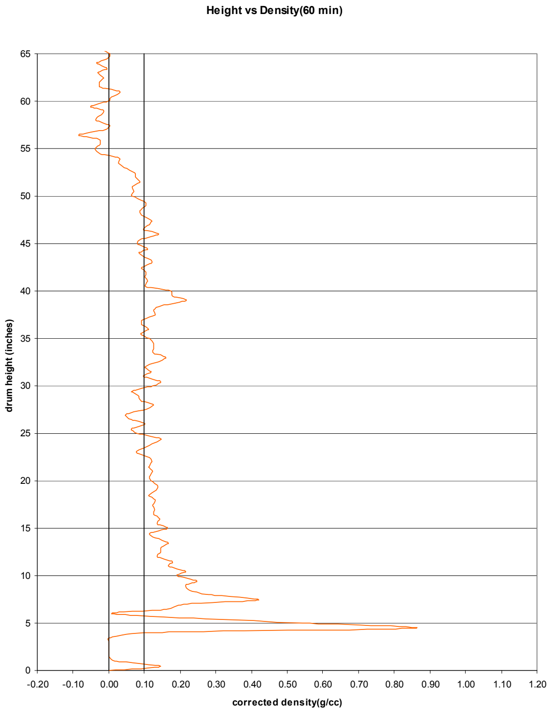


Figure 96 - Anti-Foaming Runs – Height vs. Density (Temperature and Pressure Effects on Foaming)

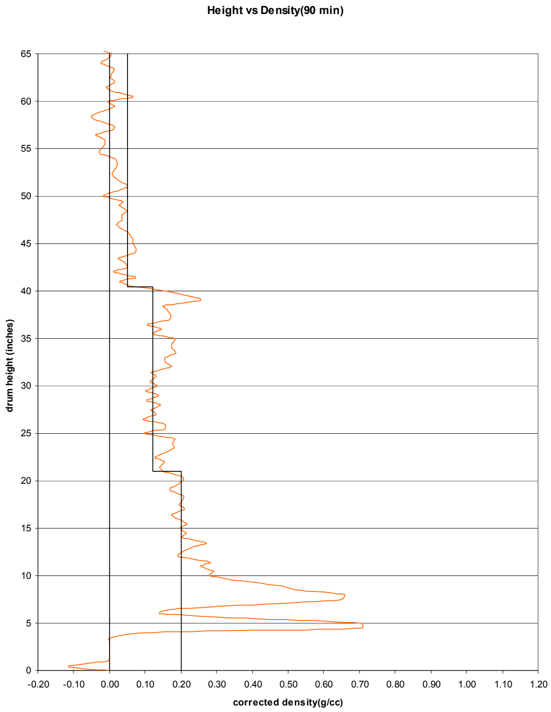
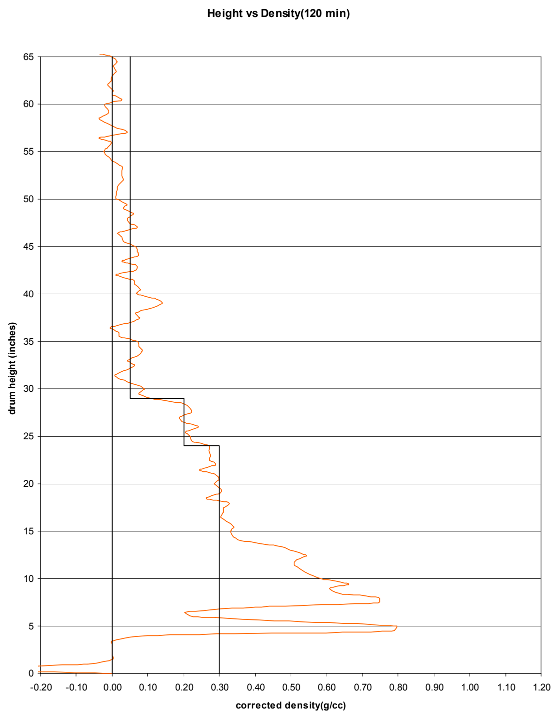


Figure 97 - Anti-Foaming Runs – Height vs. Density (Temperature and Pressure Effects on Foaming)



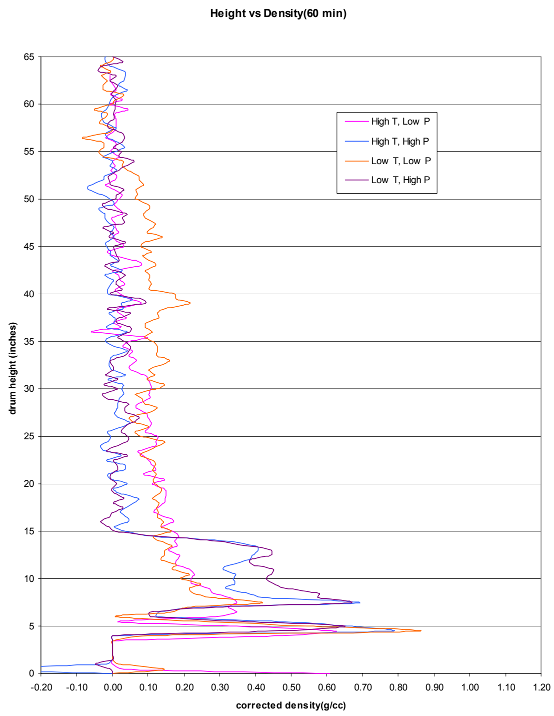


Figure 98 - Anti-Foaming Runs – Height vs. Density (Temperature and Pressure Effects on Foaming)

Figure 99 - Anti-Foaming Runs – Height vs. Density (Temperature and Pressure Effects on Foaming)

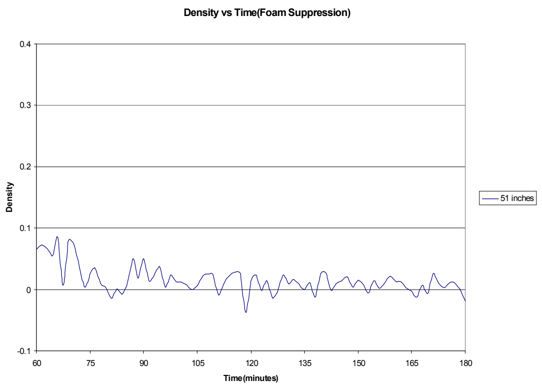


Figure 100 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

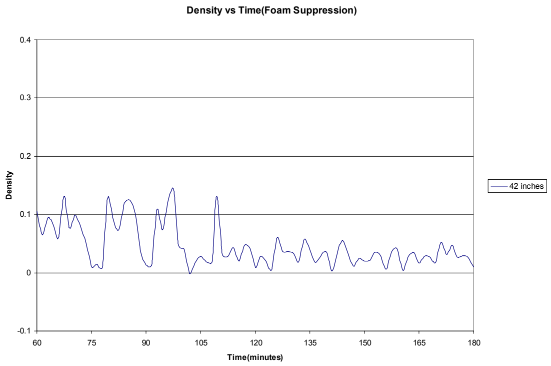


Figure 101 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

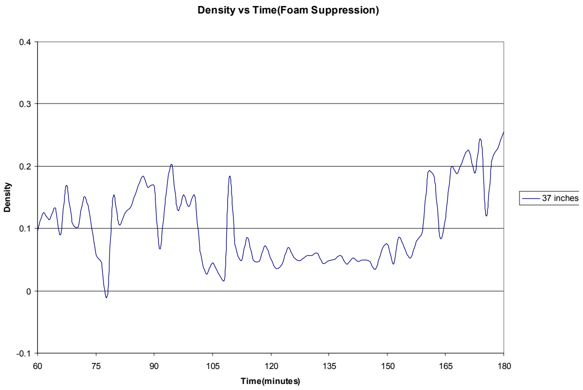


Figure 102 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

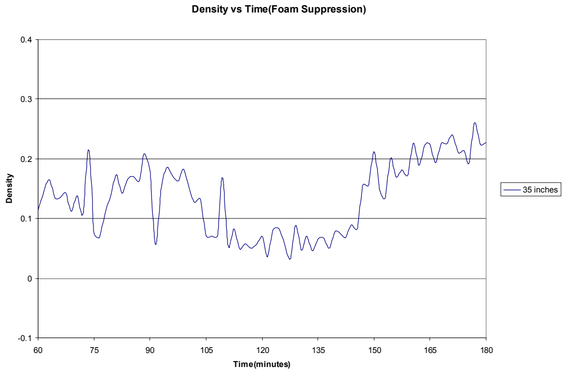


Figure 103 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

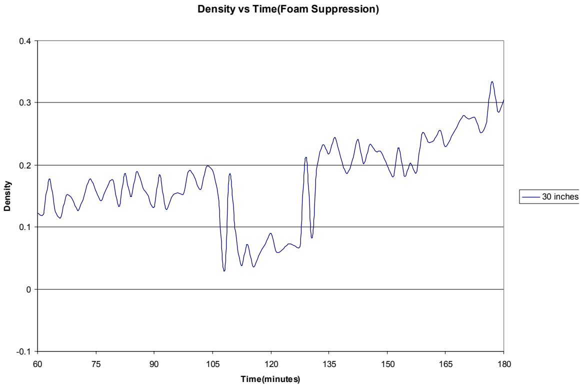


Figure 104 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

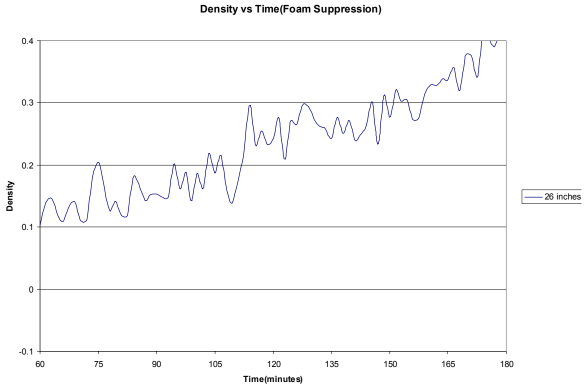


Figure 105 - Anti-Foaming Runs – Density vs. Time (Foam Suppression)

(1) <u>Feed Rate Variation (Fluid 4 and Fluid 1 Runs) – Effect of Superficial Vapor Velocity</u>

The effect of superficial vapor velocity can be seen from the runs made using the same resid at feed rates of 2400 gm/hr and 3600 gm/hr respectively. Both runs had the same Nitrogen velocity (0.25 scfh); however, the steam velocity for one of the runs was twice (40 cc/hr vs. 20 cc/hr) that of the other. Note in Figure 107 and Figure 108 that at when the resid rate was doubled, the height of the density columns more than doubled. One can also note that the densities of the coke in the drum are less for the higher vapor velocities.

Similar effects, as shown in Figure 109 and Figure 110, were observed for the second resid used. However, as discussed below, the steam velocity in this test was increased to 40 cc's after one hour and to 60 cc's after two hours. Additional tests should be made under identical conditions as conducted with the first.

The steam and nitrogen velocities for the Fluid 1 2 run are shown in Figure 106. At the start of the test, the feed rate was 3600 gm/hr with the steam velocity at 20 cc/hr and Nitrogen velocity at 0.25 scfh. After one hour the steam velocity was increased to 40 cc/hr and then increased again to 60 cc/hr after 2 hours. The Nitrogen rate was held constant at 0.25 scfh for the first 120 minutes, and then increased to 0.5 for 30 minutes before being raised to 1 scfh for the duration of the test. This run foamed over plugging the overhead lines. A drum of very loose shot was made, some one-quarter inch in size with some pebble looking shot that was three-quarters of an inch in diameter.

Examination of Figure 111 (height versus density as a function of time) showed the change in height as a function of time to be decreasing (growing at a rate of 0.1 in/min) over the last 30 minutes of the first hour of coking. However, when the steam velocity was increased to 40 cc/hr the height in the drum increased by a factor of 3 to approximately 0.3 in/min. When the Nitrogen rate was increased from 0.5 to 1 scfh after 240 minutes of coking, a new column emerged that had a gradient of 0.1 before the test ended. Additional tests will be conducted in the continuation study to further investigate these effects.

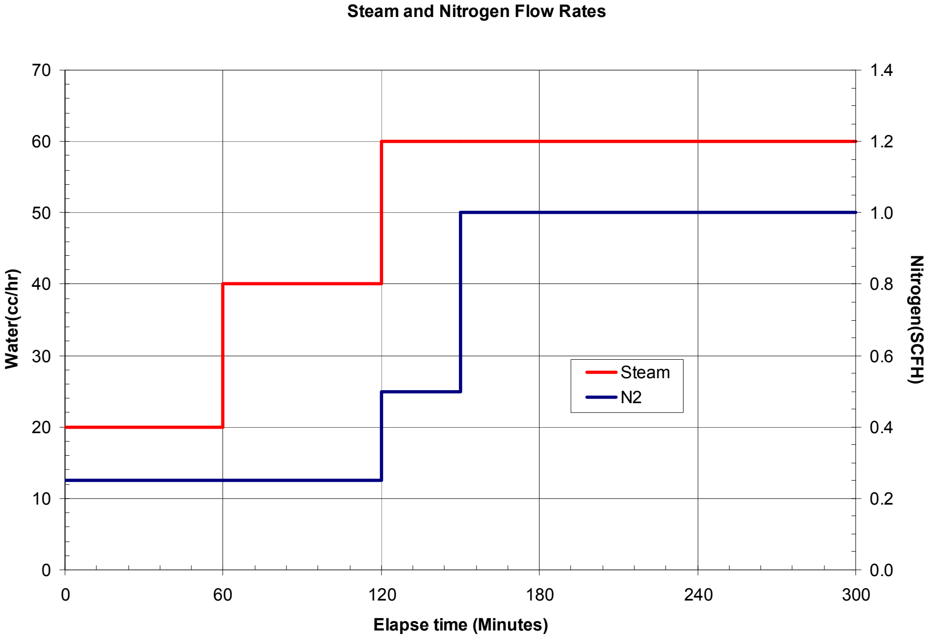


Figure 106 - Anti-Foaming Runs – Steam and Nitrogen Rates

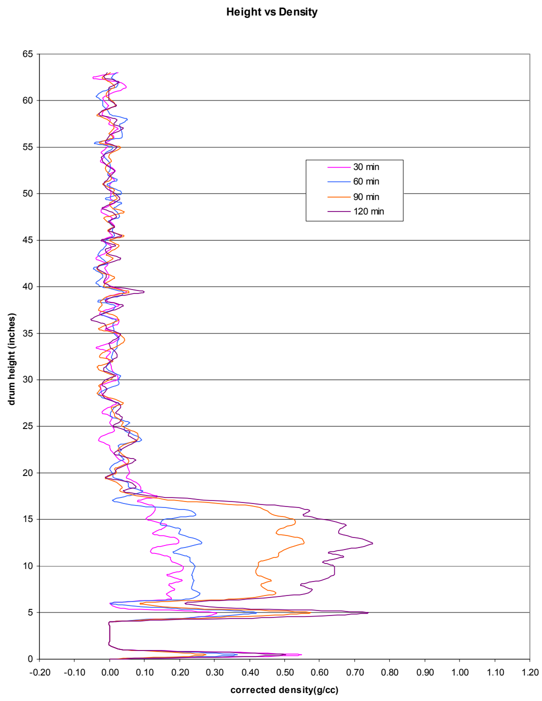


Figure 107 - Anti-Foaming Runs – Height vs. Density (2400 grams/hr feed rate)

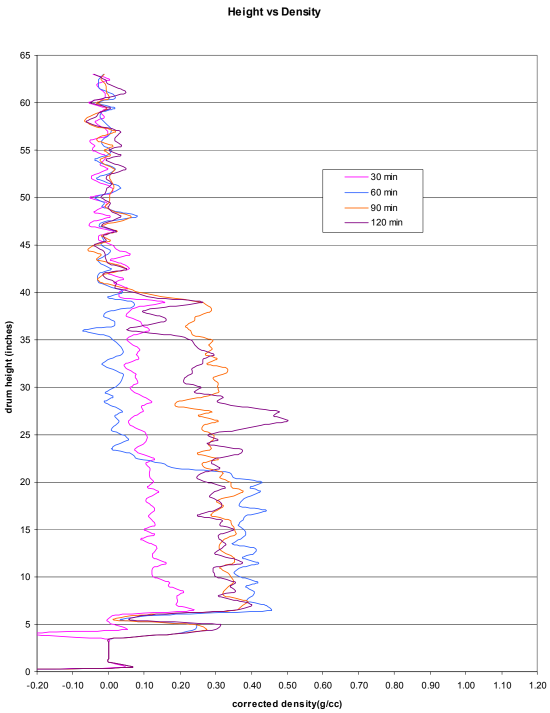


Figure 108 - Anti-Foaming Runs – Height vs. Density (3600 grams/hr feed rate)

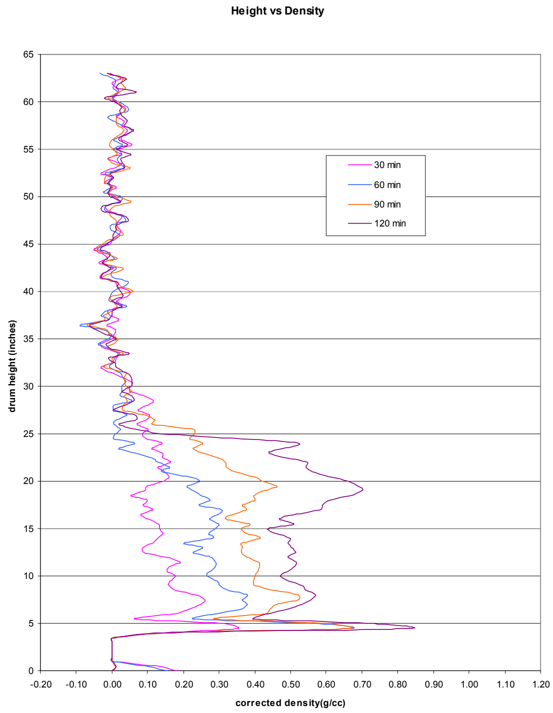


Figure 109 - Anti-Foaming Runs – Height vs. Density (2400 grams/hr feed rate)

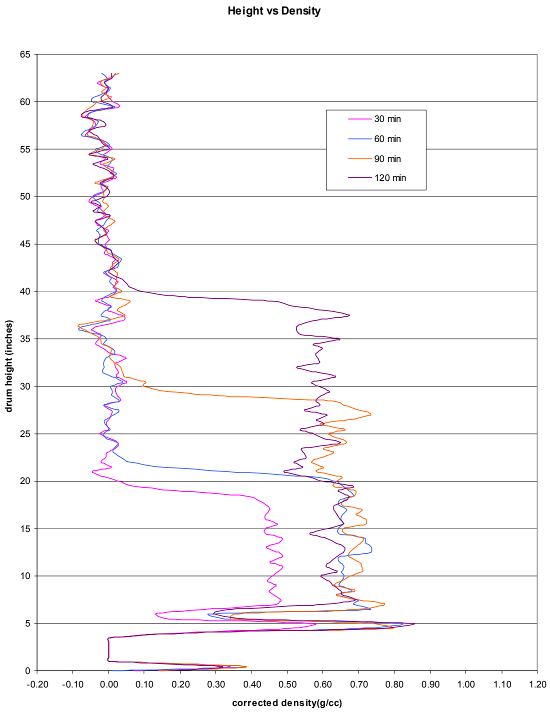


Figure 110 - Anti-Foaming Runs – Height vs. Density (3600 grams/hr feed rate)

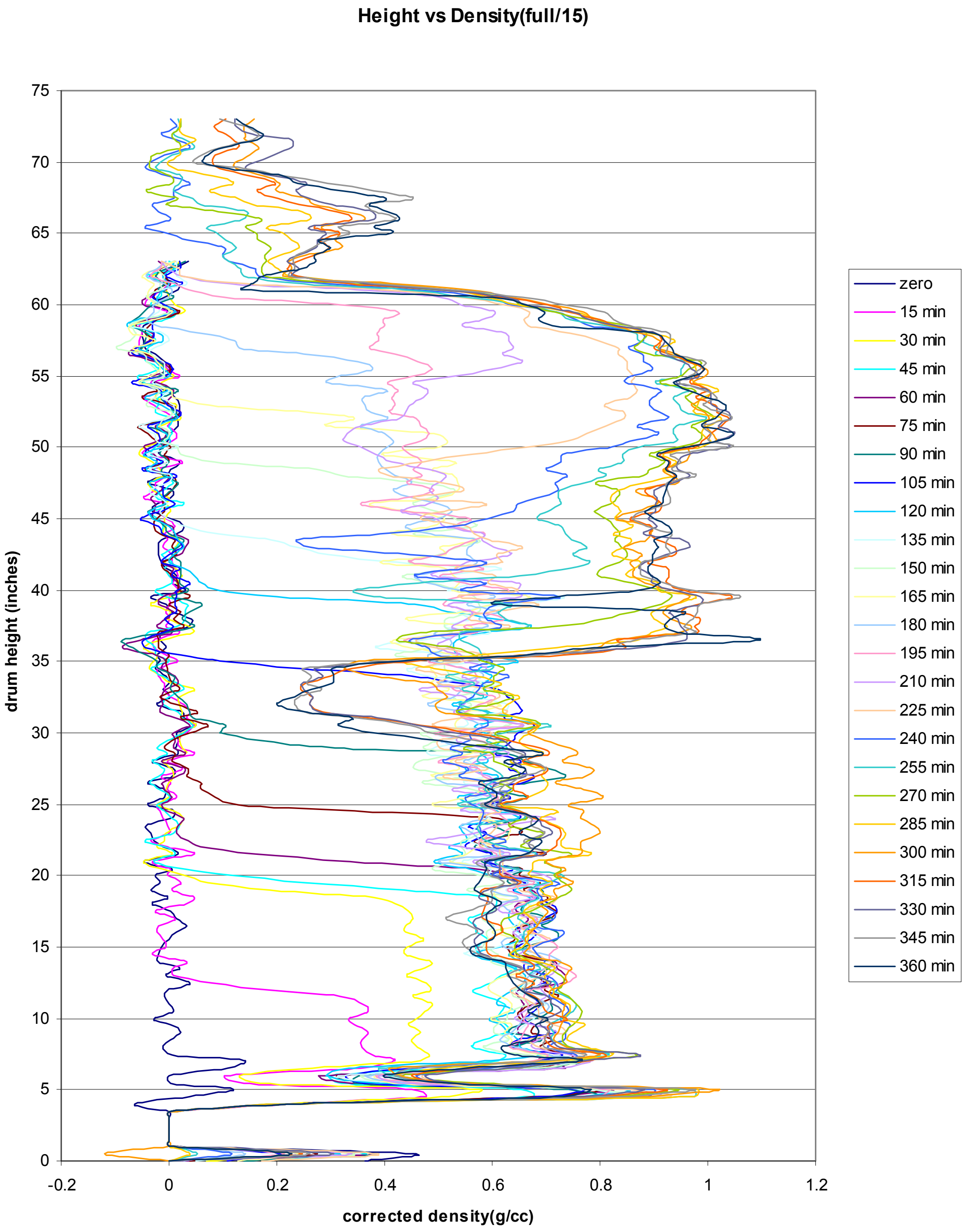


Figure 111 - Anti-Foaming Runs – Height vs. Density (Steam and Nitrogen Effects)

(2) Feed vs. Overhead Injection of Antifoam

Test were conducted to compare feed vs. overhead injection of the 100,000 cSt antifoam. In one rune the antifoam was injected in the feed while the other run was set up to inject overhead. The data for these runs are presented in Figure 112 and Figure 113 as density vs. elapsed time at 5-inch intervals in the drum. Two preliminary observations can be made. First, as shown in Figure 112 the densities fluctuated wildly for the overhead injection case (antifoam injection began at the 165 minute mark) whereas as shown in Figure 113 when the antifoam is injected in the feed the fluctuations are more subdued. It can also be seen that the coke produced when the antifoam is injected in the feed is denser than when it is injected overhead. Other tests will be conducted in the continuation study before any firm conclusions are drawn.

