THE UNIVERSITY of TULSA

Department of Chemical Engineering

Fundamentals of Delayed Coking Joint Industry Project

ANNUAL REPORT

October 2003 through September 2004

Principal Investigators
Dr. Michael Volk, Jr. & Dr. Keith Wisecarver
600 S. College Tulsa, OK 74104

October, 2004

DOE Award DE-FC26-02NT15381

Table of Contents 2004 Annual Report
October 2003 – September 2004

1. List of Tables

2. List of Figures

3. Disclaimer

4. Public Abstract

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, the delayed 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.

Despite its wide commercial use, only relatively few contractors and refiners are truly knowledgeable in delayed-coking design, so that 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. As a result of Tulsa University’s prior related research, a process model was developed that with additional work could be used to optimize existing delayed cokers over a wide range of potential feedstocks and operating conditions.

The objectives of this research program are to: utilize the current micro, batch and pilot unit facilities at The University of Tulsa to enhance the understanding of the coking process; conduct additional micro and pilot unit tests with new and in-house resids and recycles to make current optimization models more robust; conduct focused kinetic experiments to enhance the furnace tube model and to enhance liquid production while minimizing sulfur in the products; conduct detailed foaming studies to optimize the process and minimize process upsets; quantify the parameters that affect coke morphology; and to utilize the knowledge gained from the experimental and modeling studies to enhance the computer programs developed in the previous JIP for optimization of the coking process. These refined computer models will then be tested against refinery data provided by the member companies. Novel concepts will also be explored for hydrogen sulfide removal of furnace gases as well as gas injection studies to reduce over- cracking.

The following deliverables are scheduled from the two projects of the three-year JIP:

1. A novel method for enhancing liquid yields from delayed cokers and data that provide insight as to the optimum temperature to remove hydrogen sulfide from furnace gases.
2. An understanding of what causes foaming in coker drums and ways to minimize sulfur in the produced liquids.
3. An understanding of the HES impacts resulting from hot spots, poor drainage, and settling.
4. A screening model to quantify how other feedstocks and/or a combination of feedstocks will behave in a refinery, and kinetic/optimization models that can represent virtually any delayed coking unit across a wide range of process conditions and feedstocks.

Primarily graduate students, post-Doctoral Research Associates and faculty members, will conduct the research in this project.

This research project should find ways 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. Reducing foaming in the coke drum will also be studied in this project. Reducing the amount of antifoamant used in the coke drum by $0.10 per ton will save the refiners $5 million per year. During 2001, both production and consumption of petroleum coke has increased, and this trend is set to continue. Since 1992 world petroleum coke production capacity has increased by more than 40% to reach a peak of 154,607 tpd in 2001. This expansion is expected to continue with at least fifteen new coking units coming into production by 2003 providing new jobs and markets for the coke, such as a fuel source for kilns in the cement industry and for boilers in electric power plants or in the manufacture of electrodes to be consumed in carbon anodes for aluminum smelting and graphite electrodes of steel making.

Knowledge from this project will be transferred to the industry through semiannual advisory board meetings, graduate education of two Ph.D. students and two MS students and through the coordination of annual workshops for hands on experience of using computer programs that come out of the research.

5. Executive Summary

Eleven organizations are currently members of the Fundamental of Delayed Coking Continuation JIP that started June 1, 2002: Baker-Petrolite, ChevronTexaco, ExxonMobil, Foster Wheeler, Great Lakes Carbon, KBC Advanced Technologies, Marathon-Ashland, Petrobras, Shell, Suncor and the U. S. Department of Energy. PDVSA has verbally committed to rejoining the JIP. Discussions are ongoing with Kuwait National Petroleum Company and Husky Energy.

The coking test facilities include three reactors (or cokers) and ten utilities. Experiments are being conducted using the micro coker, pilot unit, and stirred batch reactor. Liquid products are analyzed in-house using simulated distillation (HP 5880a), high temperature gas chromatography (6890), detailed hydrocarbon analysis after ASTM distillation.

Significant upgrades were made to the facilities. The 5880 GC was replaced with the refurbished 5890 GC. Chemstation software was added and this instrument will be used for both DHA and sim dis analysis. The Foxboro operating system for the pilot unit (version 6.0) was replaced with the latest software package (version 7.1) and a new workstation computer. A hazop review was conducted with the aid of personnel from ChevronTexaco. As a result of the study, several modifications/enhancements were made to the facility. To minimize any potential exposure to H_2S from leaks, a 10,000cfm exhaust blower was installed. This blower is connected to an H_2S monitor that automatically triggers the blower if the H_2S levels exceed 10 ppm. Manual intervention is required to shut off the blower. A new larger feed tank was added to the system. This tank is closed and was pressure tested to 300 psig at 500 ^{O}F. The closed system eliminates any vapor losses to the atmosphere as well as any potential fire hazards. The feed tank is equipped with a rupture disk that is connected to the blowdown tank via a 1 inch heated line. The old balance was replaced with a new one that could measure larger feed weights.