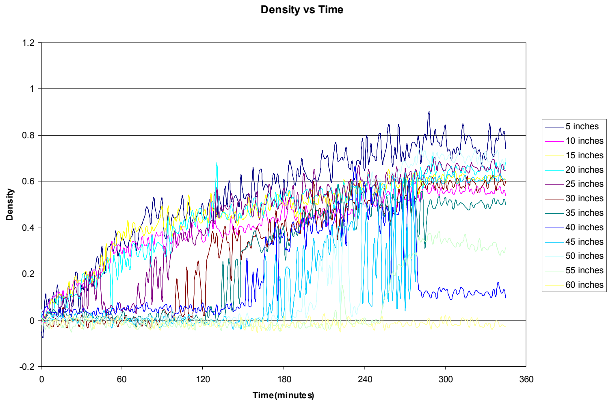


Figure 112 - Fluid 4 Anti-Foaming Runs – Density vs. Time (Overhead Injected Anti-Foam)

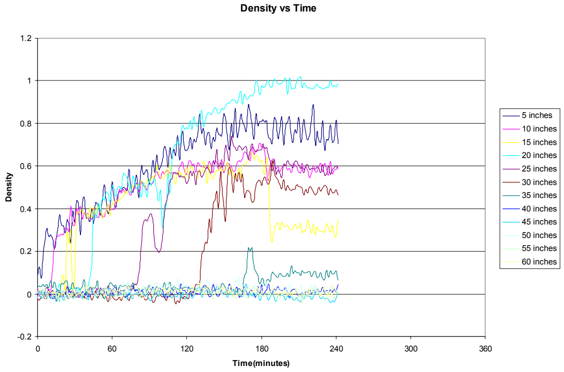


Figure 113 - Fluid 4 Anti-Foaming Runs – Density vs. Time (Feed Injected Anti-Foam)

b) Effect of Resid Composition on Foaming

Feed effects on foaming were studied first for one set of operating conditions. This data is presented as height vs. density plots in Figure 114 through Figure 117 at coking times of 60, 180, 240 and 300 minutes, respectively. On each plot, lines are drawn for a column density of 0.1 and 0.3 gm/cc. Using these density cutoffs, foam heights were calculated for the four feedstocks and are presented in Table 21 and Table 22.

Table 27 - Foam Height Calculations Using a Density of 0.3 gm/cc

Fluid	Time				Antifoam Injected
	60 min	180 min	240 min	300 min	
Fluid 3	30”	14”	10”	9”	Injected at 38 and 88 min
Fluid 4	20”	6”	5”	4”	Injected at 120, 135, & 210 min
Fluid 1	19”	7”	8”	8”	None
Fluid 2	10”	9”	1”	6”	Injected at 240 min

Table 28 - Foam Height Calculations Using a Density of 0.1 gm/cc

Fluid	Time				Antifoam Injected
	60 min	180 min	240 min	300 min	
Fluid 3	13”	9”	6”	7”	Injected at 38 and 88 min
Fluid 4	9”	5”	3”	3”	Injected at 120, 135, & 210 min
Fluid 1	2”	3”	2”	2”	None
Fluid 2	1”	6”	0”	5”	Injected at 240 min

For two of the tests, Fluid 3 and 4, antifoam was injected early in the tests. None was injected in the Fluid 1 test and antifoam wasn’t injected in the Fluid 2 run until the fifth hour. Even with antifoam injection, the Fluid 3 resid was the worst foamer. Fluid 4 would be the second worst followed by Fluid 1 and then Fluid 2. These results concur with what has been seen from the TGA studies. As will be discussed in the Batch Reactor Results section, Fluids 3 and 4 both react more quickly and at a lower temperature than the fluids tested. This implies that more vapor will be created in the furnace tube due to cracking reactions, resulting in a higher vapor velocity entering the drum and thus a higher tendency to foam.

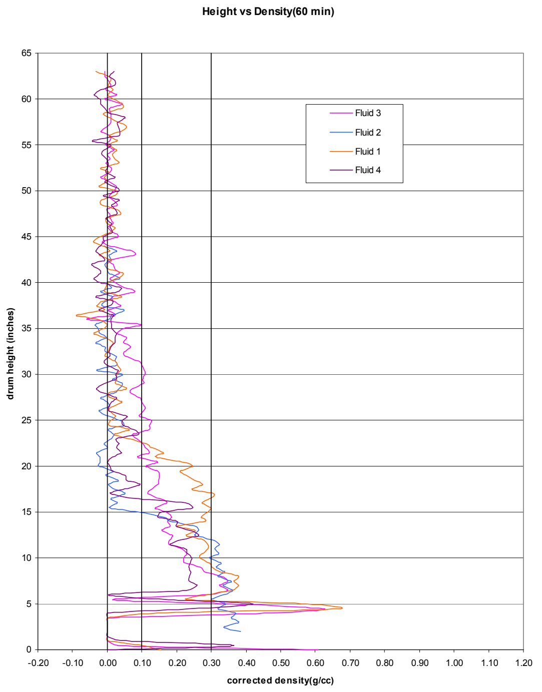


Figure 114 - Anti-Foaming Runs – Height vs. Density (Resid Effects)

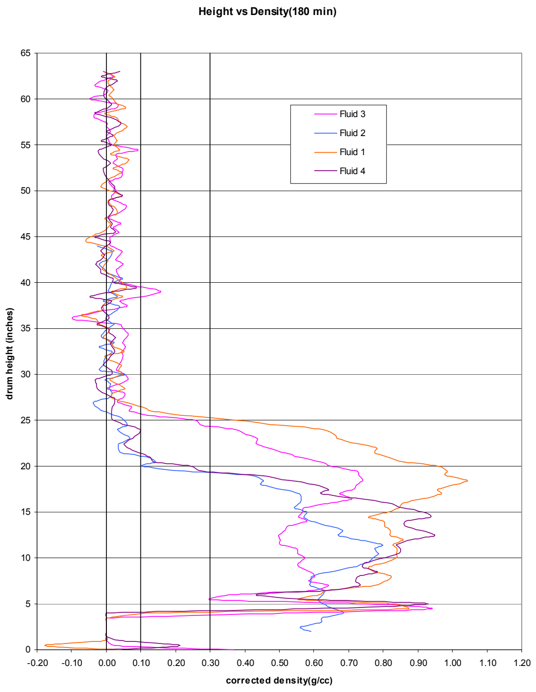


Figure 115 - Anti-Foaming Runs – Height vs. Density (Resid Effects)

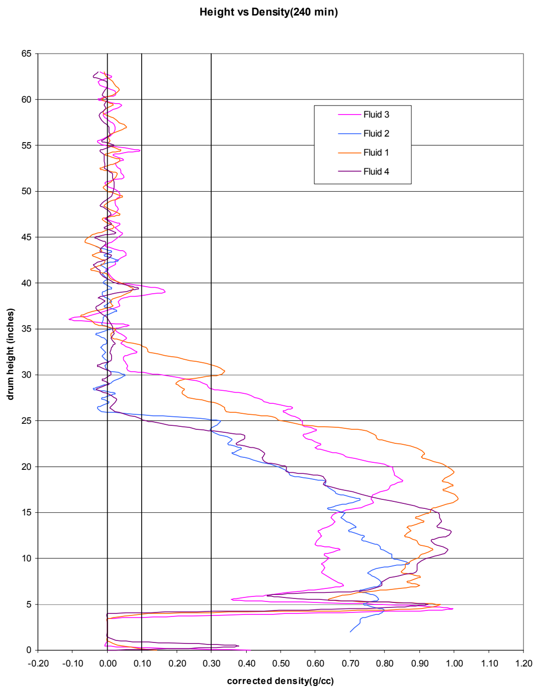


Figure 116 - Anti-Foaming Runs – Height vs. Density (Resid Effects)

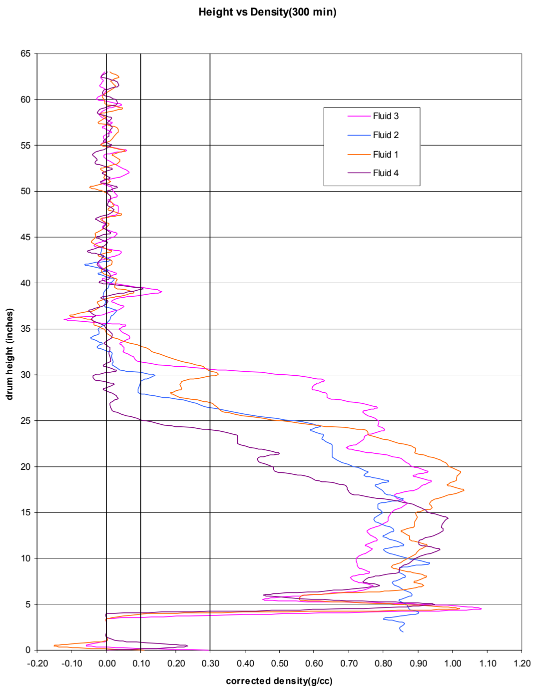


Figure 117 - Anti-Foaming Runs – Height vs. Density (Resid Effects)

11. Modeling

Five modeling efforts are discussed in this section. First are the micro-coker models. The micro-coker is a screening tool that allows for quick experimental analysis to estimate liquid, gas and coke yields and sulfur content, plus liquid sub-product yields. The associated model includes correlating the experimental yields and sulfur content plus scaling the micro-coker experimental results up to industrial values. Second are the pilot-coker models. The pilot-coker requires more extensive experimental effort and provides more detailed results. The associated models include correlating the experimental yields. Also detailed analyses of the liquid sub-products have been made and trends identified. The scaling of the pilot-coker results is discussed in the last part of this section. Third will be kinetic models from the stirred batch-coker. Included are kinetic results from TGA analysis and as a separate report will be detailed kinetic data from combining the TGA and stirred batch-coker data. Fourth is a furnace tube flow model. Based upon literature two-phase flow correlations the expected flow patterns for the pilot-coker were investigated. Finally the comparison and scale-up of the experimental to the industrial data is discussed.

A. MICRO-COKER MODELING

This section has 8 parts. The first 5 subsections deal with yield correlations. The next 3 subsections deal with the sulfur distribution in the liquid fractions. Then the ninth subsection relates to scale-up.

1. General Model

For the general model, four different characteristics of the feed have been used to determine the one that gives the best fit. These feedstock characteristics are API gravity, micro carbon residue (MCR), asphaltenes (C5+), and asphaltenes (C7+). Among these, MCR gives the best correlations for most of the products. Table 29 shows the R^2 values for all the product correlations when these four feed characteristics are used.

Table 29 - Coefficients of determination (R^2) using different feedstock characteristics

	Coke	Liquid	Gas	Gasoline	Diesel	Gas-Oil
MCR	**0.97**	**0.88**	**0.52**	**0.86**	0.75	**0.84**
Asp. C5	0.95	0.85	0.51	0.86	**0.78**	0.82
Asp. C7	0.96	0.85	0.51	0.86	**0.78**	0.83
°API	0.70	0.60	0.47	0.83	0.69	0.75

It can be seen in the table above, that micro carbon residue gives the best correlations for five out of six products. The asphaltenes content gives a better fit for the diesel correlation. The general correlations using micro carbon residue as feed characteristic are shown in Table 30. The units and range of the variables are the following: Temperature (ºF), from 900 to 950, Pressure (psig), and from 6 to 40. Microcarbon residues (wt %) range from 16 to 29.

Table 30 - General yield correlations

Product	Correlation	R^2
Liquid (%)	= -1.1139*MCR+0.0419*T-0.2897*P+1103.08*LSV+41.59	0.88
Coke (%)	= 0.9407*MCR-0.0609*T+0.1529*P-319.759*LSV+65.075	0.97
Gas (%)	= 0.1729*MCR+0.0191*T+0.13646*P-786.319*LSV-6.762	0.52
Gasoline (%)	= -0.3086*MCR+0.0137*T+0.1571*P-819.63*LSV+16.461	0.86
Diesel (%)	= -0.3339*MCR-0.02635*T-0.0392*P+70.957*LSV+50.452	0.75
Gas-Oil (%)	= -0.4714*MCR+0.0546*T-0.4076*P+1851.76*LSV-25.315	0.84

A comparison between the experimental data and the values predicted by the general correlations using micro carbon residue can be seen for coke, liquid and gas, in Figure 118.

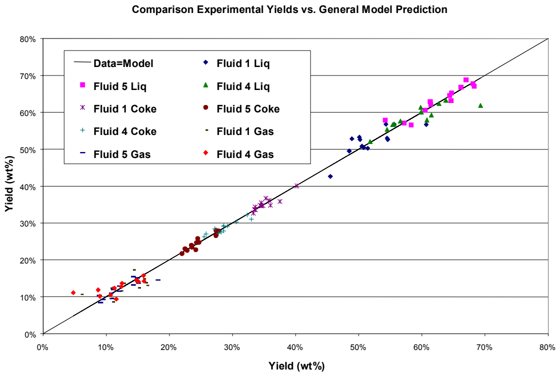


Figure 118 - Comparison Experimental Yields vs. General Model Prediction

2. Elemental Balances

The elemental balances were checked for the 10 runs with liquid analysis data available considering the yields predicted by the model (feedstock and general). The results are shown in Table 31. It can be seen that considering the yields given by the model, the closure of the elemental balances are very similar to those obtained from the actual yields. The differences observed are due to the error of the model.

Table 31 - Comparison of elemental balances obtained from actual yields and model

	Carbon		**Hydrogen**		**Sulfur**	
	Actual	G.Model	Actual	G.Model	Actual	G.Model
#5MR-2	97.7%	97.5%	95.3%	95.4%	99.1%	99.1%
#5MR-3	94.1%	94.3%	95.3%	93.1%	97.4%	96.7%
#5MR-4a	95.1%	95.2%	96.9%	97.1%	103.1%	103.1%
#5MR-5	95.8%	95.8%	96.7%	96.2%	97.2%	97.0%
#5MR-6	98.4%	98.4%	95.3%	94.4%	98.9%	99.6%
#5MR-11	97.4%	97.4%	96.2%	98.0%	99.5%	98.7%
#5MR-13	95.2%	95.1%	107.8%	108.7%	93.1%	93.2%
#4MR-1a	98.4%	98.8%	105.2%	103.1%	104.0%	100.1%
#4MR-2	101.2%	100.6%	97.0%	99.1%	90.3%	93.6%
#4MR-9	99.8%	99.6%	96.6%	97.2%	-	-
Ave. Error		**0.2%**		**1.1%**		**1.1%**

F = feedstock, G = General

3. Sulfur Distribution

Although it is known that the sulfur distribution in the products is a function of the feedstock, it is not completely clear what this effect is. Total sulfur in the feed does not provide all the information needed to describe the effect of the feedstock. Not only will the sulfur distribution depend on the type of sulfur compounds present in the feed, but it may also depend on the origin of the crude oil, kind of metallic compounds, etc. This fact makes it very difficult to find a general correlation that would consider any kind of resid.

The effect of the operating conditions, temperature, pressure, and residence time, on the sulfur distribution was studied. The amount of sulfur in the feed that goes to the liquid has been determined by difference after calculating the sulfur in the coke and gas. Even though there is some inconsistency in the data, a regression analysis show that an increase in temperature results in more sulfur going to the liquid and less to the coke and gas. An increase in pressure results in more sulfur going to the coke and gas and less to the liquid. Low residence times result in more sulfur going to the liquid and less to the coke and gas. Among these trends, the one with temperature is the clearest one. These trends suggest that in order to minimize the amount of sulfur in the liquid product, low temperature, high pressure, and high residence times are required. Incidentally, operating at these conditions means having the worst scenario possible when the objective is to maximize the liquid production. That is higher temperatures mean more cracking and thus both more liquid and more sulfur in the liquid.

This increase of sulfur in the liquid product with temperature was observed in previous research studies on coking. Data from the literature shows that higher temperatures produce an increase of the amount of sulfur in naphtha, light gas-oil, and heavy gas-oil. Another trend that has been observed in previous studies and confirmed by our data is that the sulfur in coke increases by increasing residence time. However, this change is small.

4. *Sulfur Correlations*

Empirical equations to predict sulfur distribution in products have been developed for Fluid 5 and Fluid 1. These correlations can be seen in Table 32. For these correlations, the amounts of sulfur in the products are expressed as wt% of sulfur in feed, temperature is in ºF and pressure in psig. The range of validity of these correlations is as follow: For Fluid 5, temperature between 900ºF and 950ºF, and pressure between 6 and 40 psig. For Fluid 1, temperatures between 910ºF and 950ºF, and pressures between 6 and 40 psig.

Table 32 - Feedstock sulfur recovery correlations

	Correlation	**R^2**	Ave. Err. (%)
Fluid 5			
Sulfur in Coke	=-0.041765*T+0.105642*P-586.479*S+71.4037	0.67	1.0
Sulfur in Liquid	=0.0980585*T-0.141395*P+1321.503*S-38.9963	0.79	1.4
Sulfur in Gas	=-0.0562931*T+0.035753*P-735.024*S+67.5925	0.53	1.0
Fluid 1			
Sulfur in Coke	=-0.12935*T+0.056319*P-188.1295*S+156.4702	0.83	0.7
Sulfur in Liquid	=0.352964*T-0.072662*P+1560.32*S-297.1409	0.82	2.2
Sulfur in Gas	=-0.223613*T+0.016343*P-1372.195*S+240.6707	0.76	1.7

T is in ºF, P in psig, and S is wt% of sulfur in feed

The correlations came out well in general. The worst fit is for the hydrogen sulfide gas from the Fluid 5 resid. Figure 119 and Figure 120 show a comparison between the experimental values and the values predicted by these feedstock correlations. It can be seen on these plots that for Fluid 5, the amount of sulfur that goes to the liquid is always greater than the amount that goes to the coke and gas. For Fluid 1 instead, points representing the amount of sulfur that goes to coke and liquid are found in same areas of the plot.

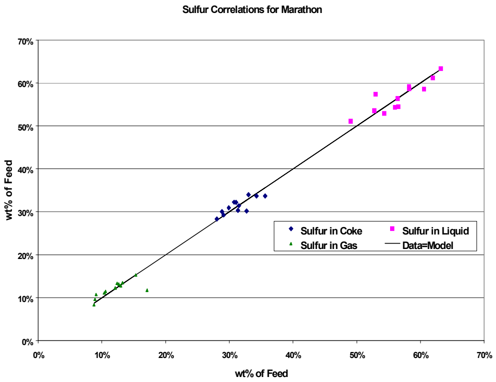


Figure 119 - Experimental values vs. sulfur model prediction for Fluid 5

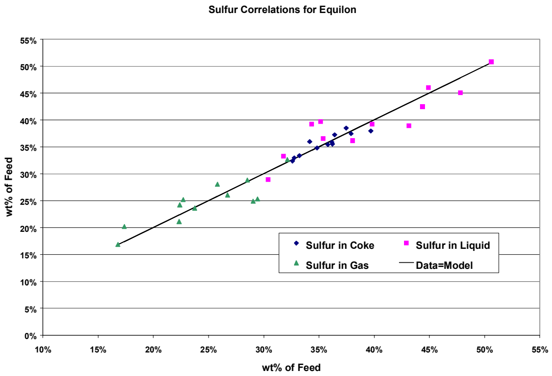


Figure 120 - Comparison experimental values and sulfur model prediction for Fluid 1

In summary the effect of operating conditions on sulfur distribution can be reasoned based upon the extent of cracking and vaporization. However one should first notice is that for Fluid 1, most of the sulfur in the feed tends to go to the coke and gas. This is in contrast for Fluid 5, more than half of the sulfur in the feed goes to the liquid. This fact suggests that sulfur compounds present in Fluid 1 resid are less stable than those in Fluid 5 resid and they are broken down to hydrogen sulfide more easily during the cracking process. It was also noticed that both feedstocks behave very similarly under changes in operating conditions. Neither feed seems to be much more sensitive to changes in any operating conditions than the other one. The higher temperature, higher residence time, and to a lesser extent lower pressure lead to more cracking and thus less sulfur in the coke and gas and more in the liquids.

5. Scale up issues

A model to predict the product yields of coking experiments for straight residues in the micro-reactor was finished. This model, which is a set of linear correlations, gives a very good prediction of the product yields when micro carbon residue and the conditions of temperature, pressure, and liquid space velocity (or feed rate) are known. However, there are two main reasons why this model could not be used to predict yields from industrial cokers. First, the liquid yields obtained in the micro-reactor have been found to be lower than those observed in refineries, and this deviation gets worse when the micro-coker is operated at the lowest feed rate, which results in liquid yields much lower than those expected in the industry. Second, the micro-coker correlations include a term to account for the effects of the residence time in the product yields, and this term does not have the same meaning for commercial units.

It is postulated that that the gas-oil fraction is being over-cracked to produce gases and lighter molecules in the range of gasoline. The simulated distillation supports this hypothesis, as the fraction of gas-oil in the liquid is much lower and the fraction of gasoline is much higher than that expected in commercial cokers. Also, some material that otherwise would leave the reactor to be part of the liquid must be converting to coke, because the coke yields are somewhat higher than the yields that one would expect in the pilot plant or industrial cokers.

The feed rate definitely has an effect on the product yields (the higher it is, the more liquid and less coke that are obtained), but it is difficult to compare the residence time or liquid space velocity in the micro-coker to that in the pilot or commercial units. The liquid space velocity in the micro-coker was defined based on the reactor volume, which makes sense for this reactor but does not for the pilot unit or commercial cokers where the reactions start before the material enters the drum.

It is obvious that some adjustments have to be made to these correlations before they can be used to predict coker yields that better match those observed in refineries. Also, the effect of the recycle is not considered in the micro-coker correlations. Future work should consider analyzing this effect and making an extra correction to the correlations. This is important since all commercial cokers operate with some recycle and this variable affects the product yields.

The first step taken to correct the correlations consists of finding a way to eliminate all the discrepancies on the residence time issue. The simplest thing to do was to fix the liquid space velocity to a certain value so this variable is eliminated from consideration when predicting the yields. The next step consists of looking at how the yields predicted by the correlations (with the liquid space velocity fixed to 0.0085 min^{-1}) compare to industrial and pilot unit yields in order to adjust them in such a way that they will predict more meaningful product yields. For this purpose, yields from pilot-coker experiments and commercial units have been compared to the yields that the micro-coker correlations would predict at those conditions of temperature and pressure for a particular feedstock. Figure 121 shows this comparison for coke, liquid, and gas yields.

The plot shows clearly that the micro-coker correlations always predict lower liquid yields and higher coke and gas yields than those obtained in the pilot or commercial units. In a first approach, the liquid and coke yields were adjusted by multiplying the results by constant factors and calculating the gas by difference in such a way that the error associated to each product were minimized simultaneously. Better results were obtained in a second approach when coke and gas were adjusted and the liquid was calculated by difference (see Figure 122). The constant factors multiplied to the results of the correlations were varied until the error for the three products was minimized. The results indicate that the coke and gas yields should be reduced by 9% and 18% respectively. The adjusted correlations were as follows:

$$\text{Coke*} = \text{Coke} \times 0.91 \qquad (1)$$

$$\text{Gas*} = \text{Gas} \times 0.82 \qquad (2)$$

$$\text{Liquid*} = 100 - (\text{Coke*} + \text{Gas*}) \qquad (3)$$

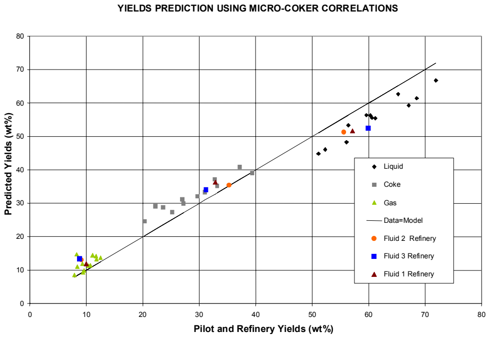


Figure 121 - Comparison Pilot Plant and Industrial Yields vs. Yields Predicted

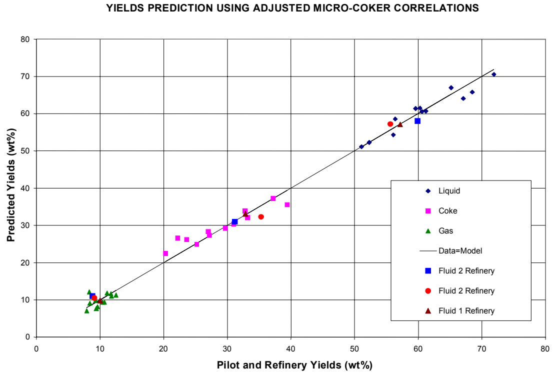


Figure 122 - Pilot Plant and Industrial Yields vs. Yields Predicted (After adjustment)

The micro-coker correlations now predict product yields that are more meaningful to the industry and that simulate better the performance of a commercial unit. It is important to mention that these corrections were made based on yields from three commercial units and data from the pilot plant that was normalized by gas. There is also a chance that these correction factors vary slightly if more or less data is considered since they were obtained by minimizing the error of the fit for those particular data points. Since the yield data from the three commercial units are at fluid temperatures above

900ºF, only data taken from the pilot unit at 890ºF or higher fluid temperatures were used to develop these correlation factors. As a result, these adjusted correlations should only be used at fluid temperatures between 900ºF and 950ºF.

A similar analysis was performed for the liquid sub-products, gasoline, diesel, and gas-oil. After plotting the yields obtained from the pilot unit experiments, and one refinery point, vs. the yield predicted by the micro-coker correlations, it is readily observed that the correlations predict a much lower gas-oil yield and higher gasoline and diesel yield that those observed in the pilot and commercial units. The causes of this phenomenon were discussed previously. The results are shown in Figure 123.

A similar procedure, to that used to adjust the main product correlations, was employed to correct the liquid sub-product correlations. Before this can be accomplished, the equations must be corrected so the summation of gasoline, diesel, and gas-oil yields adds up to the total amount of liquid. This is because these correlations give sub-product yields as percentage of the feed, and if the liquid yield was adjusted, then the liquid sub-product yields must be adjusted as well. This adjustment can also be seen as a normalization of the sub-product yields to compensate for the increase in the liquid yield prediction. The analysis to correct for the lower amount of gas-oil and the higher amount of gasoline and diesel suggest that the gasoline yield and the diesel yield should be reduced by 25% and 10% respectively. The gas-oil yield is calculated by difference. The adjusted correlations will be as follows:

$$\text{Gasoline*} = \text{Gasoline x (Liquid*/Liquid) x 0.75} \tag{4}$$

$$\text{Diesel*} = \text{Diesel x (Liquid*/Liquid) x 0.90} \tag{5}$$

$$\text{Gas-Oil*} = \text{Liquid* - (Gasoline* + Diesel*)} \tag{6}$$

A comparison of the data from pilot plant and a point from a commercial unit vs. the yields predicted by the adjusted sub-product correlations can be seen in Figure 124.

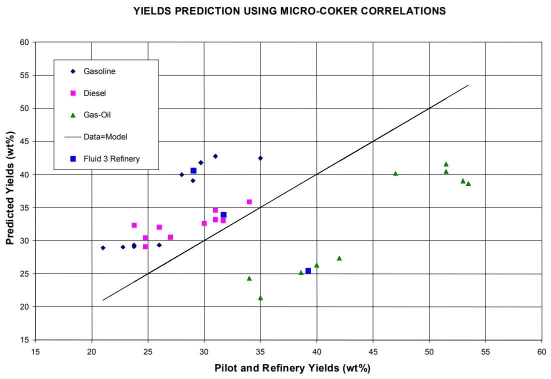


Figure 123 - Comparison Liquid Sub-Products Yields in Pilot Plant vs. Yields Predicted

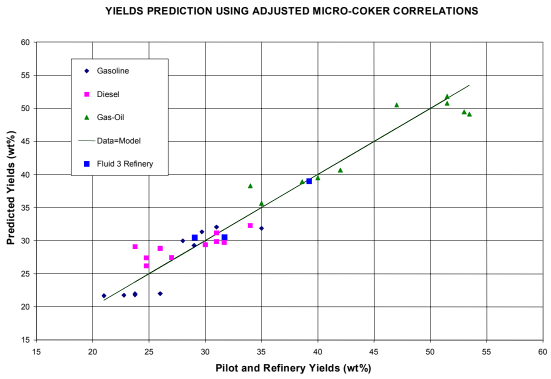


Figure 124 - Pilot Sub-Product Yields vs. Predicted Yields (After adjustment)

6. Micro-coker & Literature Models Comparison

Some comparisons can be made among the yield model developed from the micro-coker data, the graphic method proposed by Castiglioni (1983), and the rules of thumb for delayed cokers provided by Lieberman (1986). Gary and Handwerk's (2001) correlations will not be used in this first comparison because those correlations are independent of operating conditions.

Lieberman claims that ***each 8 psi reduction in coke drum pressure reduces coke yield on feed by 1.0 wt%***. The micro-coker model predicts a reduction of 1.1 wt% to 1.2 wt% for this change in drum pressure, and Castiglioni's method suggests that this reduction would be around 0.8 wt%. The three results (or estimates) are very close to each other.

Another rule of thumb mentioned by Lieberman is that ***each 10°F increase in coke drum vapor line temperature decreases coke yield by 0.8 wt%.*** The micro-coker model predicts a decrease of 0.5 wt% to 0.6 wt% for this change in temperature, and Castiglioni's method suggests that this reduction would be around 1.0 wt% to 1.3 wt%. Again, the three results are comparable. It is important to notice that there could be an important error associated with the difficult reading of the graphs proposed by Castiglioni, and sometimes the numerical values obtained from some of his plots are more a guess than a fact.

One could also compare the yield predictions by the different models using data provided by the member companies. The models to be compared would be the micro-coker correlations, Gary and Handwerk's correlations, and Castiglioni's graphic method. The comparison will be made in spite of the limitations of each model. The micro-coker model was developed using data from experiments with no recycle, so this variable is not considered. Castiglioni's graphs can lead to illogical results due to the high probability of reading wrong values from the charts. Moreover, Castiglioni's charts do not consider pressures above 30 psig or feedstocks with MCR higher than 25%, so extrapolation lines will be assumed for comparison purposes. This is an important limitation of this model. Gary and Handwerk's correlations do not include terms to account for the operating conditions and the only independent variable is the MCR of the feedstock

The yields predicted by Gary and Handwerk vs. the actual yields are shown in Table 33. As expected, the prediction is not good. Not considering the effect of operating conditions on the yields introduces a big error. It is important to mention that these correlations were developed assuming a drum pressure between 35 and 45 psig, so this may be the reason why the worst prediction is for Fluid 1 (Drum pressure = 20 psig).

Table 33 - Actual Yields vs. Gary and Handwerk's Prediction

Feedstock	Liquid (wt%)	G & H Prediction	Coke (wt%)	G & H Prediction	Gas (wt%)	G & H Prediction
Fluid 2	**55.6**	**48.6**	**35.3**	**40.0**	**9.1**	**11.4**
Fluid 3	**59.9**	**52.6**	**31.2**	**36.3**	**8.8**	**11.1**
Fluid 1	**57.2**	**41.6**	**32.8**	**46.4**	**10.0**	**12.0**
Fluid 5	**61.2**	**64.5**	**27.0**	**25.4**	**11.8**	**10.1**

The yields predicted by the micro-coker correlations vs. the actual yields are shown in Table 34. It can be observed that the prediction in general is very good. Perhaps the biggest difference is when considering feedstocks. This refinery operates with 20% recycle which results in lower liquid yields and higher coke yields than if they ran with no recycle. That may be the reason the micro-coker correlations predict a somewhat higher liquid yield and a lower coke yield than the actual results (The correlations were developed from experiments with no recycle).

Table 34 - Actual Yields vs. Micro-Coker Prediction

Feedstock	Liquid (wt%)	M-Coker Prediction	Coke (wt%)	M-Coker Prediction	Gas (wt%)	M-Coker Prediction
Fluid 2	**55.6**	**56.9**	**35.3**	**32.3**	**9.1**	**10.8**
Fluid 3	**59.9**	**58.0**	**31.2**	**31.0**	**8.8**	**11.0**
Fluid 1	**57.2**	**57.1**	**32.8**	**33.1**	**10.0**	**9.8**
Fluid 5	**61.2**	**63.9**	**27.0**	**24.7**	**11.8**	**11.4**

Since Castiglioni uses drum temperature instead of feed temperature in his method, an assumption has to be made concerning the temperature drop along the drum. A temperature drop of 100ºF between drum inlet and vapor outlet seems reasonable. The inlet temperatures would then be equivalent to drum temperatures of 815, 815, 825, and 843ºF for Fluid 2, Fluid 3, Fluid 1, and Fluid 5 respectively. A recycle of 10% was assumed for Fluid 1 because this data is not available and it is needed for Castiglioni's method.

Table 35 - Actual Yields vs. Castiglioni's Prediction

Feedstock	Liquid (wt%)	Castiglioni Prediction	Coke (wt%)	Castiglioni Prediction	Gas (wt%)	Castiglioni Prediction
Fluid 2	**55.6**	**60.6**	**35.3**	**29.9**	**9.1**	**9.5**
Fluid 3	**59.9**	**55.8**	**31.2**	**34.2**	**8.8**	**10.0**
Fluid 1	**57.2**	**52.8**	**32.8**	**38.0**	**10.0**	**9.2**
Fluid 5	**61.2**	**63.8**	**27.0**	**28.0**	**11.8**	**8.2**

The predictions are acceptable but not very good (see Figure 125). The method is in general very unpractical and inaccurate. It is difficult to work with the plots when heavy feedstocks like Fluid 1 and Fluid 2 are considered.

The micro-coker correlations seem to be at this point the easiest and most accurate way to predict coking yields. Since they have the limitation of not considering the amount of recycle, they should work better when the ratio recycle/fresh feed is small.

7. Screening Model Conclusions

Feedstock and general correlations to predict coke, liquid, gas, gasoline, diesel and gas-oil yields have been finished for the micro-reactor. The coke yield is the easiest to predict, since it depends mainly on the feedstock and little on operating conditions. The worst fits are for the gas and diesel product. Most of the correlations confirm the expected trends except for the diesel yield, which presents no clear correlation with operating conditions. The general correlations have been developed in terms of micro-carbon residue, which gave better fits than using any other feedstock characteristic. The general correlations for the six products came out very well. The elemental balances were checked using the yields predicted by the correlations, and they came out very close to those from the experimental data (the small differences are due to the error of the model). An analysis of the yield correlations shows that all the feeds behave in similar way under changes in operating conditions, and that pressure and residence time have the biggest effect on product yields.

Correlations to predict the sulfur distribution in the main products have been developed for Fluid 5 and Fluid 1. This regression analysis shows that sulfur tends to go to the liquid at higher temperatures. An increase in pressure results in more sulfur going to the coke and gas and less to the liquid. Low residence times result in more sulfur going to the liquid and less to the coke and gas. The effect of the feedstock has not been determined, as information about the thermal stability of the sulfur compounds present in the feed is required. An analysis of these correlations shows that temperature and residence time has a larger affect on the sulfur distribution than pressure does.

An industrial yield correlation or scaled up correlation has been developed. It is based upon the temperature and pressure dependence from the micro-coker with the lowest residence time and then lowering the coke and gas yields and finding liquid yield by difference.

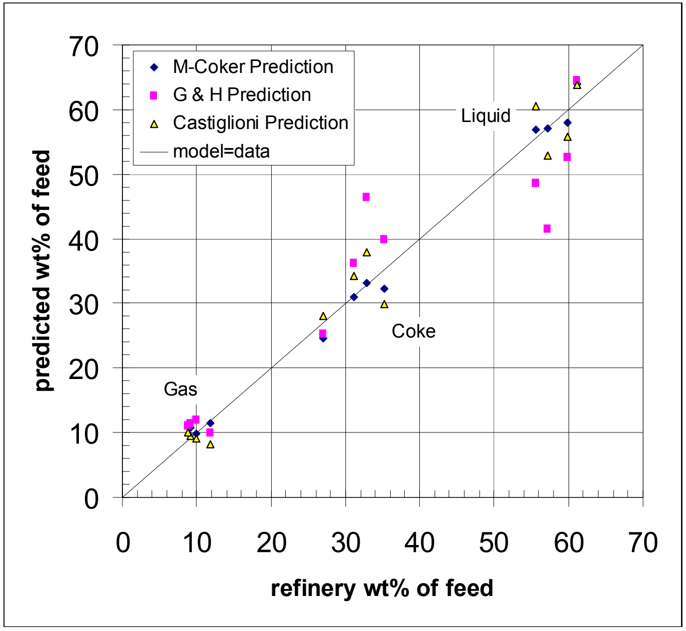


Figure 125 - Comparison of 3 Models to Refinery Yield Data

B. PROCESS OPTIMIZATION MODEL - PILOT-COKER

1. Product Yield Modeling

Runs that did not exceed a 3-hour run length and a pre-normalized recovery of 95% were not used for these correlations. Runs that had recycle oil or slurry oil added were not used because of the affects that the oils could have on the yields. A slight increase in liquid yields and a slight decrease in coke yields were noticed.

The individual correlations for each of the three products was developed using the coefficients noted in Table 36 and Table 37. The gas yields were calculated by difference where:

Table 36 - Pilot coker product correlations – Liquid

a varied from -0.0008 to -0.0037
b varied from 0.006 to .007
d varied froom -0.23 to + 0.21

These correlations were then used to develop a general correlation.

Table 37 - Pilot coker product correlations – Coke

a varies from 0.0009 to 0.0035
b varies from -0.006 to +0.008 and
d varies from 0.708 to + 1.004

Figure 126 and Figure 127 show a comparison of the experimental data and the individual resid correlations by product. Figure 128 and Figure 129 show the comparison of the experimental data and the general correlation calculated values. Individual and general correlations can predict 90% of runs within 3.0% of experimental data, see Table 38.

Table 38 - Individual and General Correlation – Percent of Runs Predicted Within 3.0% of Experimental Data

Less than 3.0%					
Coke		Liquid		Gas	
Ind. Corr.	General Corr.	Ind. Corr.	General Corr.	Ind. Corr.	General Corr.
88.73%	90.14%	90.14%	90.14%	90.14%	90.14%

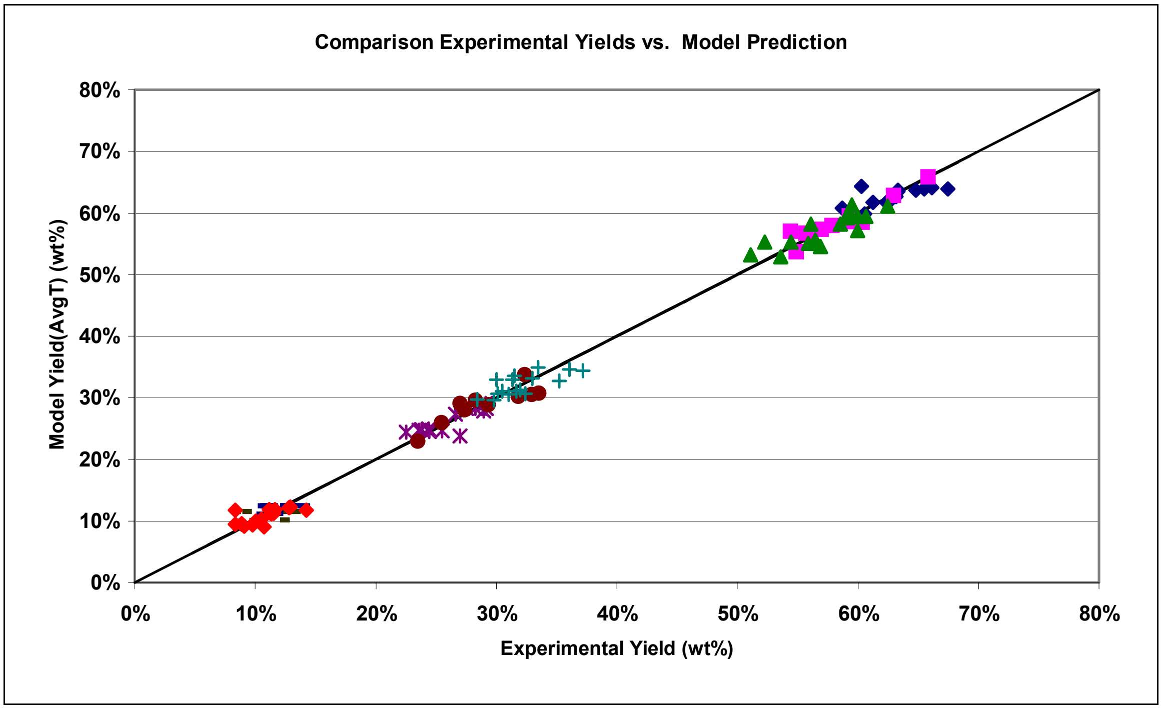


Figure 126 - Individual Resid Product Yield Correlation Comparisons

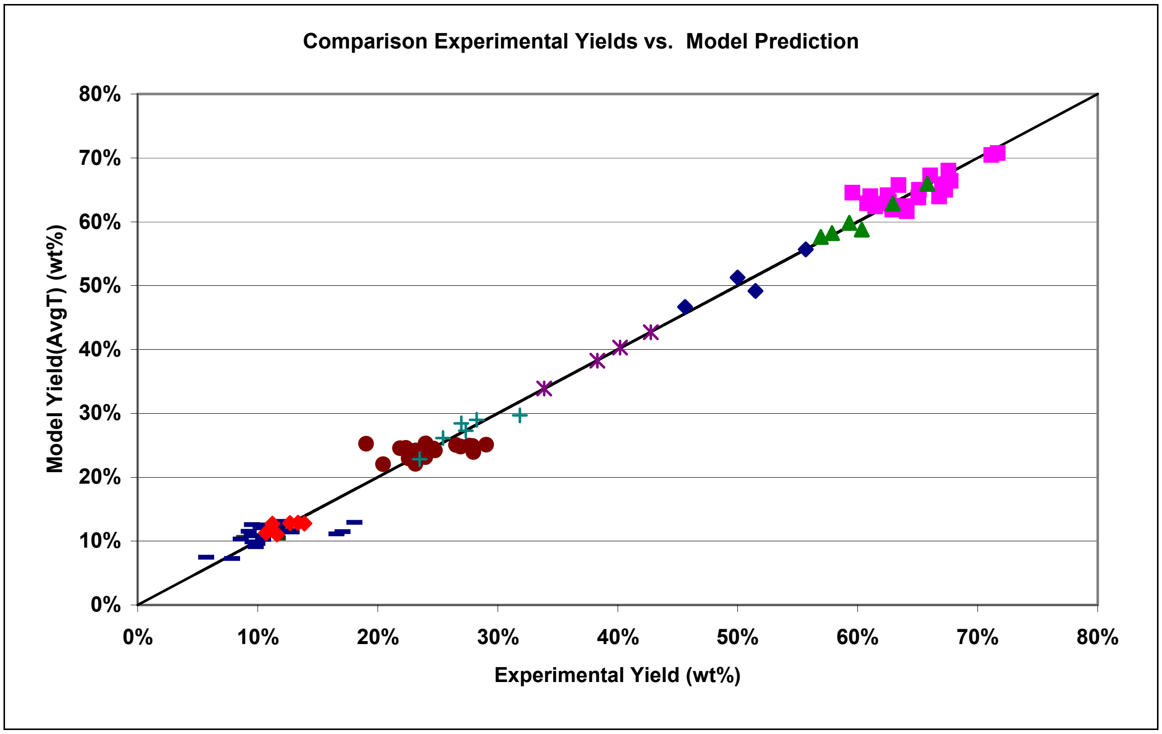


Figure 127 - Individual Resid Product Yield Correlation Comparisons

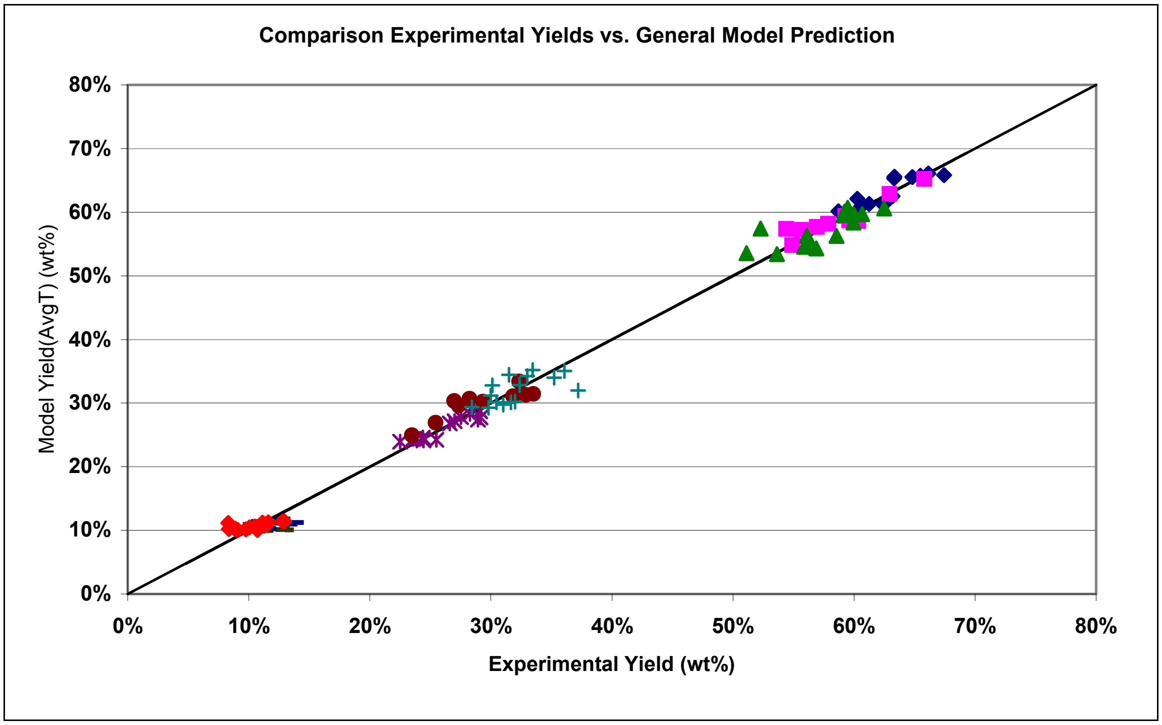


Figure 128 - General Product Yield Correlation Comparisons

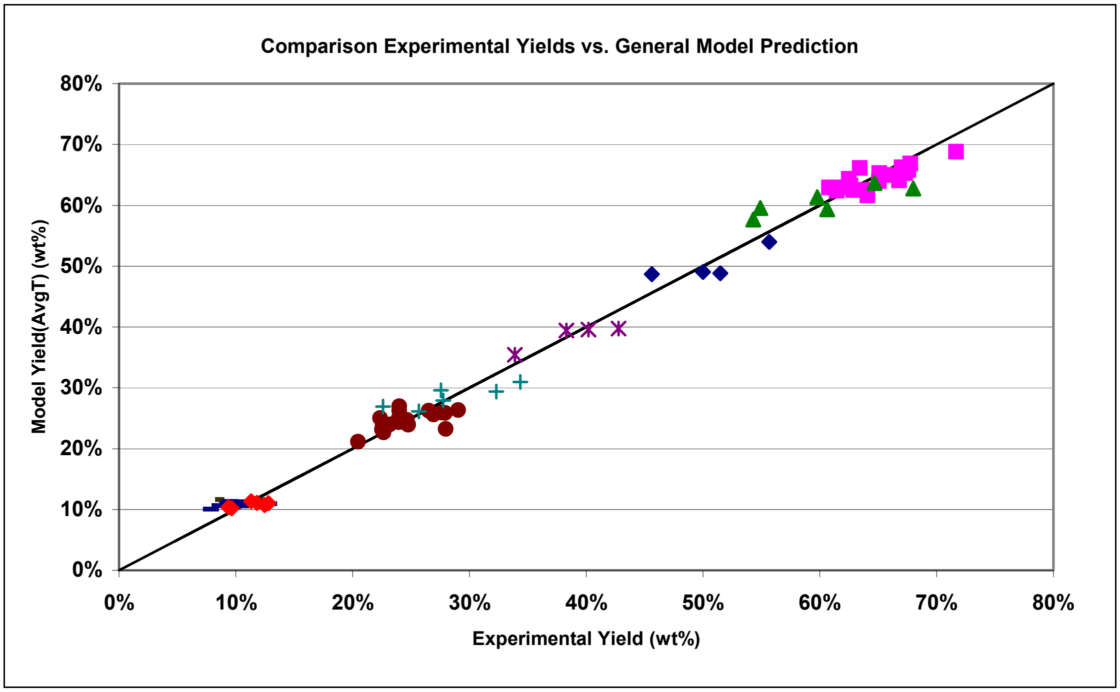


Figure 129 - General Product Yield Correlation Comparisons

2. Liquid Sub-Product Yields

In the sub-section below, the reproducibility of the liquid sub-product yields is discussed. It is not good. After much work, no acceptable general correlations were developed. However, trends were identified. Based on the repeated simulated distillation data, the preliminary correlation of this data with operating conditions is very promising. This is discussed in the second sub-section.

a) Reproducible Liquid Sub-Product Yields?

All three of these runs were considered identical runs. Their normalized product yields showed little deviations from each other. The normalized liquid yields were between 66.8 to 67.8 wt% of feed. There were some differences in the furnace output levels. However, this did not seem to have made a major impact since the temperatures at the surface of the furnace coil and the drum inlet were nearly identical. Perhaps the furnace output levels had an impact on temperatures further up the coke drum.

The first benchmark for Fluid 5, saw a 7% decrease in the gasoline production and a 6-7% increase in the gas oil production from the other two runs. The other two benchmarks had very similar liquid product yields despite the fact that they had the most deviations from each other in the temperature profiles. There are notable differences seen in the temperature and pressure profile graphs, therefore, the benchmark tests cannot be considered identical. It is believed that a major contributor in the fluctuation of the benchmark liquid products is the large temperature drop seen in seven of the eight drum temperatures during the first hour of feed injection. The two runs that have the lowest gas oil yields, saw large temperature drops while the other did not see these temperature drops.