New resids were obtained from ExxonMobil (Maya Heavy Canadian and Cerro Negro) and from Marathon (Rose Pitch). Feedstock properties were obtained for the three new resids and coking runs were made on both the pilot coker and microcoker.

The microreactor project is now complete. Tests run in the past year include repeat parametric runs, runs made with 5 and 10% recycle, five runs made with 100% recycle, and 13 tests conducted with the three new resids: four using the heavy Canadian, two with Cerro Negro and seven with the Rose Pitch. The Suncor resid showed an increase in coke yield with increasing recycle (0 to 100%) at low temperature and high pressure whereas for Marathon, little change was observed. However, at a high temperature and low pressure, runs using Marathon recycle showed a decrease in coke yield with an increase in recycle. The effect of feedstock composition and operating conditions on product yields were successfully correlated for the nine resids used. When the new resids were added, a better correlation was found when asphaltenes were included. When the experimental data was compared to available correlations found in the literature, differences in the yield predictions varied by as much as 11%. Microreactor results were documented and a user friendly GUI was added to the microcoker model for member utilization.

Forty-three batch reactor tests have been completed to date. Tests were run at pressures of 15, 40 and 60 psig. The higher pressure runs are producing significantly different data than the 15 or 40 psig runs. The components for building the apparatus for conducting the SARA analysis were assembled and testing begun.

Development of the first pass kinetic model was completed as was the first draft of the final report. The stirred-batch reactor model was developed using both the stirred-batch coker experiments and the thermogravimetric analysis (TGA) data. The model parameters, such as the activation energies and Arrenius factors, are found from the TGA while the stoichiometric coefficients are found from the stirred-batch coker. It predicts gas, gas components, liquid, liquid subproducts and coke yields fairly well. The model is currently undergoing Beta testing.

Parametric and superficial velocity tests were carried out using the Heavy Canadian and the Rose Pitch resids. A transition in morphology from agglomerated shot to transitional sponge was seen with an increase in superficial velocity for the Heavy Canadian resid. Foaming tendencies observed for the Rose Pitch runs were different than those observed for all the other runs. For the Rose Pitch resid, a shift in morphology from shot coke at 900 ^{O}F/15 psig to sponge coke at 930 ^{O}F/40 psig was observed.

Work continued on the foam model that relates foaming tendencies to resid properties. These efforts extend the work of Pelton by correlating foam volumes for various times during a run with resid properties, run operating conditions, coke morphology and pore size distribution, the crude oil components that lead to enhanced foam growth or promote the foam formation and antifoam effects. Coke pore size distribution is also accounted for.

The design of a glass coker to study foaming was finalized and equipment components ordered. A second system is being sought from Great Lakes Carbon. Shakedown tests will begin next quarter. The results from this study will provide insight as to what effect resid properties have on foam bubble size, foam quality and foaming tendencies.

The coil fouling data base was updated with the results from the runs using the three new risids. These resids have API’s that are lower than the six resids used in the first phase of study. These tests showed that the lower the API the higher the fouling. A trend in pressure was also seen, that is, the higher the pressure, the higher the fouling rate. To put the data in a form that is more useable by the refinery operators, a fouling rate per unit surface area (gms/ft^2-hour) was calculated.

Coke morphology descriptions for the three new resids were added to the electronic database. The effects of pressure and temperature on morphology were quantified. Fifty plugs were drilled and permeability and porosity measurements made. A relationship between porosity and permeability as a function of morphology was observed. Thirty samples, one from each morphology group per resid, were picked for capillary pressure analysis. This data gives pore throat size distributions from .001 to 100 um and allows one to quantify the porosity as micro, meso and macro. Capillary pressure data are being gathered on both refinery produced coke and coke produced with the pilot. Preliminary results indicate very similar morphologies are being produced. For each sample, thin sections are also being made and scanning electron photographs are being taken to provide visualization of the porosity and pore throat geometry.

Coke morphology was seen to have an important effect on quenching. Hard dense sponge or agglomerated shot coke cooled very slowly, whereas the presence of loose shot or void spaces within the coke rum correspond to very fast cooling. Effort were begun to modify the existing quench model to account for varying porosity/permeability within the coke bed.

An overall structure for the delayed coker software was developed. The current model is mainly correlated data. In the long-run, it is proposed that we transition from correlated data to more mechanistic modeling of the delayed coking process.

The address for the Delayed Coking Web Site is http://www.tudcp.utulsa.edu. The web site has become a useful tool to welcome visitors and tell them about the JIP. It is segmented such that visitors can gain general information while the “Members Only” site contains confidential information generated in the JIP. There is a reading room, applications, a tour of the facility, a place to meet the personnel, JIP news, experimental data from the three cokers, models and correlations, and a discussion board. During the last quarter, data from the tests conducted were posted.

A tentative date for the thirteenth Advisory Board Meeting is Wednesday and Thursday, May 18-19, 2005. The meeting will be held at the University of Tulsa in ACAC. The meeting on the 18th will begin at 1 pm and adjourn at 5 pm. A social is planned that evening in the Presidents Lounge from 5 to 9 pm. The meeting on the 19th will begin at 7 am and adjourn at 2:30 pm.