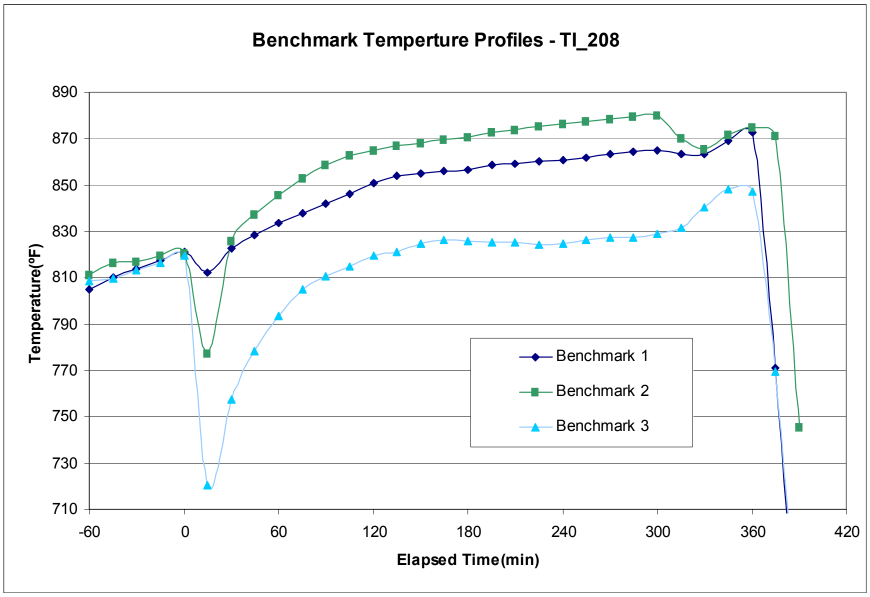


Figure 130 - Benchmark temperature profile comparisons – overhead temperature (TI_208)

The higher temperatures of run 1 would cause more of the gas oils to be vaporized before they are converted to coke or cracked to smaller liquids. Thus the gasoline content would decrease. Further investigation of the temperature and pressure profiles, along with coke levels and vapor flow rates, could lead to a better understanding of why the liquid products saw such variations. If this investigation does not result in an improvement of the correlations, more runs will need to be made. After making changes to the coker unit design and the controls system, a great improvement in the reproducibility of data has been seen.

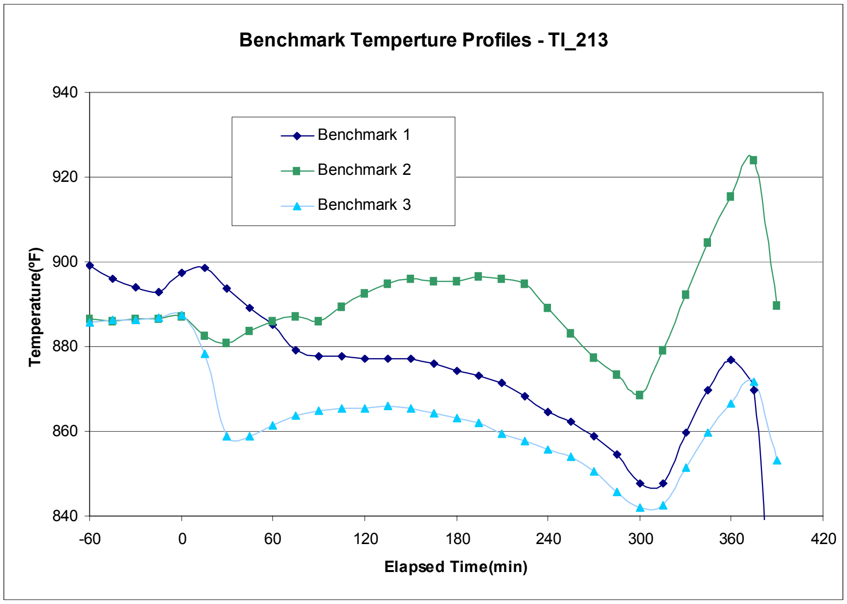


Figure 131 - Benchmark temperature profile comparisons – interior drum temperature (TI_213)

So the pilot-coker temperature profiles were revisited to see how this data can be used to better predict the liquid sub-product yields. Also the operating procedure for the new pilot-coker was modified to collect the first hour's liquids separately for SimDis analysis before recombining.

b) Old Pilot-coker liquid yields via new SimDis data correlated to Pressure, Average TI_208 and MCR (Pilot)

As discussed above, the correlation of the liquid sub-products (gasoline, diesel and gas oil) yields was previously unsuccessful. However using the new SimDis data progress was made. The correlation coefficients were much better to the general correlation

Figure 132 shows the comparison of the old model to data based on the old SimDis data. The correlation is quite poor (note both 3/8" and ¼" coil data are included). Figure 133 show the comparison of the new model to data based on the new SimDis data.

(note only ¼" coil data are included). The correlation is seen to be tremendously improved.

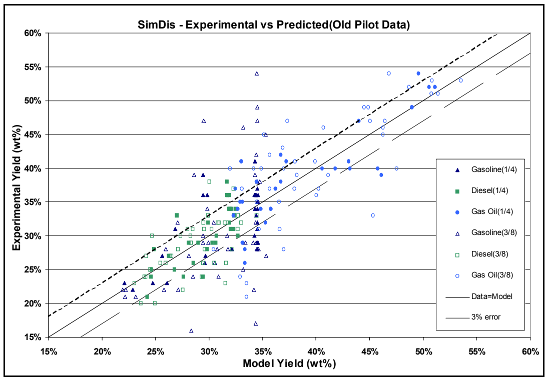


Figure 132 - Old Pilot SimDis Data – General Correlation Yield Comparisons (All runs)

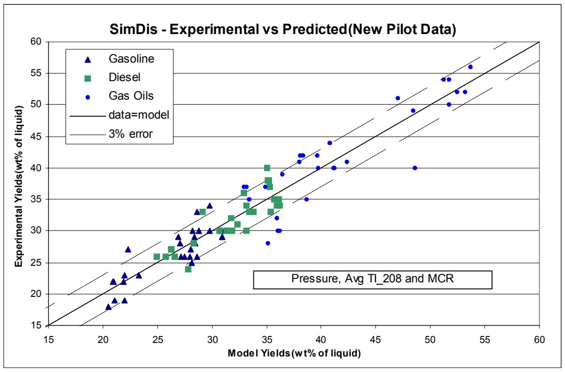


Figure 133 - New pilot SimDis data – general correlation yield comparisons (All ¼" runs)

C. STIRRED BATCH-COKER CORRELATIONS

Correlations using the feedstock properties have been developed by employing the batch-coker. Table 39 shows the feedstock properties along with the coke produced in feedstock runs. The heating rate was medium (85 % output) and the pressure was 40 psig.

Coke production was found to be a strong function of MCR, Asphaltene, H/C ratio, and API. Figure 134 through Figure 137 show how these properties correlate with the coke yield in weight %.

Table 39 - Feedstock properties used for the correlations

Feed	MCR	Asph	Ni	V	H/C	H Content	API	Coke
Fluid 6	21.77	8.56	63.94	68.17	12.14%	10.73%	5.4	29.6
Fluid 5	16.25	2.35	36.85	55.2	12.89%	11.06%	9.7	24.3
Fluid 2	25.74	15.27	106.62	688.6	11.74%	10.02%	3.3	32.7
Fluid 1	29.4	24.6	132.05	700	11.25%	9.39%	1.1	38.8
Fluid 4	21.15	12.97	121.29	316.19	11.84%	9.83%	1.6	30.1
Fluid 3	20.25	8.75	183.3	139.46	11.84%	10.10%	4.3	30.7

Figure 134 shows that when MCR increases coke increases linearly. MCR can be defined as the tendency of the resid to produce coke. It is clear that this property can predict coke very accurately. Asphaltene content can also predict coke yield since an increase in asphaltene, mostly aromatics, would increase coke (see Figure 135).

Table 40 - Actual Coke vs. MCR Correlation Prediction

Feed	Coke	Cal. Coke	% Error
Fluid 6	29.6	30.4	2.6%
Fluid 5	24.3	24.9	2.4%
Fluid 2	32.7	34.3	5.0%
Fluid 1	38.8	38.0	2.1%

Fluid 4	30.1	29.8	1.1%
Fluid 3	30.7	28.9	6.0%

Table 41 - Actual Coke vs. Predicted Coke by Asphaltene Correlation

Feed	Coke	Cal. Coke	% Error
Fluid 6	29.6	28.9	2.3%
Fluid 5	24.3	25.1	3.4%
Fluid 2	32.7	33.0	1.0%
Fluid 1	38.8	38.7	0.2%
Fluid 4	30.1	31.6	5.0%
Fluid 3	30.7	29.0	5.4%

The MCR content correlation gave the most error in predicting Fluid 2 and Fluid 3 yields as shown in Table 40 while asphaltene correlation gave the most error in predicting Fluid 4 and Fluid 3 yields as shown in Table 41. Fluid 4 has a higher MCR and asphaltene content than Fluid 3. Nevertheless, Fluid 3 produced higher coke that could not be confirmed by the correlation. As shown in Table 39, Fluid 4 has a higher MCR and Asphaltene content than those of Fluid 3; also it has equal H/C ratio, lower Hydrogen content and lower API. These values would suggest that Fluid 4 should produce higher coke yield than Fluid 3 would. In reality, Fluid 3 yielded slightly higher coke in the batch-coker experiment. This is maybe due to the nickel and vanadium. Ni/V ratio in Fluid 3 resid is greater than one and in all the other residua studied it is less than one.

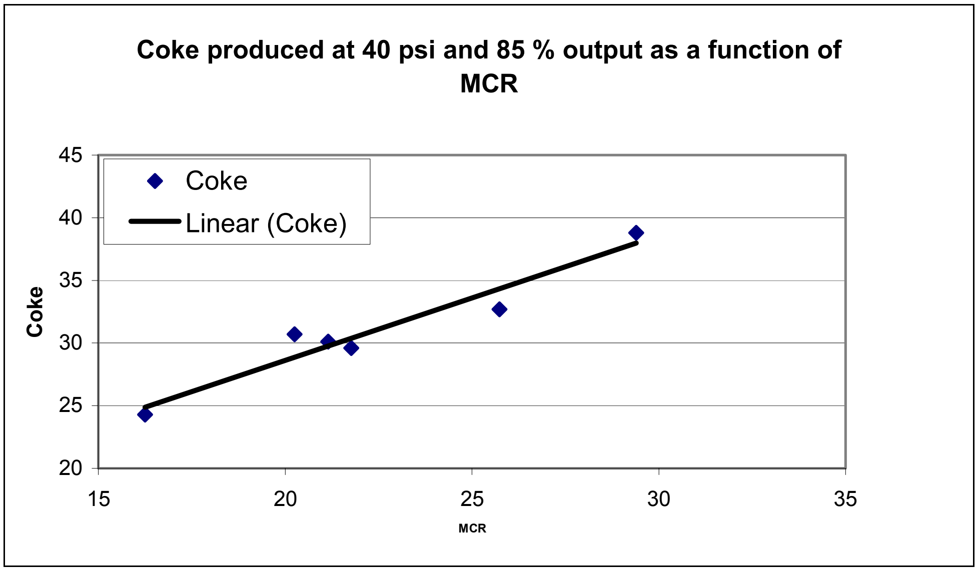


Figure 134 - Coke produced at 40 psig and 85% output as a function of MCR

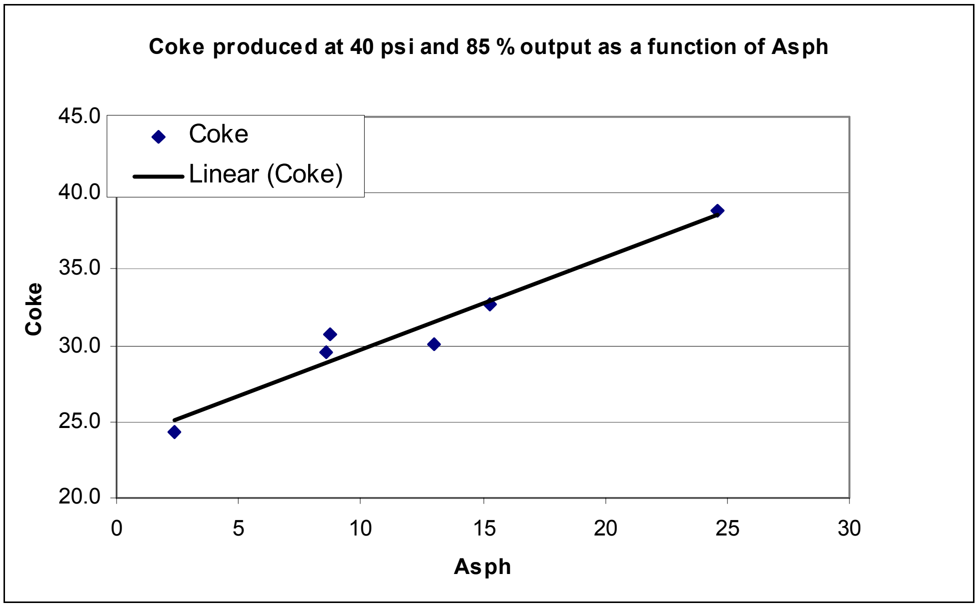


Figure 135 - Coke produced at 40 psig and 85% output as a function of Asphaltene

Figure 136 shows the relationship between the coke yield and H/C ratio. Coke yield decreases with increasing H/C ratio. H/C ratio is a measure of aromaticity. A lower H/C ratio means more aromatic compounds exist in the feed structure. Coke yield also decreases when API increases (lower density) as can be depicted from Figure 137.

Table 42 - Actual Coke vs. Predicted Coke by H/C Correlation

Feed	Coke (wt%)	Cal. Coke (wt%)	% Error
Fluid 6	29.6	29.4	0.7%
Fluid 5	24.3	23.2	4.7%
Fluid 2	32.7	32.7	0.0%
Fluid 1	38.8	36.8	5.2%
Fluid 4	30.1	31.9	5.9%
Fluid 3	30.7	31.9	3.8%

Table 43 - Actual Coke vs. Predicted Coke by API Correlation

Feed	Coke (wt%)	Cal. Coke (wt%)	% Error
Fluid 6	29.6	29.5	0.2%
Fluid 5	24.3	24.1	0.9%
Fluid 2	32.7	32.2	1.5%
Fluid 1	38.8	35.0	9.8%
Fluid 4	30.1	34.4	14.2%
Fluid 3	30.7	30.9	0.8%

H/C and API correlations have the most error in predicting Fluid 4 and Fluid 1 coke yields, as shown in Table 42 and Table 43. The other feedstock predictions have less than 5% error.

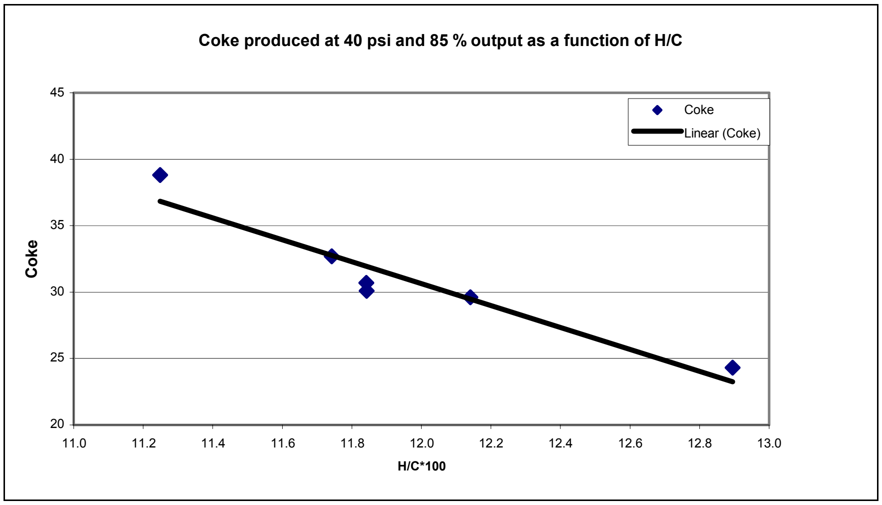


Figure 136 - Coke produced at 40 psig and 85% output as a function of H/C

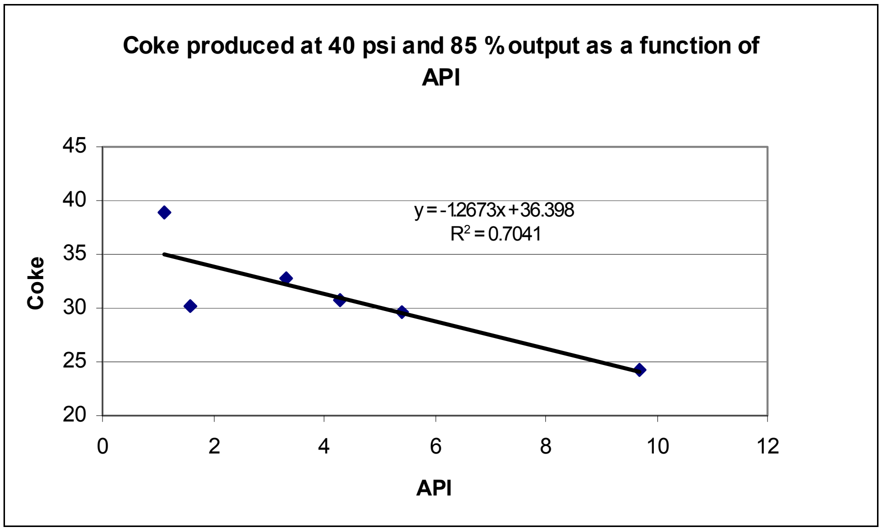


Figure 137 - Coke produced at 40 psig and 85% output as a function of API

Another good correlation can be derived from two properties, namely MCR content and H/C ratio. The prediction of this correlation is given in Table 44. It is generally an accurate and easy correlation to use with Fluid 3 being the only feedstock that gave higher than 5% error. Knowing only the MCR and H/C ratio, which are easily measured in a laboratory, would enable one to predict the coke yield.

Table 44 - Actual Coke vs. Predicted Coke by H/C and MCR Correlation

Feed	Coke	Cal. Coke	% Error
Fluid 6	29.6	30.0	1.4%
Fluid 5	24.3	24.0	1.2%
Fluid 2	32.7	34.3	4.8%
Fluid 1	38.8	38.3	1.3%
Fluid 4	30.1	29.6	1.7%
Fluid 3	30.7	28.7	6.5%

Liquid and gas yields were predicted with the same accuracy as predicted for the coke yields.

Table 45 shows the actual product yields vs. the calculated product yields. The Table shows the correlation predicts all product yields with very good accuracy.

Table 45 - Actual product yields vs. predicted product yields

Feed	Coke	Calc. Coke	Liquid	Calc. Liquid	Gas	Calc. Gas
Fluid 6	29.6	30.0	59.7	59.3	10.7	10.7
Fluid 5	24.3	24.0	65.2	64.9	10.5	11.1
Fluid 2	32.7	34.3	55.2	55.7	12.1	10.0
Fluid 1	38.8	38.3	50.8	52.3	10.5	9.4
Fluid 4	30.1	29.6	57.6	60.6	12.3	9.8
Fluid 3	30.7	28.7	59.4	61.2	9.9	10.1

H/C ratio correlates very well with gas oil, diesel, and total liquid as shown in Figure 138, Figure 139, and Figure 140, respectively. The predictions using these correlations is shown in Table 45 and Table 46.

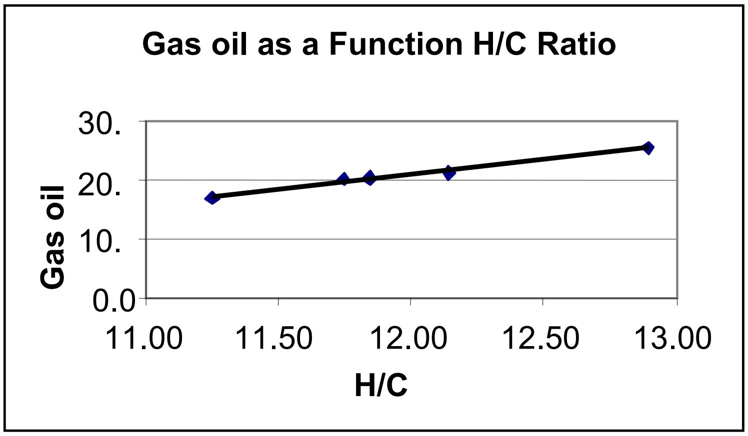


Figure 138 - Gas oil correlation

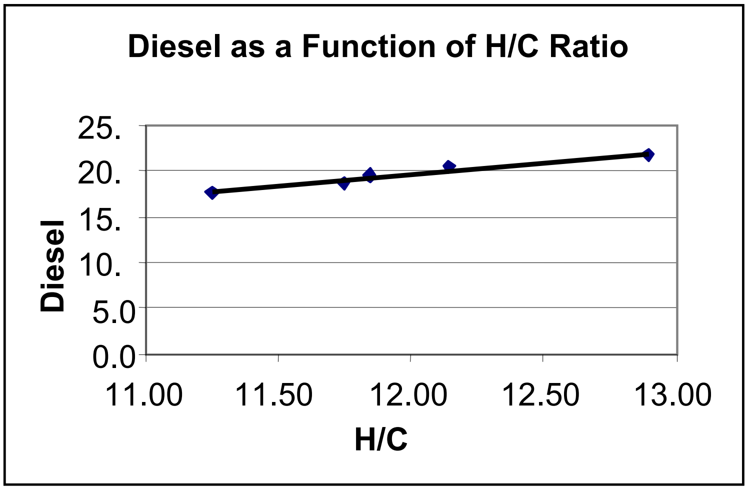


Figure 139 - Diesel correlation

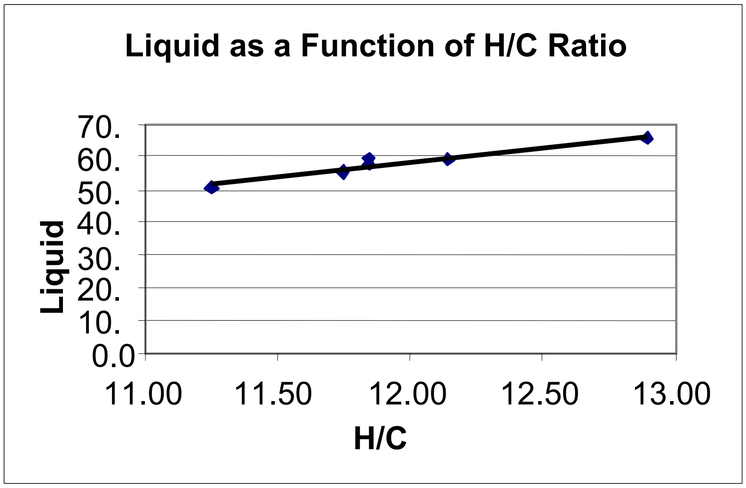


Figure 140 - Liquid correlation

Table 46 - Liquid cut predictions using the H/C correlations for liquid and liquid fractions

Feed	Liquid	Calc. Liquid	Gas oil	Calc. Gasoil	Diesel	Calc. Diesel	Gasoline	Calc. Gasoline
Fluid 6	59.0	59.6	21.3	21.8	20.5	20.1	17.5	17.7
Fluid 5	65.6	66.1	25.7	25.7	21.7	22.0	18.2	18.5
Fluid 2	55.6	56.1	20.2	19.7	18.8	19.1	16.6	17.4
Fluid 1	50.8	51.9	17.0	17.2	17.5	17.8	16.3	16.9
Fluid 4	57.6	57.0	20.3	20.2	19.3	19.3	17.9	17.5
Fluid 3	59.4	57.0	20.5	20.2	19.6	19.3	19.1	17.5

Table 47 - Percent error in predicting liquid and liquid fractions

Feed	Error % Liquid	Error % Gasoil	Error % Diesel	Error % Gasoline
Fluid 6	0.9	2.5	2.1	1.5
Fluid 5	0.7	0.3	1.6	1.4
Fluid 2	1.0	2.1	1.4	4.4
Fluid 1	2.1	1.4	1.7	3.8
Fluid 4	1.0	0.4	0.3	2.6
Fluid 3	4.0	1.3	1.6	8.4

D. KINETIC MODEL - STIRRED BATCH-COKER

The goal of the kinetic analysis is to enable prediction of the reaction rate in furnace tube for each feedstock, to determine the effect of feedstock properties on reaction kinetics, to predict rate of formation of products (gas, liquid, coke) and liquid product distribution, and to determine the effect of residence time on product yield and liquid distribution. Kinetic data were obtained in two ways: through stirred-batch reactor experiments, and through thermogravimetric analysis. Both of these methods have advantages and disadvantages. The stirred batch reactor gives good information on product distributions but has limited temperature control and a limited amount data over time for each run (typically four liquid samples are obtained during a coking run). Thermogravimetric analysis (TGA) gives excellent temperature control with a large data set (feed loss vs. time), but provides no information on product distributions. Since these methods complement each other, both of these methods were used for kinetic analysis. The TGA data was analyzed first to facilitate development of a kinetic model which will then be compared to the stirred-batch reactor data for validation. The model will then be modified using the analysis of the boiling point curves (by HTGC) of the stirred-batch reactor residue samples and of the condensate products, as well as the on-line GC analysis of the gas products.

The kinetic parameters have been derived from the TGA data using the following equation, as discussed in the January 2002 Quarterly Report:

$$\ln\left(-\frac{\ln[(1-x_A)]}{T^2}\right)=\ln\left[\left(\frac{A_0R}{E}\right)\left(1-2\frac{RT}{E}\right)\right]-\frac{E}{RT}$$

This equation is known as the Coats-Redfern equation, except that we use A_0 which has the following form:

$$k=A_0\left(\frac{dT}{dt}\right)^n e^{\left(\frac{-E}{RT}\right)}\quad \text{where } n=0 \text{ for isothermal system}$$

$$\text{and } n=1 \text{ for nonisothermal system}$$

and

$$A=A_0\left(\frac{dT}{dt}\right)^n$$

The left hand side of the Coats-Redfern equation vs. $1/T$ should give straight line. However, since our samples are mixtures of thousands of components, a straight line would not necessarily be expected over the entire range of the kinetic experiment. Figure 141 shows real TGA data from one of the resids plotted against a straight line. A realistic model should use more than one activation energy to account for the compositional changes due to reaction and to the complexity of the feed.

As an example of the dependence of the activation energy on conversion, the slopes of the Coats-Redfern equation for each 10 % conversion of the feed were calculated for the one of the resids at 5°C/min heating rate; the results are plotted in Figure 142. If we find the slope of the Coats-Redfern equation between each two adjacent points, this will give us the trend of the activation energy but with a great deal of scatter due to background noise in the data; Figure 143 shows such a plot for the this resid at 5°C/min.

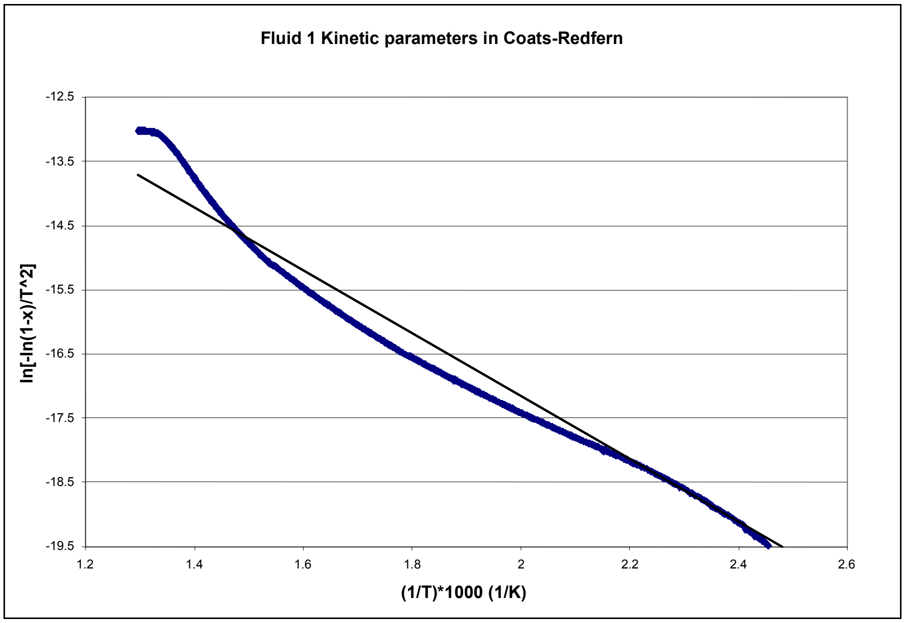


Figure 141 - Kinetic parameters in Coats-Redfern equation

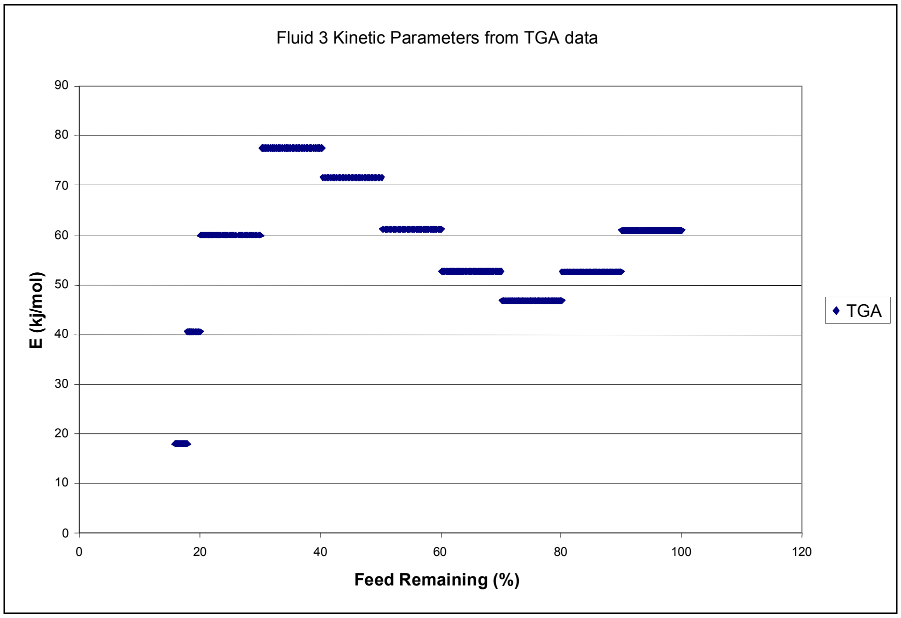


Figure 142 - Activation energy as a function of the feed remaining (5°C/min)

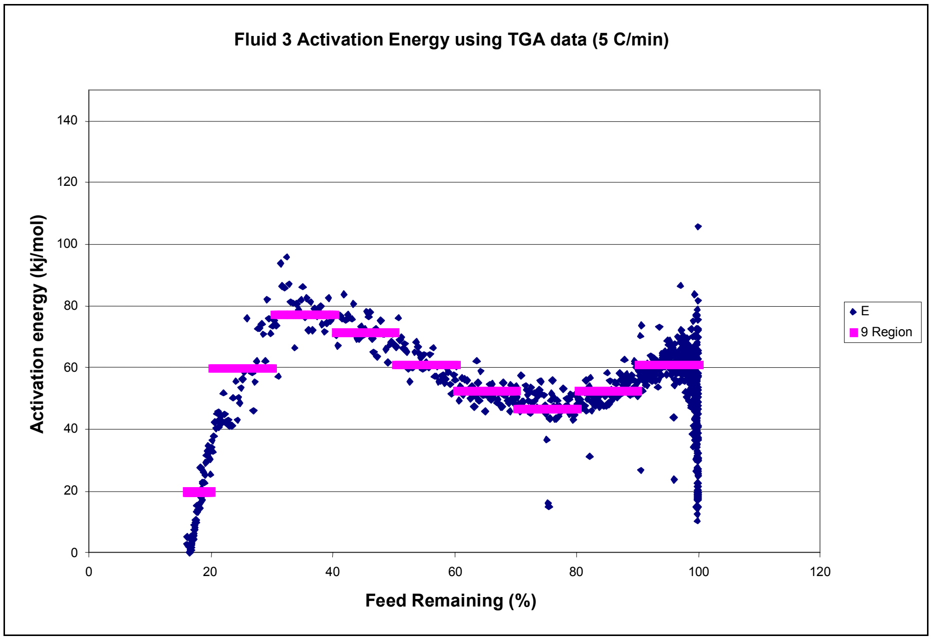


Figure 143 - Activation energy as a function of the feed remaining (5 °C/min)

If the activation energy depends on the conversion of the feed, the same activation energy will be obtained at the same conversion regardless of the heating rate. Figure 144 shows the dependence of the activation energy on the conversion of the feed for one of the resids. Several points can be noticed from this graph. First, the trend of the activation energy curve is the same regardless of the heating rate. Second, the 20°C/min heating rate gives a slightly higher activation energy. Third, the 20°C/min heating rate has unreacted material remaining at the end of the nonisothermal run. This can be seen by the high activation energy at the end of the curve. The last point worth mentioning is that the shape of curves of the activation energy for the resides were the same.

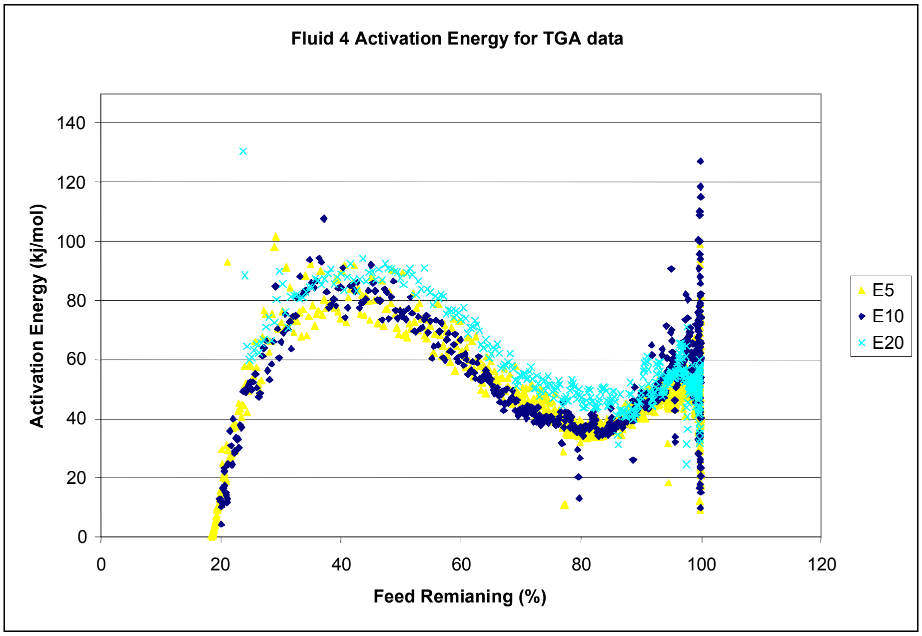


Figure 144 - Activation energy as a function of the feed remaining

Knowing that the activation energy is really changing with compositional changes, more than one activation energy is needed to characterize the reactions and predict the conversion. Figure 145 shows the activation energy for at 10°C/min. Three activation energies can predict the conversion as a function of temperature. As can be seen in Figure 146, the resulting fit is extremely good.

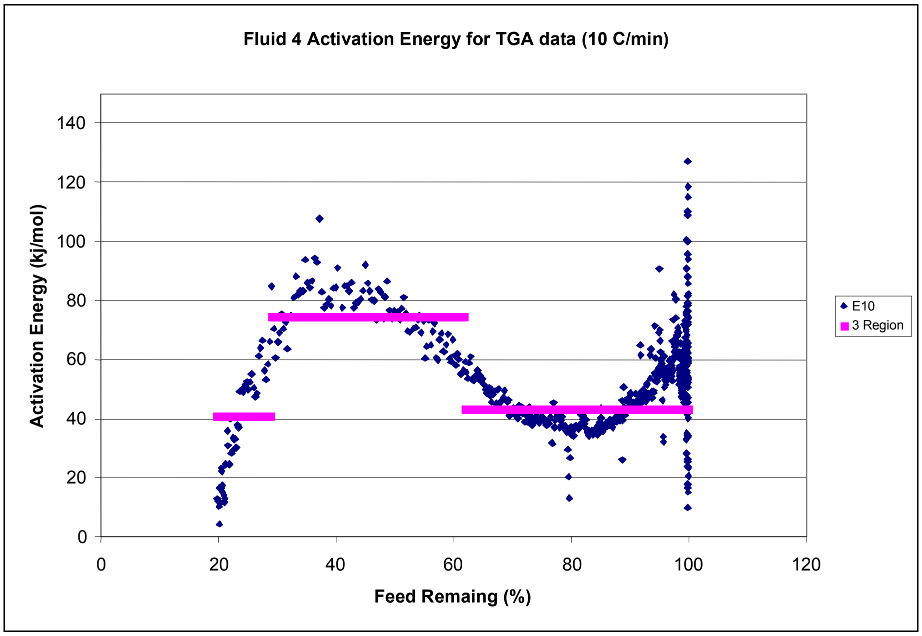


Figure 145 - Activation energy as a function of the feed remaining (10°C/min)

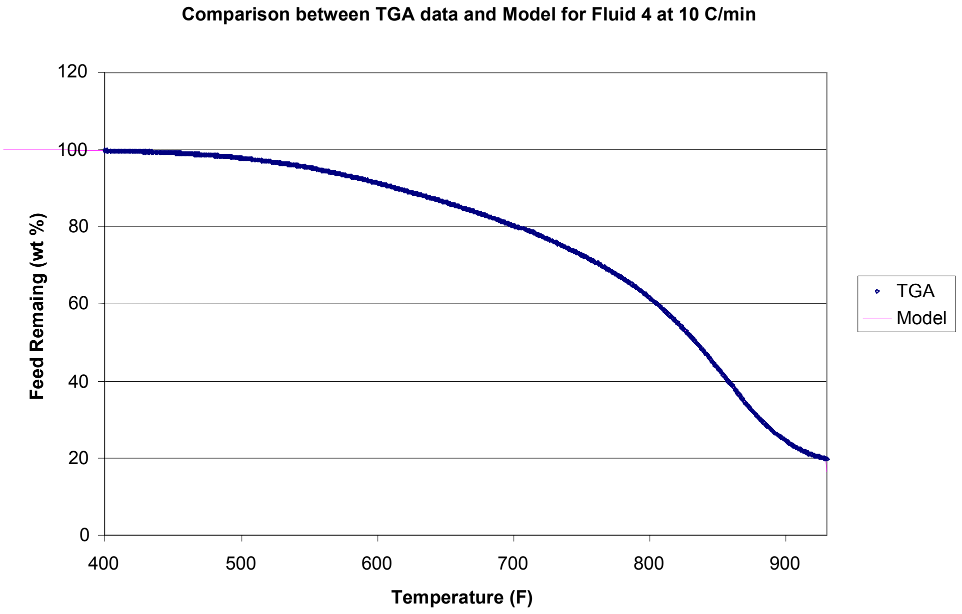


Figure 146 - Comparison between TGA data and Model for at 10°C/min

The same procedure can be applied for all feedstocks to find their activation energies. Figure 147, Figure 148, and Figure 149 show the activation energies for three different resids. These three graphs have the same shape, implying that the chemical structures of the feed are the similar.

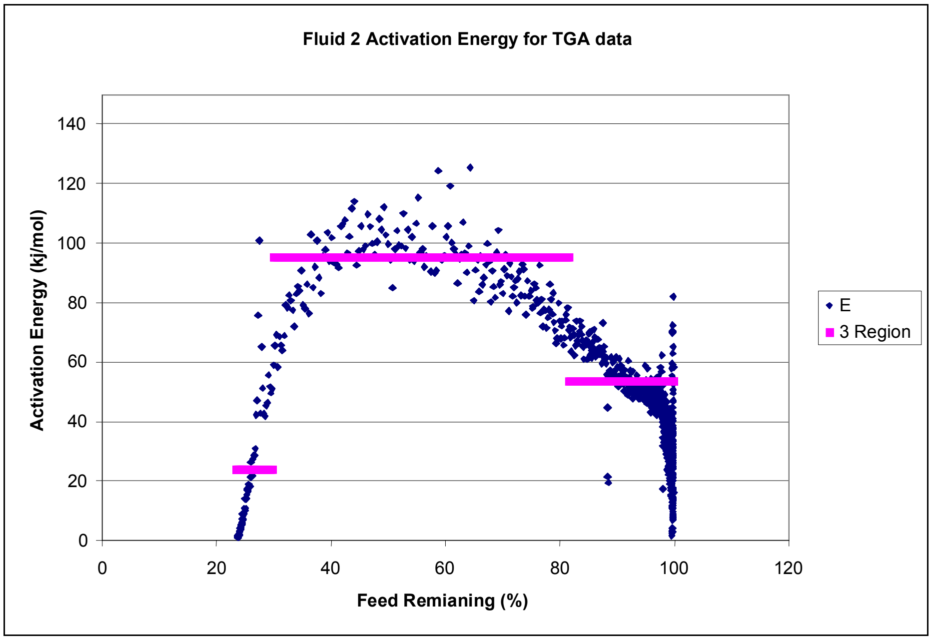


Figure 147 - Activation energy as a function of the feed remaining (5°C/min)

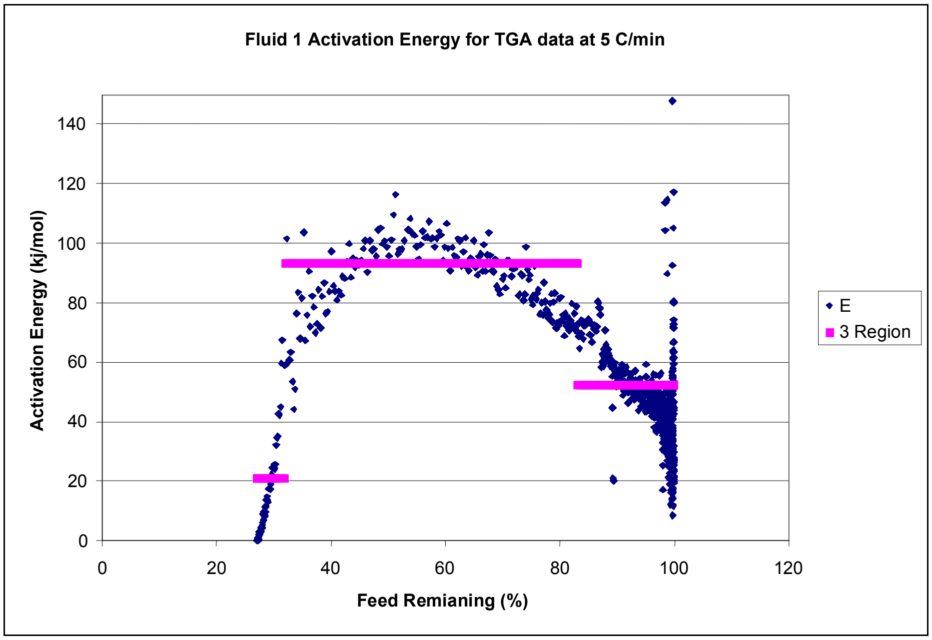


Figure 148 - Activation energy as a function of the feed remaining (5°C/min)

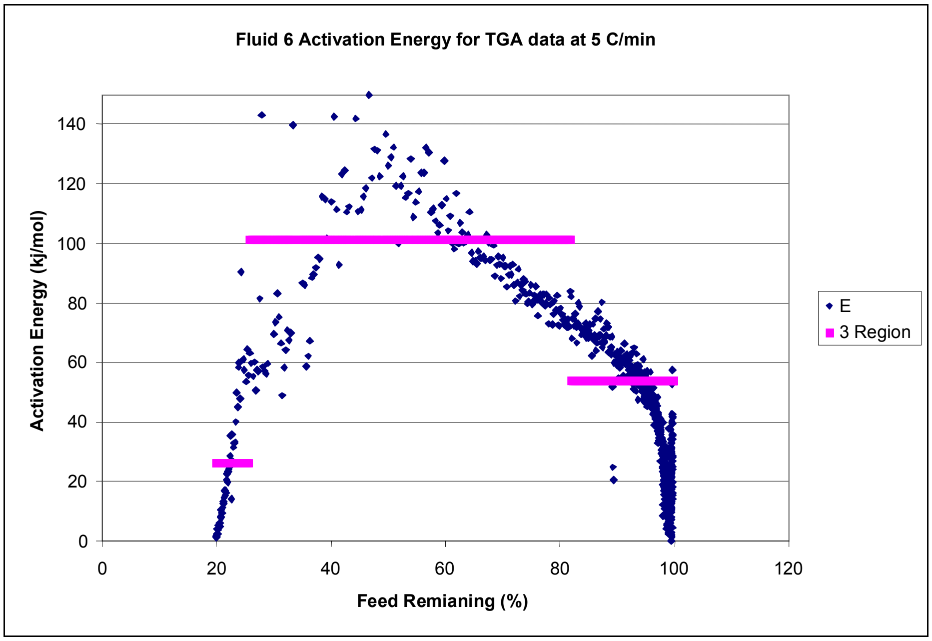


Figure 149 - Activation energy as a function of the feed remaining (5°C/min)

E. FURNACE TUBE MODEL

A preliminary model was developed to predict the two-phase flow regimes for the furnace tube, both for horizontal and inclined flow. The flow pattern in this case is a function of the resid properties (density, viscosity, and surface tension), which are estimated at the temperature and pressure of interest, as well as the angle of inclination of the pipe. Results show that the flow pattern in the pilot unit furnace changes from intermittent to annular due to vaporization of the feedstock. The vaporization results in a large increase in gas velocity, leading to the pattern transition from intermittent to annular flow. For the commercial delayed coking process, the high mixture velocity at the furnace outlet is expected to result in the annular flow regime. Typical flow patter maps, with the operating point for the pilot unit labeled, are shown in Figure 150 to Figure 154.

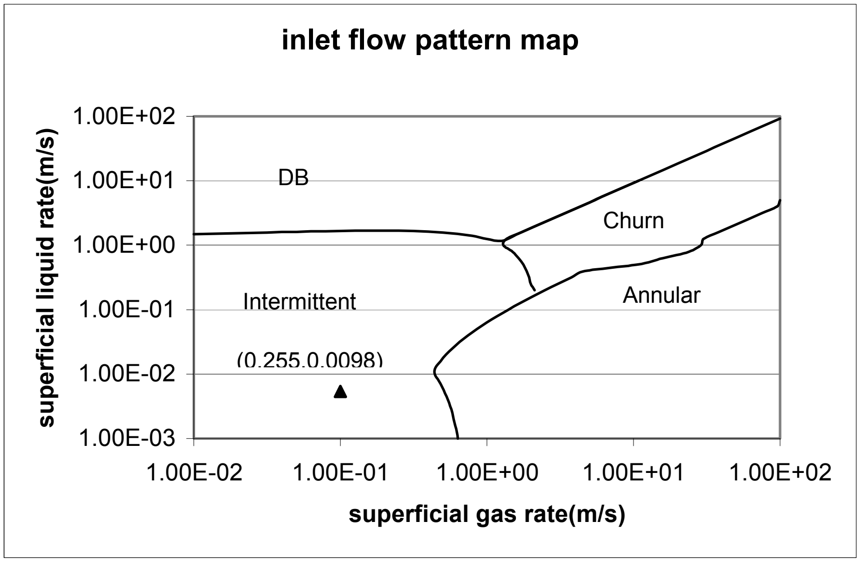


Figure 150 - Flow pattern map at furnace inlet

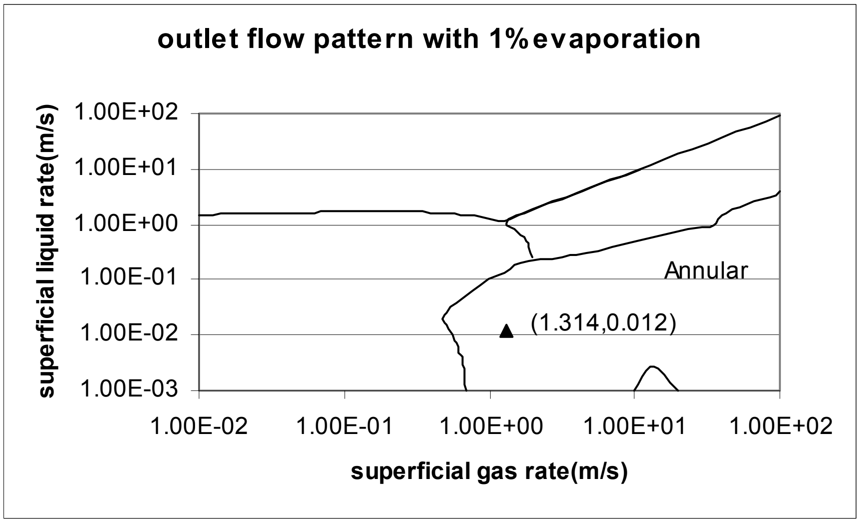


Figure 151 - Flow pattern map at furnace outlet with 1% vaporization

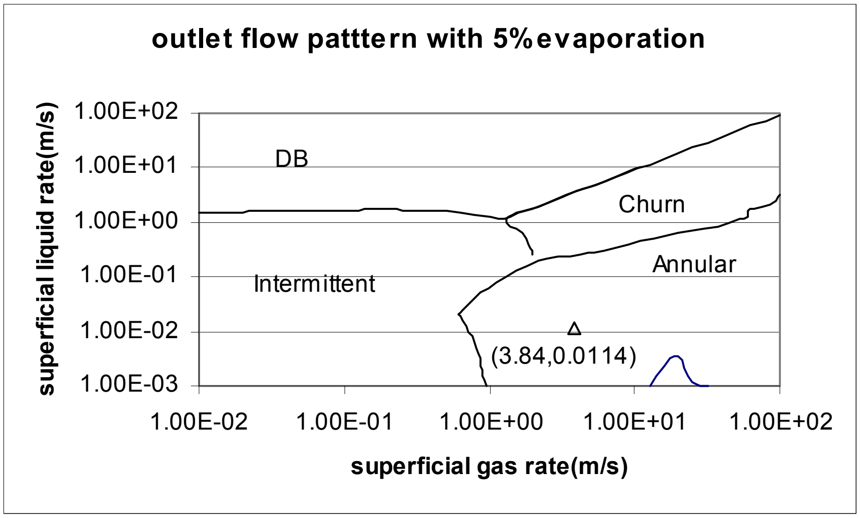


Figure 152 - Flow pattern map at furnace outlet with 5% vaporization

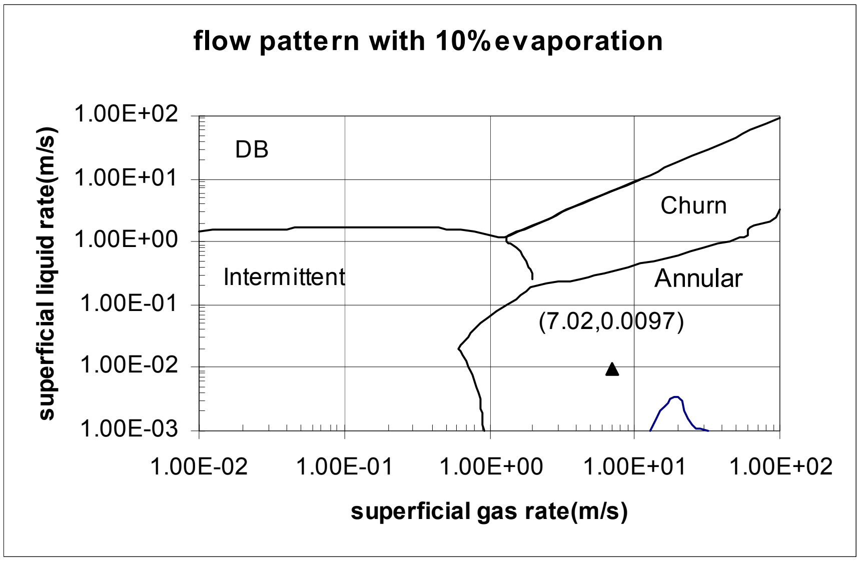


Figure 153 - Flow pattern map at furnace outlet with 10% vaporization

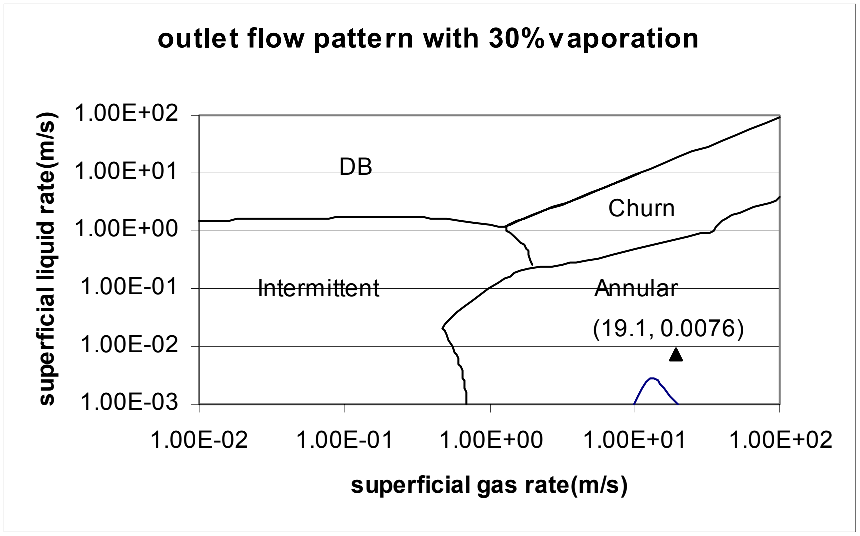


Figure 154 - Flow pattern map at furnace outlet with 30% vaporization

This flow pattern model, supplemented with kinetic data on the feed vaporization rate and with heat transfer correlations, will result in the development of a full furnace tube model that is able to predict heat transfer rates and fluid velocities entering the coking drum.

F. SCALE UP COMPARISONS

1. Comparison between mirco-coker, pilot coker, and stirred-batch coker

Figure 155 through Figure 160 show the average normalized coke, liquid and gas recoveries for each feedstock as well as the % volatile matter and SimDis results for the micro-coker, pilot-coker and batch reactor. Although these data only give a rough comparison, since variations in temperature and other reactor parameters (e.g., heating rate, flow rate) are not shown, it can be seen that there is generally more variation in liquid and coke yields between feedstocks than there is with operating conditions (temperature, pressure, flow rate, or reactor type).

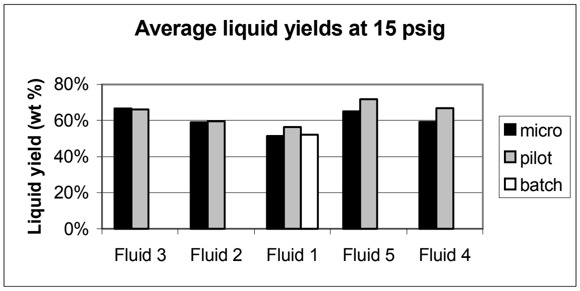


Figure 155 - Average Liquid Yields for the Three Coking Units at 15 psig

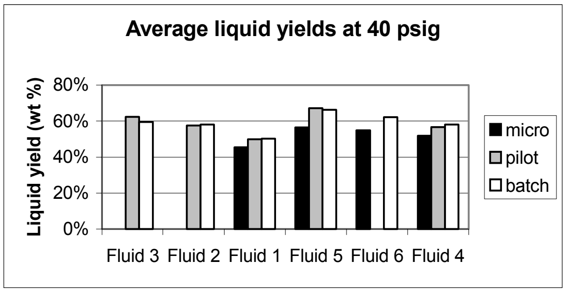


Figure 156 - Average Liquid Yields for the Three Coking Units at 40 psig

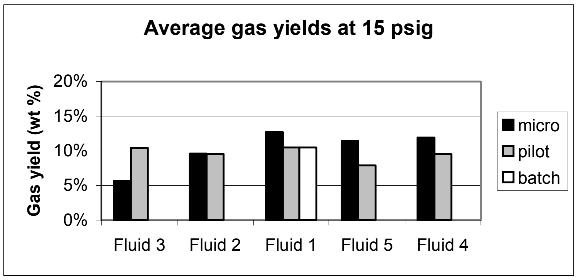


Figure 157 - Average Gas Yields for the Three Coking Units at 15 psig

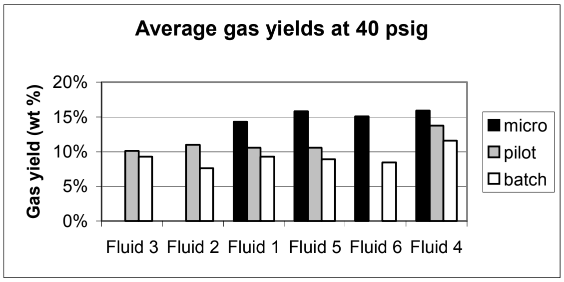


Figure 158 - Average Gas Yields for the Three Coking Units at 40 psig

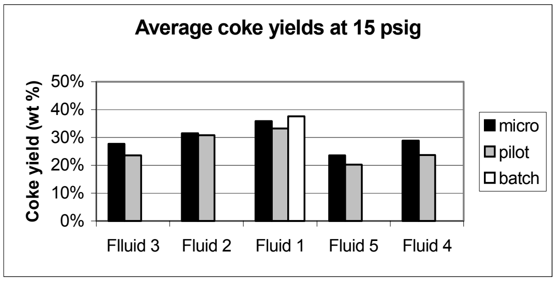


Figure 159 - Average Coke Yields for the Three Coking Units at 15 psig

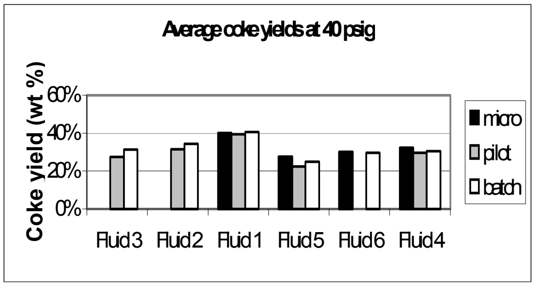


Figure 160 - Average Coke Yields for the Three Coking Units at 40 psig

The most important variables affecting product yields are the feedstock properties, the pressure, and the temperature-time history of the sample. Lower pressures give higher liquid yields because heavier liquids will be vaporized and leave the system before reacting further. The temperature-time history within the reactor has a more complicated effect. Many different chemical reactions occur in delayed coking; some are favored at lower temperatures while others are favored at higher temperatures. One would therefore expect that the heating rate would be an important variable for the batch reactor. For the micro-coker and pilot coker the residence time within the drum, and to a lesser extent within the portion of the furnace tube where the temperature is high enough for reaction to occur, and the temperature profile within these parts of the system will affect the product yields and quality.

The micro-coker runs and pilot-coker runs are somewhat easier to compare with each other than with the batch reactor runs due to the significant differences in operating conditions in the batch reactor. However, there are some notable differences in the way the micro-coker and pilot-coker are run. The micro-coker uses a cold feed (~630 °F), and the entire coke drum is heated to the control temperature (900°F, 930°F, or 950°F). On the other hand, the feed temperature to the pilot unit is much higher, and temperature control is in the furnace tube. The drum overhead temperature is considerably below the feed temperature, as is seen in refinery operation. Most of the coking reactions are therefore taking place at a lower temperature in the pilot unit than in the micro-coker at the same nominal temperature.

As seen in Figure 155 and Figure 156, the pilot coker and batch reactor in most cases show higher liquid yields than the micro-coker; the only exceptions are for the Fluid 2 and Fluid 3 resids, for which there are only one micro-coker run each, that show approximately the same liquid yield as the pilot coker. The difference in liquid yield is noteworthy because, as noted above, the micro-coker runs at a higher average drum temperature than the pilot coker or batch reactor. Ordinarily, one would expect higher liquid yields at higher temperatures, and this is indeed the trend seen from analyzing the pilot and micro-coker data separately (that is, higher liquid yields are seen for each unit when the temperature is raised). Apparently, the difference in the time-temperature history of the sample within the reactor (i.e., the gradual heating of the resid in the batch reactor and in the furnace tube for the pilot coker vs. the sudden heating of the relatively cold feed in the micro-coker) is causing this observed difference in liquid yields. These time-temperature histories for the three reactors are illustrated (in a qualitative way) in Figure 161.

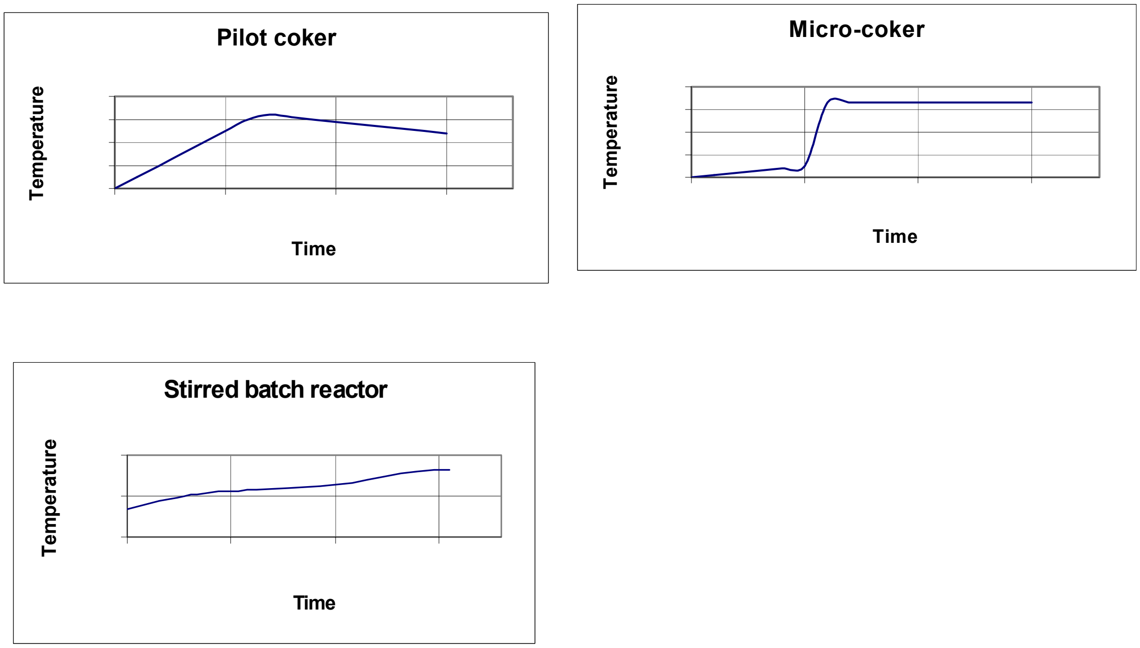


Figure 161 - Temperature vs. Time Trends for Pilot-Coker, Mirco Coker, and Stirred Batch Reactor

As seen in Figure 157 and Figure 158, the gas yield is notably higher for the micro-coker than for the batch reactor or pilot coker, also indicating that a change in reaction pathways is occurring under the micro-coker conditions.

For the coke yield, Figure 159 and Figure 160 show that the pilot coker has a somewhat smaller coke yield than either the micro-coker or batch reactor for every feedstock. The coke drum in the pilot coker operates at a somewhat higher temperature than the average temperature in the batch reactor. At higher temperatures, liquid products tend to vaporize and leave the reactor before converting completely to coke, thus resulting in lower coke yields. For the micro-reactor, it seems that the change in reactions favored at the very rapid heating rate experienced by the resid tends to also promote higher coke formation.

Figure 162 through Figure 167 show the average gasoline, diesel, and gas oil yields (as a % of the total liquids) at 15 and at 40 psig. The micro-coker gives, for most feedstocks, notably more gasoline and less gas oil than the other two units. The pilot coker and batch reactor tend to give roughly the same yields of gasoline, diesel and gas oil. Again, this difference for the micro-coker appears to be due to the significantly different temperature-time history of the resid in the micro-coker.

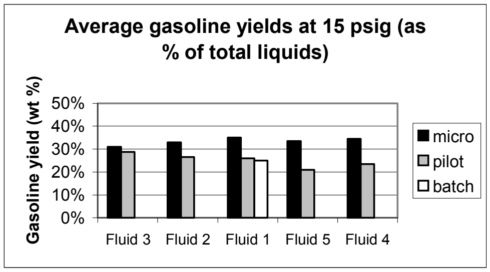


Figure 162 - Average Gasoline Yields for the Three Coking Units at 15 psig

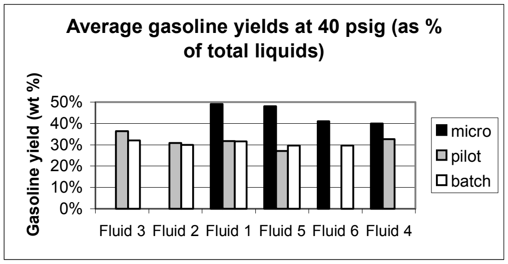


Figure 163 - Average Gasoline Yields for the Three Coking Units at 40 psig

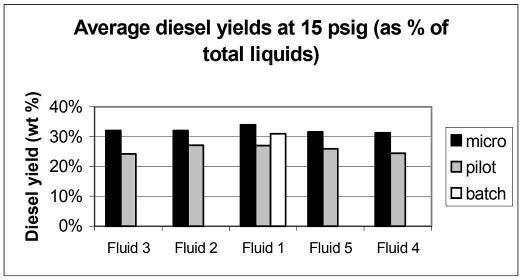


Figure 164 - Average Diesel Yields for the Three Coking Units at 15 psig

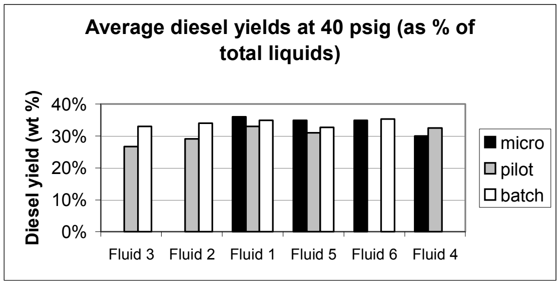


Figure 165 - Average Diesel Yields for the Three Coking Units at 40 psig

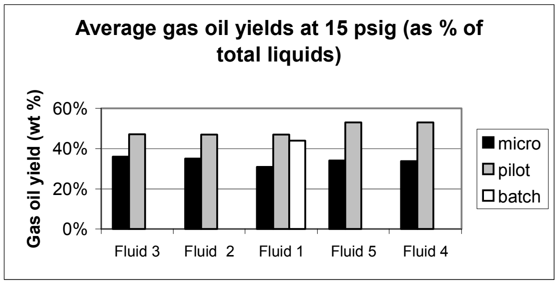


Figure 166 - Average Gas Oil Yields for the Three Coking Units at 15 psig

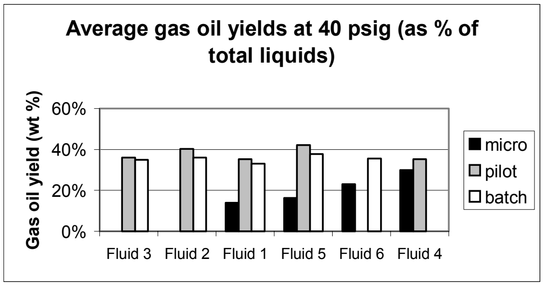


Figure 167 - Average Gas Oil Yields for the Three Coking Units at 40 psig

2. Comparison with refinery data

Delayed coking refinery operating data was provided by all six companies that donated feedstock to the JIP. These data were used to compare experimental results from the project with refinery operating results. Unfortunately, in most cases the refinery conditions (temperature and pressure) did not exactly match what were used in the experiments. For consistency and to allow a direct comparison between feedstocks, experimental runs were made at 6, 15, and 40 psig and (nominal) feed temperatures of 900, 930, and 950°F. Table 48 shows the refinery operating conditions for the six resids.

Table 48 - Refinery Operating Conditions

Resid	Feed Temp (F)	Ovhd Temp (F)	Pressure (psi)
Fluid 1	920-925	–	20-25
Fluid 3*	915	–	35-50
Fluid 6	903	829	50
Fluid 5	–	822	50-55
Fluid 2	816-834	915	35
Fluid 4	925-930	–	35

There were also some problems with limitations on the data. As shown in Table 48, three of the data sets were missing overhead temperature data, and one was missing feed temperature data. Also, much of the supplied data gave limited information on liquid product boiling point distributions. In addition, the data supplied by one refinery was for a different feedstock than was supplied to the JIP (apparently they blend feedstocks for their delayed coking process and the donated feedstock was an unblended sample).

Due to these limitations, comparisons to the experimental data were rather qualitative in nature. Figure 168 and Figure 169 show a graphical comparison of refinery with experimental product yields for two of the fluids tested. In all cases, the experimental data is seen to correspond well to the refinery data, within the limitations of the operating conditions.

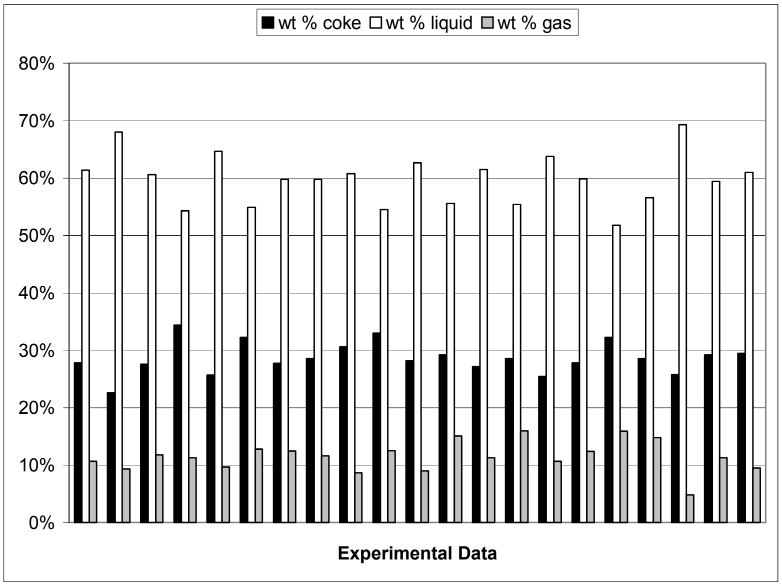


Figure 168 - Comparison of Refinery Yields with Pilot and Micro-Coker Data

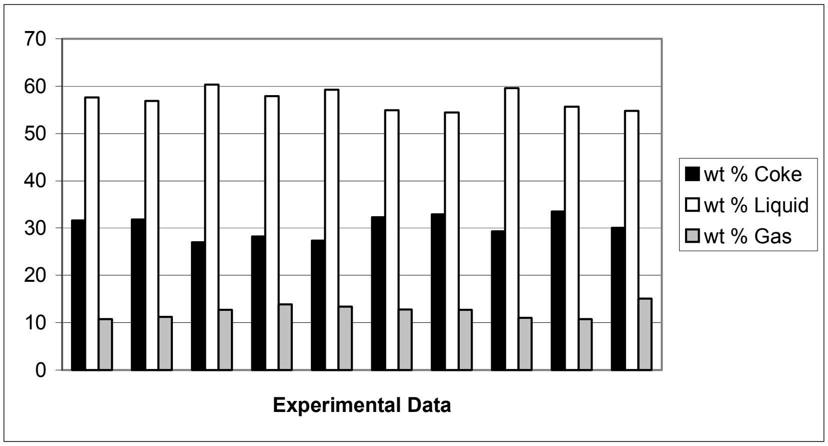


Figure 169 - Comparison of Fluid 6 refinery yields with pilot and micro-coker data

Liquid product boiling point distribution comparisons are shown in Figure 170. Again, the comparison is good within the limitations of the varying operating conditions.

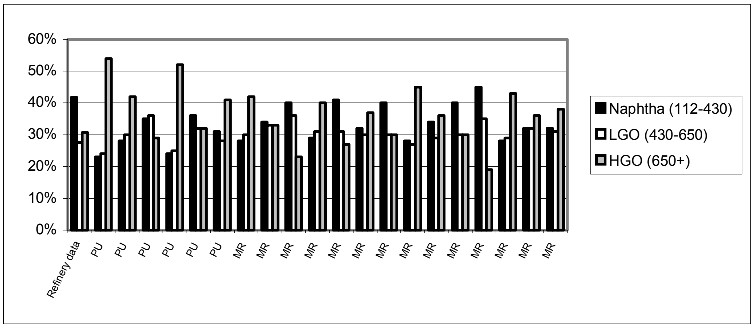


Figure 170 - Comparison of Refinery Liquid Properties with Pilot and Micro-Coker Data

12. Recommendations

A. MICRO REACTOR STUDY

The micro-coker is a screening tool that allows for quick experimental analysis to estimate liquid, gas and coke yields and sulfur content, plus liquid sub-product yields. Results from this JIP show the micro reactor produces results that are scaleable to industry. However, this model was built using only three feedstocks and the range of several key parameters such as asphaltene content, MCR, recycle and metals (Ni, V) were not broad enough for a robust model. Also, comparison of the micro-coker operating conditions with the pilot coker show that the same feed temperature results in overcracking in the micro-coker because there is no temperature drop through the reactor as there is in the coke drum of the pilot unit. Lower reactor temperatures should be utilized in the micro-coker, corresponding to the average drum temperature in the pilot coker rather than the feed temperature, so that a better comparison in the product yields for the two units can be obtained.

B. BATCH REACTOR STUDY

A larger database of kinetic studies is needed in order to better determine how feedstock properties affect the kinetics. Analytical measurements for the batch reactor experiments should be modified to include SARA analyses on the reactor samples and PiONA analyses on the product liquids. Product sampling of the condensed liquids should be modified to allow more frequently sampling during the run. Use of a wider variety of feedstocks should also be considered, as well as runs at higher pressure to better simulate furnace tube conditions. The batch reactor can also be used to for study of novel processing schemes, such as injection of gas during reaction to reduce gas-phase cracking and removal of H_2S evolved at the onset of the coking reactions.

C. PILOT UNIT STUDIES

While conducting parametric studies, runs were made with and without antifoams. Contrary to refinery experience, antifoams were successfully injected with the feed. Preliminary foaming studies have proven the usefulness of the gamma densitometer in measuring foam and coke formation. Additional studies should be done to gain a better understanding of the foaming process in order to minimize or eliminate process upsets as well as optimize the use of antifoams to increase refinery margins. The impact of superficial velocity should be quantified by varying feed rate to the pilot coker, and/or conducting studies using drums different sizes, to achieve superficial velocities more closely resembling those of industrial units.

Temperature profile data in the drum can be used to determine cool down rates during steam stripping, which should correlate to coke morphology. This can provide valuable safety information to refiners. The temperature profiles also can potentially be correlated to foam levels and, in conjunction with furnace heat output data, may allow energy balances to be made on the drum, shedding light on heats of reaction and vaporization rates.

Fouling can be studied in more detail by cutting slices from spent furnace coils and examining the coke microscopically to determine how the coke is deposited and what factors increase coke deposition.

To expand the properties of the feedstocks studied, other feedstocks should considered. These may be other types of feedstocks such as solvent deasphalted pitch or lube oil or other resids such as Cerro Negro, Arabian Light, etc.

D. MODELING

The Delayed Coking Model is a lumping model based on boiling point distributions. It assumes that any material that is cracked into components light enough to become vapor will leave the drum without further cracking, while any cracked material that is heavy enough to stay in the drum will become heavier (through condensation or polymerization reactions) to eventually form coke. A larger database of kinetic studies is needed in order to better determine how feedstock properties affect the kinetics. Enhanced batch reactor studies (discussed above) would will allow us to enhance our kinetic model to include olefin-producing reactions, naphthene ring-opening and dehydrogenation reactions, and aromatic condensation reactions. These principles expand modeling beyond correlated data available from this Joint Industry Project or from a member company's limited database of process operation.

13. Conclusions

A. MICRO REACTOR STUDY

Results of this study show the micro-coker to be an effective screening tool, producing small quantities of coke, liquids and gases for testing over a very short operating period. The results from the micro-coker compare favorably with pilot scale and commercial results in terms of product yields, liquid product distribution and properties, and coke properties. Some differences between the micro-coker and pilot unit results were noted, specifically the somewhat lower liquid yields and higher gas and coke yields, and higher gasoline yields in the micro-coker. These differences are due to the differences in the way the micro-coker and pilot-coker are run. The micro-coker uses a cold feed (~630 °F), and the entire coke drum is heated to the control temperature (900°F, 930°F, or 950°F). On the other hand, the feed temperature to the pilot unit is much higher, and temperature control is in the furnace tube. The drum overhead temperature is considerably below the feed temperature, as is seen in refinery operation. Most of the coking reactions are therefore taking place at a lower temperature in the pilot unit than in the micro-coker at the same nominal temperature. This means that, compared to the pilot unit, the micro-coker tends to overcrack the feed, resulting in more gas and coke and less liquids, specifically less gas oil.

B. BATCH REACTOR STUDY

Kinetic studies were carried out using both the stirred-batch reactor and thermogravimetric analysis (TGA). The TGA studies give excellent temperature control with a large data set (feed loss vs. time), but provide no information on product distributions. This data has resulted in a simple kinetic model of resid conversion. The stirred batch reactor gives good information on product distributions but has limited temperature control and a limited amount data over time for each run (typically four liquid samples are obtained during a coking run). Combined with information from the TGA, a more detailed kinetic model can be developed that includes prediction of the boiling point distribution of the products.

The stirred-batch reactor experiments were carried out until complete reaction occurred, i.e. until complete conversion of the feed to coke and vapor (condensate and gas) products. This aspect of the experiments allowed a comparison of the end products of the stirred-batch coking reactions to the results of the micro-coker and pilot unit studies. Results showed that the product yields (coke, liquid and gas) match very well with what was achieved in the pilot unit under comparable temperatures and pressures.

C. PILOT UNIT STUDIES

The pilot unit was successfully run to obtain reliable and reproducible coking data. Results from the pilot unit correspond well with results from refinery operation from the same feedstocks at similar operating conditions. Analysis of the gas, liquid and coke products have given valuable information on the liquid product subfraction yields, sulfur distributions, and coke morphology as a function of feedstock and operating conditions. Both shot and sponge morphologies were produced with this facility.

Preliminary studies have been carried out using the modified pilot unit for foam detection. Use of the gamma densitometer was successfully demonstrated to detect foam formation, foam collapse (both spontaneous and from antifoam addition), and coke morphology. Problems were encountered while trying to control the foaming facility using fluid temperatures because of the temperature fluctuations (± 20 °F). By controlling the tests using skin temperature, reproducible data was obtained. This data was compared to the data generated in the parametric studies using the 3' drum. Excellent agreement was obtained. Foam could be observed and collapsed using the 100,000 cSt antifoam. A preliminary estimate of foam density is < 0.3 gm/cm^3. Very little foaming was observed for the Fluid 3 resid at 40 psig as a function of temperature. Significant foaming, filling the drum two-thirds full before injecting antifoam, was observed for the lower pressure runs. It was observed that when the feed rate was increased, the height of the foam column more than doubled at an equivalent time and that the column was not as dense. Steam velocity was observed to have a similar effect. Injection of the antifoam in the feed suppressed foaming and produced a denser coke. Of the four resids, Fluid 3 was the worst foamer followed by Fluid 4, Fluid 1, then Fluid 2. These results concur with what was observed in the batch reactor tests. Additional testing and data processing must be carried out before any final conclusions are drawn.

Seventeen fouling tests were run with the pilot unit. Two different application techniques were used for the anti-coking agent; one where the coil was pre-treated and one where it was only added to the feed. The pre-treating agent passivated the metal surface inhibiting the lay down of coke precursors. This pre-treatment resulted in energy savings due to quicker warm-up as well as from only having to apply a 5^{o}F delta T rather than 10^{o}F for the test where the coil wasn't pre-treated. The additives also improved the heat transfer to the fluid and where the resistance to energy transfer analogy could be applied resulted in less fouling. An increase in temperature by as much as 20^{o}F was observed when a combination of anti-coking agent was used with a stabilizer. There were no distinguishable differences observed in the coke morphology produced from run to run. The coke morphology was described as a very small tightly aggregated shot. No BB shot was observed. The coke generated in the fouling studies was nearly identical to that described from the pilot unit runs that were called transitional.

D. MODELING

Correlations to predict the product yields for the micro-reactor were developed. Sets of correlations for several feedstocks (Fluid 5, Fluid 1, Fluid 4) were developed to predict product and liquid subfraction yields as a function of temperature, pressure, and liquid space velocity. A general correlation was also developed based on temperature, pressure, liquid space velocity, and feedstock microcarbon residue. Correlations were also produced to predict sulfur distribution among gas, liquid and coke products. All correlations show very good agreement between experiment and prediction. The product yield correlations were adjusted with correction factors, which account for the overcracking mentioned above, to allow prediction of the pilot unit results.

Correlations (both general and feedstock-specific) were also developed from the pilot unit studies to predict product distributions, with very good agreement between experiment and prediction. Results from the revised SimDis data were used to successfully correlate liquid product distribution data.

Results from the stirred-batch reactor were also used to develop some simple rule-of-thumb correlations for coke, liquid, and gas yields.

A preliminary model was developed to predict the two-phase flow regimes for the furnace tube, both for horizontal and inclined flow. The flow pattern in this case is a function of the resid properties (density, viscosity, and surface tension), which are estimated at the temperature and pressure of interest, as well as the angle of inclination of the pipe. Results show that the flow pattern in the pilot unit furnace changes from intermittent to annular due to vaporization of the feedstock. The vaporization results in a large increase in gas velocity, leading to the pattern transition from intermittent to annular flow. For the commercial delayed coking process, the high mixture velocity at the furnace outlet is expected to result in the annular flow regime.

14. References

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15. Nomenclature

AIChE	(American Institute of Chemical Engineers)
BM	Benchmark
CD	(Computer disk)
DHA	(Detailed Hydrocarbon Analysis)
DOE	(Department of Energy)
FMB	(Foxboro Bus Modules)
GC	(Gas Chromogragh)
H_2S	(Hydrogen Sulfide)
HES	(Health, Environmental & Safety)
HTGC	(High Temperature Gas Chromatography)
JIP	(Joint Industry Project)
LLC	(Limited Liability Company)
MCR	(Micro Carbon Residue)
Ni	(Nickel)
NPRA	(National Petroleum Refining Association)
PFPD	(Pulsed Flame Polarigraphic Detector)
PiONA	(Paraffins, Iosparaffins, Naphthenes & Aromatics)
SARA	(Saturates, Aromatics, Resins & Asphaltenes)
TCD	Thermal Conductivity Detector
V	(Vanadium)

16. Appendices

A. EQUIPMENT OPERATING PROCEEDURES

1. Micro-coker Operating Procedure

1. Take bottom off of sample shell and grease the o-rings and seals with the grease provided for this purpose.
2. Heat the oil (~240 g) on hot plate to liquid so it can be poured into the sample cylinder.
3. Weigh the sample cylinder with heating mantle, valve and thermocouple attached to the sample cylinder and get tare weight.
4. Put in ring stand and pour the oil but let the oil cool down just a little before pouring in so not quite so liquid. Do not get any on the sides of the sample cylinder. Re-weigh and let sit overnight to cool all.
5. Weigh the removable liner and put it in reactor.
6. Coke may go into the line going to the first trap (metal); if this happens during the run, stop the run and clean it out. That line should also be tared just in case and reweighed after the run.
7. Tare the moisture/oil trap before the run also.
8. Tare the two glass traps with fittings and joints intact.
9. Prepare the wet test meter ready. Fill with DI H2O, if possible, to top of the meniscus in the aide glass tube. Fill up the differential tube to 0 mark. Temperature and differential readings will be read.
10. Weigh the cylinder with oil and put into place. Start stirrer and set at 180 rpm.
11. Turn on the heater to sample cylinder, pre-heater and reactor; see settings for temperatures. Be sure the 3 way valve after the back pressure gauge is in the vent position while the sample is heating up. Do not get the sample too hot or it will go through the system too fast. It should be just runny.
12. Manually run the plunger down to the resid and then back off about 10-15 cc. Be sure the 3 way valve on the nitrogen line is in the vent position while running the plunger down. After the plunger is in place turn off the nitrogen to the sample cylinder and let it run through the rotameter into the reactor.
13. Nitrogen pressure gauge should read 20-22 psi, with a rotameter setting of 9.25.
14. Back pressure regulator should be set at 6.1.
15. After the sample is ready to go and syringe pump is set, turn the pump to auto setting to 10-15, turn the 3 way valve after BP gauge back to the wet test meter and let run. Be sure the clutch is in with slide bar in the lock position (slide bar out to get cylinder out).
16. Open the valve to the pre-heater just a little bit. Do not open all the way, as this will cause problems. After all the oil has been injected and the pump stops, shut the valve and let run. It takes about 70 minutes for a run.
17. Take the temperature readings on all heated zones about every 10 minutes and record on data sheet.

2. Stirred batch-coker Operating Procedure

1. Weigh the liner empty.
2. Weigh the liquid sample tubes.
3. Weigh the condensate cylinders.
4. Pour ~1.2 gallons of the hot resid sample inside the liner (approximately 60% of the liner volume) so the final coke, approximately 30% of the charge, will form mainly below the agitator allowing simple disassembly after the run.
5. Weigh the liner with the sample in it.
6. Place the liner inside the reactor.
7. Check on all internals including the stirrer.
8. Place the reactor gasket in place and tighten the reactor lid.
9. Purge the reactor with nitrogen for one hour to displace the air in the system.
10. Pressurize the system with nitrogen to the required test pressure (between 15 and 40 psig) and check for leaks.
11. Turn the heater on and set the controller output to 85%, 55%, or other predetermined value.
12. Enter a value for the stirrer speed in AC inverter.
13. Turn the magnetic drive manually to make sure that the stirrer can turn.
14. Push the run button in the AC inverter to start the magnetic drive stirrer.
15. Record gas volume, temperature, and pressure every 15 minutes.
16. Take liquid samples, as described below in sampling procedure, at 775°F, 800°F, 825°F, and 850°F.
17. Record time and temperature at which the sample is drawn.
18. Weigh the sample tube again and get tare weight.
19. Continue the test until gas production diminishes indicating the end of the run.
20. Turn the heaters off and start purging with nitrogen for 1 hr.
21. Cool the reactor overnight
22. Dismantle the reactor.
23. Take the final weight of the liner.
24. Solvent wash the lid and attached internals.

3. Stirred batch-coker processed resid sampling procedure

A schematic diagram for the sampling tube is given in Figure 171, Figure 172, and Figure 173. The following sampling procedure is applied when sampling the liquid from the reactor.

1. Weigh the sampling tubes beforehand and label them.

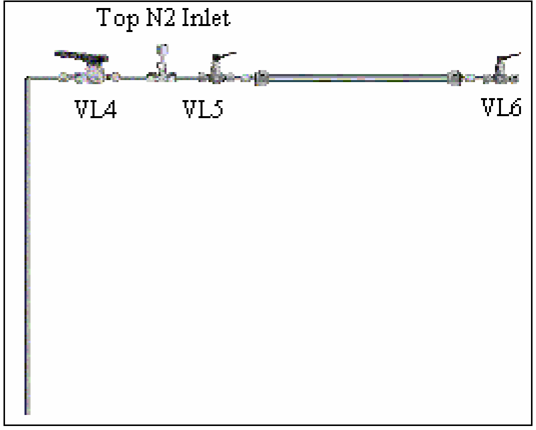

Figure 171 - Schematic diagram of the sampling tube

2. Slide the sampling tube into the sample port – the seal nut should be loosened to allow the sampling tube entry.
3. Open VL2 and tighten the nut without applying excessive torque.
4. Check for leaks between the sampling tube and the seal nut. If there is a leak, tighten the nut but don't over tighten it since that will prevent the tube from sliding.
5. Purge the sampling tube and sampling port with nitrogen by opening VL2, VL4, VL5, and VL6.
6. Close the valve in the sequence from outside to inside (VL6 and then VL5).
7. Release the pressure between VL5 and VL6 (toggle valves) by pushing down the handle of VL6.
8. Open the top nitrogen line valve (not shown in the figures) and check for a leak between the seals and the sampling tube. If there is a leak, tighten the seal nut with a wrench but make sure you can still slide the tube vertically in both directions.
9. Make sure that the nitrogen pressure is higher than the reactor pressure to prevent early sampling in the vapor phase.
10. If there is no leak, open the sample port valve, VL1.
11. Push the sample tube through the sample port valve and into the liquid – the tube should be pushed down until it

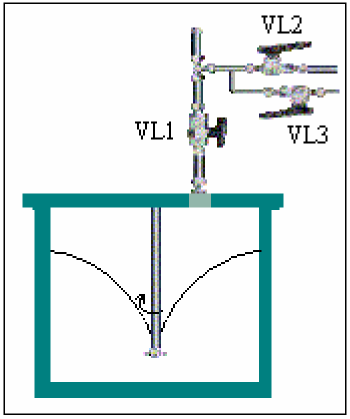

Figure 172 - Schematic diagram of the reactor and sampling port

hits the bottom of the liner. This way you can make sure that you are in the liquid phase.

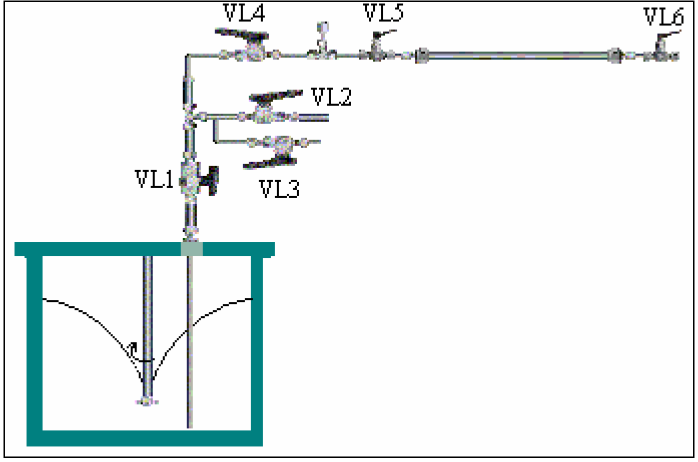

Figure 173 - Schematic diagram of the reactor with the sampling tube inserted

12. Close the top nitrogen valve and open VL5. The sample now should be going to the sample compartment. With the pressure already exists between VL4 and the reactor, the sample bomb will not be completely filled. This sample should be enough for testing. If more liquid is desired, close VL5 and push down VL6 and release it very rapidly to relieve the pressure in the sampling bomb. The tube plug at the end of VL6 will prevent the liquid from jetting out. Open VL5 for more liquid sample and shut it off.
13. Open the top nitrogen valve to push the sample in the lower side of the sampling tube back to the reactor.
14. Pull up the sampling tube slowly and watch for leaks at the seal nut. This step should be done carefully without bending the sampling tube. If leak is detected, tighten the nut with the wrench and continue pulling up the sampling tube until it passes VL1 and then close VL1. Don’t pull yet the sampling tube completely out of the sampling port.
15. Close the nitrogen lines, the top nitrogen valve and VL2.
16. Open VL3 to relieve the pressure in the sampling port.
17. Pull out the sampling tube completely out of the sampling port.
18. Take the final weight. The sample weight will be the difference between the empty sampling tube and the final weight.

4. Pilot-coker Operating Procedure

Delayed Coking/Visbreaking Pilot Unit Operating Procedures

Written/Updated by Chris A. Paul 3/22/95

<u>Delayed Coking Operation</u>

I. Start-Up and Normal Operating Procedures

A. Operator needs to assemble, weigh, and install empty coke drum reactor.

1. Assemble coke drum reactor top and bottom hubs using seal rings, flange clamp assemblies and clamp bolts.
2. Inspect seal rings before use. Use a new seal ring if the old one appears excessively worn, and you do not believe it will hold pressure.
3. Use a torque wrench when tightening the clamp bolts to apply approximately **55 ft-lbs** of torque. Don't forget to put in the hanger sleeves between the top nuts and bolts.
4. Install winch eyelet fitting into reactor top hub. Don't forget to put in the 1" plug.
5. Weigh coke drum reactor with bottom and top hubs, seal rings, clamp assemblies, and winch eyelet fitting (without reactor main thermowell).
6. Enter weight into I/A system manual input screen.
7. Hang reactor on unit using winch, and mount reactor from the top clamp assembly to overhead unistrut.
8. Remove eyelet fitting and connect top hub to block fitting using 1" spool piece.

   a. Make sure nitronic nut is on the end connected to the reactor top hub. Use "Anti-Seize" to lubricate fittings which will be exposed to high temperatures.

   b. The block fitting will need to be stripped and disconnected in order to connect it to the spool piece from the reactor top hub.
9. Weigh preheater coil.
10. Enter weight into I/A system manual input screen.
11. Connect coke drum reactor bottom hub to coker preheater coil outlet.
12. Connect coker preheater inlet to process feed line.
13. Install reactor main thermowell and connect thermocouples (TI-208 through TI-215) to extension leads.
14. "Anti-Seize" can be used to lubricate the fittings being connected in steps 11-13 which will also be exposed to high temperatures.

B. Pressure test unit, establish N2 flow, and insulate exposed areas.

1. Block out all rotameters (PDT-201, LT-601, and LT-611).
2. Check blowdown line to T-211 (Blowdown Pot above coke drum) to see that coking rupture disk (rated for 250 psig @400 F) is in place. If it is not in place, install it.
3. Using cylinder N2, pressure test unit for 1 hour at ~140 psig. (Pressure relief valves on T-601 and T-611 Product Separators are set for 150 psig.)

   a. Block in the unit. PIC-611 can be used in manual control set to the fully closed position.

b. After blocking out the rotameters, open the nitrogen cylinder.

c. Slowly open the Hoke block valves in the high pressure nitrogen line and the metering valve which will open flow of nitrogen to the unit.

d. Watch PI-200 and PI-201 pressure gauges. When they both read 140 psig, close the block valve and close the N2 cylinder.

e. While waiting one hour, soap all the coke drum fittings, top and bottom hub sealing surfaces, and the overhead block valve fittings to inspect for leaks.

f. If the last run was visbreaking using P control valve PIC-201, soap the control valve (PIC-201) spool piece connections.

g. If the pressure drop after 1 hour is < 5 psig, the pressure test was good.

h. Bleed off the pressure through the PIC-611 bypass valve or through the blowdown valve (in the N2 line to T-211 at the top of the coke drum) or by slightly opening PIC-611 using manual control.

i. Set PIC-611 back to automatic control with a setpoint at the operating pressure for the upcoming run.

4. After pressure test, turn on plant N2 (at PDT-201, LT-601, and LT-611) to line the unit out at operating pressure (PIC-611) and to establish total N2 flow of approximately 1-3 SCFH (set the flow indicators on the three pairs of rotameters to 0. 5).

5. Install TI-207 (Drum Outlet Skin T). TI-207 should be positioned with the end touching the skin of the spool piece which connects the coke drum reactor top hub with the block fitting overhead. Wire it in place to the spool piece with the end touching the top of the nitronic nut at the reactor top hub.

6. Insert kaowool between TI-207 and the ceramic wall of the furnace all around the spool piece to prevent excess heat loss out the top of the furnace.

7. Wrap the top block above the reactor, the reactor internal thermowell nut, and any other exposed areas.

8. Put TI-131 into position on the preheater inlet line skin just outside the furnace.

9. Wrap the end of the feed line to the preheater inlet at the bottom of the furnace and insert kaowool into any of the furnace grooves where heat may be lost.

C. Turn on steam and glycol, and fill water graduates

1. Open steam flow (supply and return) at the steam manifold to steam tracers (1-6).

2. Open glycol block valves around E-611 (Overhead Condenser) and the gas meter knockout pot glycol line.

3. a. Fill T-030 (Diluent Water Feed Graduate) with distilled water.

b. Fill the Diluent Water burette to the 0 cc mark.

4. a. Fill T-035 (Quench Water Feed Graduate) with distilled water.

b. Fill the Quench Water burette to the 0 cc mark.

D. Operator should line up feed system flow and prime diluent water line.

1. Line up flow inside the Hot Box from the Feed Drum. Check the level of feed inside the drum.
2. Line up flow from P-001 (Hot Box Feed Pump) to FV-005 (Overfill Protection Valve). Leave FV-005 closed, but line up rest of flow through F1 (Feed Filter) to T-023 (Charge Tank).
3. Line up flow from T-023 to AOV-131 back to Hot Box so that P-025 (Feed Booster Pump) discharge will circulate to T-023 and P-026 (Main Charge Pump) discharge will return to Hot Box.
4. Check stroke settings on all 4 barrels of P-026 to see that they are set to the appropriate values for diluent water, charge, and quench water. For a smooth charge flow, use both charge barrels (to lower the pulsations of the feed).
5. Start P-026 with VR feed barrels blocked out in order to line out the diluent water flow rate at a stroke setting to pump ~100 cc/hr for about 5 minutes to fill the lines from the water graduate to the feed inlet line. Cut back the stroke to that of the desired diluent water flow rate for the run (~10-20 cc/hr).
6. Line out the quench water flow rate to ~10-20 cc/hr also.
7. Check the weight of charge (WT-23). If it is at least 2000 g, start P-025 to begin circulating the charge.
8. Check to see that AOV-131 is in the "closed" (to recycle) position.
9. Open the VR feed barrels of P-026 to begin flow of VR back to the hot box recycle loop.

E. Initialize Run in the AT&T

1. Close out the previous run. Shutdown logs will print out.
2. Enter the Run Number in the AT&T. Run number is in the format 274-YR-XXXX .

F. From Foxboro I/A screen (B46:Unit 274:Coker:Sequence), hit START button to begin coking sequence program.

1. Sequence program will change unit status to "**Start-Up**".
2. Program will bring up unit set up screen. Select COKER, and select one of the two control modes, most likely COKE MODE. The program will wait for the operator to hit the CONTINUE SEQUENCE button.
3. Program will bring up operator start of run manual entry screen and will wait for all data to be entered.

4. Enter all manual inputs on the start of run manual input screen.

Estimated Coke Yield (31. 0) wt%
Approximate Flow Rate (FI-23) (1100) g/hr
Limits of Flow (FI-23) (1050) to (1150) g/hr
Estimated Coke Density (0. 50) g/cc
Reactor Fill % (75. 0) vol% of Rx
Hours to Steam Strip Coke (1. 5) hrs

Temperature Setpoints

a. TIC-23 (Feed Tank) (250) °F
b. TIC-131 (Line Heater) (300) °F
c. TI-200 (PreHTR Out) (940) TIC-201 Setpt . °F
d. TI-208 (Drum Outlet) (800) TIC-206 Setpt. °F
e. 205 Bias from TI-208 (-105) TIC-205 setpt. °F
f. 204 Bias from TI-208 (-105) TIC-204 setpt. °F
g. 203 Bias from TI-208 (-65) TIC-203 setpt. °F
h. 202 Bias from TI-208 (-20) TIC-202 setpt. °F

Pressure Setpoint

a. PIC-611 (Drum Outlet) (40) psig

$$\text{Run Length (hrs)} = \frac{\text{Rx Vol (cc)xRx Fill \%xCoke Density (g/cc)}}{\text{Feed Flow Rate (g/hr) x Est Coke Yield (wt\%)}}$$

G. Hit CONTINUE SEQUENCE button on manual input screen to begin sequence program below. (Send message to operator to check the inputs or call the engineer if run length is outside reasonable limits. When acceptable inputs have been entered to calculate a reasonable run length, display the run length, print screen, and continue with sequence program below.)

1. Sequence program will turn on power to THTR-23 (Feed Tank Htr), THTR-131 (Feed Line Htr), THTR-201 through THTR-206 (Furnace Zone Heaters).
2. Sequence program will turn on the "Coking Mode" furnace control scheme.
   a. Use TI-200 (from F. 9. c. above) as remote measurement for TIC-201.

b. Use TI-208 (from F. 9. d. above) as remote measurement for TIC-206.

c. Add Bias-205 to TI-208 to get (heater wall T) setpoint for TIC-205.

d. Add Bias-204 to TI-208 to get (heater wall T) setpoint for TIC-204.

e. Add Bias-203 to TI-208 to get (heater wall T) setpoint for TIC-203.

f. Add Bias-202 to TI-208 to get (heater wall T) setpoint for TIC-202.

g. Read the setpoints entered or calculated from F. 9. of the manual input screen into the TIC's (23, 131, 201-206).

4. Check status of FV-005 (Overfill Protection Valve). Put it in "Closed" position if it is not already.
5. Check status of AOV-131 (3-Way Charge Flow Valve). Put it in "Closed" (Recycle) position if it is not already.
6. Check WT-23 (Feed Weight). WT-23 was zeroed with charge level at bottom of dip tube.

If WT-23 < <u>10,000</u> g. , open FV005. (10,000 g of charge =~ 2. 5 gal)

a. Sequence program will check to see if P-001 (Hot Box Feed Pump) is on; if not, it will turn it on or alarm if there are problems.

b. When WT-23 > <u>21,590</u> g. , close FV005.
(21,590 g of charge =~ 5. 5 gal)
  1. If after 1 hour WT-23 is still not > 21,590 g, sound an alarm.
  2. If there is no flow, the operator might need to stroke valve FV-005 on and off to resume flow.
  3. If no one responds (WT-23 is still < 21,590 g) after 30 minutes, turn off P-001, THTR-131, 201-206, close FV-005, and end the sequence program.

c. Turn off P-001.

7. Start P-025 (Feed Booster Pump) if it is not already running.
8. Start P-026 (Main Charge Pump).
9. Change unit status to "**<u>On-Line</u>**".
10. Check the following variables with deviation alarms suppressed until all are lined out.

a. Check to see that FI-23 (20 minute moving average Feed Hourly Flow Rate) is **within limits of flow** entered in F. 5. above.

b. Check TI-200 (PreHTR Outlet) to be within **+/- 5 ^{o}F** of TIC-201 setpoint (TI-200 is measurement) entered in F. 9. c. above.

c. Check TI-208 (Drum Outlet Vapor) to be within **+/- 10 ^{o}F** of TIC-206 setpoint (TI-208 is measurement for TIC-206).

d. Check TI-202 through TI-205 to be within **+/- 5 ^{o}F** of TIC-202 through TIC-205 setpoints (TIC-206 setpoint + Bias).

  - e. Check PT-611 (Drum Outlet) to be within **+/- 2 psig** of PIC-611 (F. 10. a. above).
  - f. Check FI-612 (Gas Flow) to be within **+/- 1. 0 SCFH** of setpoint.
  - g. Check TE-23 (Feed Tank) and TE-131 (Feed Line) to be within **+/- 10 ^{o}F** of TIC-23 and TIC-131, respectively.
  - h. Check PDI-201 to be below **30 psig**.
  - i. Check LIC-601 and LIC-611 to both be below **75%.**
  - j. Flow of diluent and quench water can be checked optionally by the operator (if available). To calculate an approximate flow rate/hr, fill the burette with water and open flow from the burette to the pump (while blocking the flow from the graduate). Time the flow for one or more minutes and calculate an hourly flow rate.
  - k. If the variables above are not lined out after 90 minutes, activate the deviation alarms for the variables to identify the variable(s) not lined out, and sound an alarm to notify the operator to check the unit.
    1. If no one responds (the variables are not lined out after 30 more minutes), turn off THTR-131, 201-206, P-026, and end the sequence program.

11. When the unit is lined out, throw AOV-131 to “Open” (To Unit) position which will cut in charge to the heater and coke drum.
12. Activate the deviation alarms described in 10, if they have not been activated already. Suppress FI-612’s alarm, since gas flow rate is expected to increase when charge is cut in.
13. Change unit status to “**<u>On Test</u>**”, and print on-line log sheets.
14. Start timer counting the run length (hrs).
15. After run length time is up, throw AOV-131 to “Closed” (Recycle) position which will cut out charge but continue diluent water (steam) and quench water (if used).
16. Change unit status to “**<u>Steam Stripping</u>**”.
17. Start timer counting the time (hrs) to steam strip coke (F. 8. above) and display time remaining.
18. After steam strip time is up, stop P-026 (Main Charge Pump) which will cut diluent water (steam) and quench water flow and also charge flow to hot box through the recycle loop.
19. Suppress all alarms described in 10.
20. Turn off power to THTR-201 through THTR-206 (Furnace Zone Heaters) and THTR-131 (Feed Line Heater).
21. Change unit status to “**<u>Shutdown</u>**”, and print on test and steam strip log sheets.
22. Change TIC-206 remote measurement (TI-208) back to TI-206 so that a shutdown will not be caused when TI-208 is unplugged.
23. Sound alarm so operator will know run is over.

24. When alarm is acknowledged, prompt operator that it is time to remove the main reactor internal thermowell (so that it will not become stuck in the coke).
    a. Depressure the unit by bleeding off the pressure (set PIC-611 to local manual control with setpoint of 0 psig or bleed through PIC-611 bypass or the blowdown valve (in the N2 line to T-211 at the top of the coke drum). Leave the N2 flow on in order to maintain gas flow through the unit.
    b. Open the baffle in the trunk ventillation line at the top of the reactor. **Be careful when working near the furnace since the furnace and overhead lines are very hot.**
    c. Strip any insulation from the thermowell nut and disconnect the thermocouple leads (TI-208 through TI-215).
    d. When the unit is depressured (PI-200 and PI-201 pressure gauges read 0 psig), break the main thermowell fitting loose, and pull out the thermowell using the overhead winch. **Use a face shield when breaking the thermowell fitting to remove the thermowell.**
    e. Put a plug nut into the top block fitting.
    f. Set PIC-611 to local automatic control with a setpoint of 25 psig.
    g. Check to see that the nitrogen flow comes back (plant N2 at PDT-201, LT-601, and LT-611) to line the unit out at 25 psig (PIC-611) and establish total N2 flow of approximately 1-3 SCFH (set the flow indicators on the three pairs of rotameters to 0. 5).
    h. When N2 flow is re-established, the unit can cool overnight and the day operator can drain the products.
    i. Block out all 4 charge barrels of P-026 to prevent any backflow to the feed graduates.
25. Operator will press the ACK button on the I/A to acknowledge that the main thermowell was removed and to continue the batch sequence program.
26. Prompt operator to enter the end of run manual inputs. Bring up an ACK button for the operator to press after entering the end of run inputs.
27. After performing I. H-J. and II. A. 5. to obtain and enter the needed data, operator will hit the ACK button on the I/A sequence screen to finish the sequence program. A message will be sent to the printer indicating that the sequence was completed.

H. At the end of the run after unit cools (overnight), the day operator needs to drain and weigh products and record readings as outlined below. Be sure to use the grounding straps when draining the products to prevent any static buildup.

1. Dump the levels from both product separators (T-601 and T-611) by setting LIC-601 and LIC-611 setpoints to 0% level (output = 100% open) or by opening the LIC-601 and LIC-611 bypass valves until all liquid is drained into the product receivers (T-901 and T-911).
2. Tare an empty container, drain the heavy product from T-901 receiver and weigh it. Enter weight into end of run manual entry screen.
3. Drain the water and light product from T-911 receiver, use a separatory funnel to separate the water from the light product, and weigh the light product using a tared container. Enter weight of light product into I/A system. Keep light product covered as much as possible to avoid evaporation of light components.
4. Drain the gas meter knockout pot. Separate water from light product if necessary, and weigh the light product. Enter weight into end of run manual entry screen.
5. Add any water product from the gas meter knockout pot to the water product drained from T-911 and weigh the total water product. Enter weight into end of run manual entry screen.
6. When heavy product cools to ~100 to 130 ^{o}F, blend the light product and any light product from the gas meter KO pot with the heavy product under the fume hood.
    a. Take a gravity of the total liquid product and record it in the manual entry screen.
    b. Pour up appropriate samples of total liquid product. Samples will be needed for C5&lighter, simdis, sulfur, etc.
    c. Store the remaining total liquid product in the cold box to avoid loss of light components.
7. Take readings from the water graduates and water burettes and enter values into manual entry screen.
    a. Volume (cc) of T-030 (Diluent Water) +/- 5-10 cc
    b. Volume (cc) of T-035 (Quench Water) +/- 5-10 cc
    c. Volume of Diluent Water burette, +/- 0. 1 cc
    d. Volume of Quench Water burette, +/- 0. 1 cc

I. Turn off the plant nitrogen flow (plant N2 at PDT-201, LT-601, and LT-611) and bleed off the pressure (set PIC-611 to 0 psig or bleed through PIC-611 bypass or the blowdown valve (in the N2 line to T-211 at the top of the coke drum).

J. Operator needs to remove and weigh the preheater coil and coke drum reactor.

1. Disconnect top and bottom reactor hubs and the preheater from the process lines.
2. Remove TI-131 thermowell from the preheater coil.
3. Disconnect the preheater coil from the coke drum reactor bottom hub and weigh the preheater (plus any coke buildup).
4. Enter weight of the preheater into the end of run manual input screen.

5. Install winch eyelet fitting into reactor top hub (don't forget the 1" plug) and hang reactor from winch.
6. Dismount reactor from the top clamp assembly to overhead unistrut. Lower reactor down from the unit using winch.
7. Weigh reactor (full of coke) with bottom and top hubs, clamps, and winch eyelet fitting (without reactor main thermowell but with 1" plug).
8. Enter coke drum weight into end of run manual input screen.

K. Summary of end of run manual inputs. Use PC MS Access to enter the following data into TRENDS.

Beginning of Run Data

1. Reactor Wt Empty (from B. 5. above) grams
2. Preheater Wt Empty (from B. 10. above) grams
3. Charge API Gravity @ 60F (3. 7) °API
4. Diluent Water Reading (T-030) (2000) cc (+/- 5 or 10 ccs)
5. Quench Water Reading (T-035) (2000) cc (+/- 5 or 10 ccs)

End of Run Data

Weight API Gravity

6. Heavy Product (from H. 2.)grams
7. Light Product (from H. 3.)grams
8. Gas Meter KO Lt Prd (from H. 4.)grams
9. Total Liquid Product (from H. 6. a.)°API
10. Total Water Product (from H. 5.)grams
    (T-611 H2O + Gas Meter KO H2O)
11. Diluent Water Reading (T-030) (H. 7. a.) cc (+/- 5 or 10 ccs)
12. Quench Water Reading (T-035) (H. 7. b.) cc (+/- 5 or 10 ccs)
13. Diluent Water Burette Reading (H. 7. c.) cc (+/- 0. 1 cc)
14. Quench Water Burette Reading (H. 7. d.) cc (+/- 0. 1 cc)

15. Reactor Wt + Coke Wt (from J. 6.) grams
16. Preheater Wt + Coke Wt (from J. 2.) grams
17. Length of Coke "rod" (from II. A. 5.)inches
18. Operator will press a button to acknowledge all entries.
19. If any entries are missing or outside of reasonable limits, send message to operator. Otherwise, print screen.
20. MS Access will perform the following calculations and store the results into TRENDS. All weights are in grams.

COKEWT = (15) - (1) HTRCOKE = (16) - (2)
DH2OFD = (4) - (11) + (13) FDAPI = (3)
QH2OFD = (5) - (12) + (14) TLPWT = (6) + (7) + (8)
H2OPWT = (10) TLPAPI = (9)

$$\text{COKEDENS (g/cc)} = \frac{(15) - (1)}{(17) * 115.83333}$$

II. Turnaround Items

A. When ready for coke removal, remove coke drum reactor top and bottom hubs.

1. Loosen clamp bolts and remove top and bottom hubs.
2. Remove coke from top and bottom hubs. Bake out in a furnace overnight at 900-1000 F if necessary.
3. Replace hubs with pipe flange pieces if coke will not come out and the coke drilling tool will need to be used. Otherwise, just remove the coke.
4. Tighten clamp bolts just enough to hold flanges together. BE CAREFUL NOT TO OVERTIGHTEN THE BOLTS SINCE THIS WILL CAUSE EXCESSIVE WEAR AND TEAR ON THE SEAL RINGS WHICH COST $125 EACH TO REPLACE. Never exceed 55 ft-lbs of torque on the bolts.
5. Determine the approximate length of the "rod" of coke and enter the value into the end of run manual entry screen.

B. Send coke drum reactor full of coke back to the shop for coke removal if the coke is difficult to remove.

1. Use a drill with coke drilling tool if coke is difficult to remove.
2. Use a wire brush drill attachment to brush coke from drum inside wall. Be sure to dispose of any coke fines removed while wire brushing and do not mix it with the coke for sampling since it will contain a high amount of Fe and metals due to wear particles from the wire brush.
3. Return the rest of the coke for storage and sampling.
4. Samples of pulverized coke are needed for VCM, Moisture, Sulfur, etc.

C. Inspect overhead vapor lines and clean out periodically.

D. Replace preheater coil with spare and burn out used preheater coil overnight in a furnace at 900-1000 F after each run.

1. (RMJ, insert preheater burnout procedure here)
2.
3.

E. If next run uses a different charge stock, feed system must be purged.

1. Stop P-025 (Feed Booster Pump).
2. Drain feed tank and all feed lines. Clean tank with toluene or other suitable solvent.
3. Line up drum or container of new feed inside hot box.
4. Purge hot box to unit feed recycle loop with new feed.

III. Emergency Shutdown Procedures

A. If high ΔP (> 50 psig) is detected, the I/A will perform the following.

1. Throw AOV-131 to "To Slop" position which will cut out charge.
2. Stop P-026 (Main Charge Pump) which will cut diluent water (steam) and quench water flow and also charge flow.
3. Turn off power to THTR-201 through THTR-206 (Furnace Zone Heaters) and THTR-131 (Feed Line Heater).
4. Change unit status to "**Emergency Shutdown**", and sound alarm. Print log sheets up to point of shutdown.
5. After alarm is acknowledged, bring up end of run manual entry screen.
6. Operator should notify engineer in charge that emergency shutdown occurred.
7. I/A should ask whether to continue sequence program or end the program and slop the run. The engineer will determine if the run was long enough to use the data or to slop the run.
8. If we are going to use the data, continue with I. H-K. as a normal run.
9. If we choose to slop the run, end the sequence program.
   a. Drain receivers and slop all products.
   b. Proceed with I. I-J. but do not bother to weigh the reactor.
10. Proceed with II. Turnaround Items.

B. If a high Furnace Zone T (>1000 °F) is detected, the I/A will perform the following.

1. Throw AOV-131 to "To Slop" position which will cut out charge but continue diluent water (steam) and quench water.
2. Turn off power to THTR-201 through THTR-206 (Furnace Zone Heaters) and THTR-131 (Feed Line Heater).
3. Change unit status to "**Emergency Shutdown**", and sound alarm. Print log sheets up to point of shutdown.
4. Start timer counting the time (hrs) to steam strip coke (I. F. 8.), or continue with steam strip if unit shutdown during steam stripping step.
5. After alarm is acknowledged, indicate that unit is steam stripping and display time remaining.
6. Operator should notify engineer in charge that emergency shutdown occurred.
7. After steam strip time is up, stop P-026 (Main Charge Pump) which will cut diluent water (steam) and quench water flow and also charge flow to hot box slop drum.
8. Print on test and steam strip log sheets.
9. Sound alarm so operator will know steam stripping is over.
10. After alarm is acknowledged, bring up end of run manual entry screen.

11. I/A should ask whether to continue sequence program or end the program and slop the run. The engineer will determine if the run was long enough to use the data or to slop the run.
12. If we are going to use the data, continue with I. H-K. as a normal run.
13. If we choose to slop the run, end the sequence program.
    - a. Drain receivers and slop all products.
    - b. Proceed with I. I-J. but do not bother to weigh the reactor.
14. Proceed with II. Turnaround Items, and have electrician and instrument man check out furnace, wiring, and thermocouples.

C. Loss of Charge Pump

1. Loss of P-025 will cut charge supply to P-026 and will cut circulation of the feed to T-023.
    - a. Try to restart P-025.
    - b. If P-025 cannot be restarted and unit is not “On Test”, bypass P-025 (if possible) and line up flow from P-026 to T-023 to keep charge circulating to the feed tank.
    - c. If unit is “On Test”,bypass P-025 (if possible) and keep charge flowing to the unit until run is over.
    - d. Have crafts work on P-025.
2. Loss of P-026 will stop charge, diluent water, and quench water flow to the unit.
    - a. Try to restart P-026.
    - b. If P-026 cannot be restarted and unit is “On-Line” or “On Test” but not within two hours of completing the run, throw AOV-131 to “To Slop” position, change unit status back to “Start-Up”, drain receivers and slop all products, proceed with shutdown (I. I-J.) but do not bother to weigh the reactor, and have crafts work on P-026.
    - c. If P-026 cannot be restarted and unit is “On Test” within two hours of finishing the run or the unit is “Steam Stripping”, continue the run with the “Steam Stripping” step. Even though steam and quench water will be cut off, nitrogen flow will serve to strip the coke. Continue with normal shutdown (I. H-K.), and have crafts work on P-026.

D. Loss of Plant Nitrogen

1. Loss of plant nitrogen will lose the PDT-201 reading and level controls LT-601 and LT-611.
    - a. If unit is “On Test”, finish the run without PDT-201 (block it in).
    - b. Block in LT-601 and LT-611.
    - b. Drain T-601 and T-611 periodically using the bypass valves to the level control valves (LIC-601 and LIC-611).

E. Loss of Instrument Air

1. Loss of instrument air will lose control of FSOV-005 (Overfill protection valve) and AOV-131 (Three-way valve).
    - a. FSOV-005 has a bypass which will require manual operation.

b. AOV-131 has no bypass or manual operating alternative. The only time the operation of AOV-131 would be critical is at the end of the run when it is time to cut charge. This can be accomplished instead of using AOV-131 by setting the stroke of the charge barrels (B and C) of P-026 to 0 (no flow).

F. Loss of Electric Power

1. All pumps, electrical heaters, and the feed scale (WT-23) will shut down. Foxboro has a UPS backup so there will still be control for the unit.
2. Turn off all pumps, electrical heaters, and the scale while the power is off. Acknowledge all state alarms.
3. If the unit was "On-Line" or "On Test" during the power failure and the power comes on within 15 minutes, we can try to continue the run where it left off.
    a. Restart pumps and turn on heaters.
    b. The scale will probably need to be zeroed. This can be accomplished by lifting the charge tank (T-023) from the scale and zeroing the scale before putting the tank and contents back on the scale. The weight can then be checked with the weight before the power outage.
    c. Check the furnace temperatures as they come back up to make sure TE-200 and TE-207 meet their targets.
4. If the power does not come back up within 15 minutes, the run will have to end.
    a. If the unit is "On-Line" or "On Test" but not within two hours of completing the run, throw AOV-131 to "To Slop" position, change unit status back to "Start-Up", drain receivers and slop all products, proceed with shutdown (I. I-J.) but do not bother to weigh the reactor.
    b. If the unit is "On Test" within two hours of finishing the run or the unit is "Steam Stripping", continue the run with the "Steam Stripping" step. Even though steam and quench water will be cut off, nitrogen flow will serve to strip the coke.
    c. Continue with normal shutdown (I. H-K.).
5. If TE-23 drops below 300 ^{o}F before power is restored, drain the feed from the feed tank and put it in the hot box.

G. Loss of Steam

1. Loss of steam will cause some of the feed and heavy product lines to cool which may result in a loss of flow.
2. The hot box feed pump (P-001) should be turned off to prevent its motor from burning out if the charge becomes too heavy to pump.

B. ERROR ANALYSIS

An error analysis was conducted to determine the variables contributing most to the errors in the material balance for the micro-coker. The following method was used. If a value *y* is calculated from *n* given variables:

$$y = f(x_1, x_2, \ldots, x_n)$$

then the uncertainty in *y* may be calculated as follows:

$$\varepsilon_y = \left[\left(\frac{\partial y}{\partial x_1} \varepsilon_{x_1} \right)^2 + \left(\frac{\partial y}{\partial x_2} \varepsilon_{x_2} \right)^2 + \ldots + \left(\frac{\partial y}{\partial x_n} \varepsilon_{x_n} \right)^2 \right]^{1/2}$$

where ε_x represents the uncertainties in the variable in the subscript.

For the micro-coker, the measured variables with their assumed errors are as given in Table 49.

Table 49 - Micro-coker measure error estimates

Variable	Error estimates
Weights	0.02%, with a minimum error of 0.1 grams
Pressure	0.1 psi
Temperature	0.5 degrees
System Volume	0.05 liters
GC Reading	0.005
Wet Test Meter Volume	3%

Results of this analysis are shown in Table 50 for one of the Fluid 1 runs.

Table 50 - Error Analysis for Micro-Coker

VARIABLE	VALUE	ERROR
Amount Fed	145 grams	1.3 grams
Amount of Coke	48.2 grams	0.3 grams
Amount of Liquid	69.0 grams	0.8 grams
Amount of Gas	23.9 grams	1.9 grams
Total Mass Recovered	141.1 grams	2.1 grams
% Recovery	97.3%	1.7%

Analyses for other runs give results very similar to this. It can be seen that the largest error is due to the gas measurement, although there is a significant error in the feed weight.

It was also seen that the variables having the largest effect on the error are the weights and the wet test meter volume; the other variables make an insignificant contribution to the overall error.

Comparison of the mean error for the % recovery (1.7%) also compares favorably with the average % recovery obtained experimentally from the micro-coker runs.

These results suggest that the experimental data can be best normalized by correcting each weight (feed, coke, liquid and gas) in proportion to the numbers in Table 50.

A similar analysis was conducted for the pilot unit. Since the measured variables and calculation method are different than for the micro-coker, the error analysis might be expected to yield different results. The error estimates for the pilot unit are shown in Table 51, and the results of the error analysis are shown in Table 51.

Table 51 - Pilot unit measurement error estimates

Variable	Error estimates
Weight-Liquid	0.02%, with a minimum error of 0.1 grams
Weight-Feed Tank	0.20%
N2 in the system	0.1 liters
Pressure	0.1 psi
Final Temperature	0.5 F
N2 flow rate	0.05 ml/min
N2 flow time	1 min
Temperature at Wet Test Meter	0.5 C
System Volume	0.05 liters
GC Value	0.005
Pressure at Wet Test Meter	0.1 psi
Wet Test Meter Reading	3%

Table 52 - Error Analysis for one of the pilot unit runs

VARIABLE	VALUE	ERROR
Amount Fed	6300 grams	15.1 grams
Amount of Coke	1538.2 grams	13.3 grams
Amount of Liquid	4187.9 grams	1.6 grams
Amount of Gas	327.0 grams	27.8 grams
Total Mass Recovered	6053.1 grams	30.9 grams
% Recovery	96.1%	0.5%

It should be noted that the pilot unit analysis does not consider analysis of material holdup in the feed and overhead lines, which were not measured.

For both the micro-coker and pilot unit, the largest error is due to the gas measurement. Based on these results, it seems appropriate to normalize the material balances by correcting the gas flows to achieve 100% closure.