6. Experimental Methods

A. *SCOPE OF PROBLEM*

Three state-of-the-art test facilities were developed for use in the previous JIP. The facilities were used to generate high-quality data. These facilities, with some minor modifications to improve them, are now being utilized to gather large quantities of coking related data to enhance the capabilities of the predictive models developed during the first three years of the Fundamentals of Delayed Coking Joint Industry Project (JIP). The work plans for this Joint Industry Project show the work being conducted with two major projects:

> Project 1 – Small Scale Reactor Studies - conducts studies with the micro and batch reactors to generate sufficient data to enhance the robustness of the screening model and to better understand the reaction kinetics in the furnace tube and coke drum. Methods for removing sulfur, for enhancing liquid production, as well as ways to reduce sulfur in the liquids to help refiners meet the upcoming stringent sulfur requirements will also be studied.
>
> Project 2 – Pilot Unit Studies - conducts detailed studies to enhance the robustness of the process optimization model and to better understand the foaming process thereby minimizing or eliminating process upsets as well as optimizing the use of antifoams thereby increasing refinery margins. Concurrent studies on the produced coke will provide a better understanding as to what parameters affect coke morphology as well as provide insight as to why settling, poor drainage and hotspots occur in coke drums minimizing health and safety hazards.

Results from these Projects will be used to further develop correlations for product yields and properties, as well as to develop mechanistic models for the furnace tube and coke drum that account for reaction kinetics and energy effects (i.e., heats of reaction, heats of vaporization, and heat transfer effects).

B. *PROGRAM CHRONOLOGY*

The schedule for completing the complex and interrelated tasks over a three year period is shown in Table 1 and Table 2. Table 1 and Table 2 also show when significant deliverables in the form of report, models, and data will be provided to the participants. Those items colored blue are complete while those in red show when the task is scheduled for completion.

Table 1 - Pilot Unit/Foaming Studies

	2002							2003												2004												2005								
Tasks	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Foaming Studies With In-house Resids																																								
1. Comparison of Injection Strategies	1	5																																						
2. Parametric Tests																																								
2 Resids Not Tested (Pet & Mar)			3	5	5	3																																		
4 Resids Tested in Phase I						1	4	4	3																															
3 Resids (Eq, Sun & Mar) with Recycle															1	2	2	2	2	1		2											🟩 3	🟩 2						
3. Refinery Condition Tests																		1															🟥 1	🟥 1						
4. Antifoam Optimization Studies																																								
Continuous Injection (100K cSt)											1		1	1	1	1																								
Feed Line Injection (100KcSt)											1	1	1	1	1	1																								
Intermittent Injection (100K cSt)										3					1																									
Carrier Viscosity (600K cSt)																																								
Continuous											1	1	1	1		1																								
Intermittent											1	1	1		1	1																								
Dilute vs Neat Injection										1		1																												
5. Superficial Velocity Studies																																								
2" drum @ 2400 gm/hr																				4																				
3" drum @ 1200 gm/hr																					4																			
3" drum @ 3600 gm/hr																						4																		
6. Morphology Studies	1	5	3	5	5	4	4	4	3	4	3	2	2	3	4	3	2	3	2	5	4	6											🟥 4	🟥 3						
7. Quenching Studies					1	2	2	2	1	3	3	2	2	3	4	4																								
8. Foaming Model Devel. & Valid																																								
Parametric							Development	🟦	🟦	🟦	🟦	🟦	🟦	🟦				Val	🟦																					
Foaming + Optimization													Development	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦					🟦	🟦	🟥	🟥	🟥	🟥	🟥	🟥						
Quenching							Development	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦																								
Model Enhancement Studies																																								
1. Obtain 3 New Resids																2		1																						
2. Parametric and Feedstock Studies																							6		6		4													
3. Recycle Studies - 1 Resid																														🟩 5	🟩 5	🟩 2								
4. Superficial Velocity Studies																																								
3" drum @ 2400 gm/hr																								1		1			🟥 1											
3" drum @ 3600 gm/hr																								1	1				🟥 1											
3" drum @ 4800 gm/hr																								1		1			🟥 1											
3" drum @ 6000 gm/hr																								1		1			🟥 1											
5. Refinery Condition Tests																																								
6. Morphology Studies																							6	4	7	3	4	🟦	🟥 4	🟥 5	🟥 5	🟥 2	🟥 4	🟥 3						
7. Quenching Studies																							2	1	2	1	2	🟦	🟥 3	🟥 3	🟥 3	🟥 1	🟥 3	🟥 3						
8. Model Enhancements																																								
Foaming																						🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥 Enhancement	🟥	🟥	🟥	🟥	🟥	🟥		🟥 Val	🟥		
Quenching																										🟦	🟦	🟦	🟥 Enhancement	🟥	🟥	🟥	🟥	🟥	🟥	🟥				
Final report																																						🟥	🟥	🟥

Table 2 - Small Scale Reactor Studies

	2002							2003												2004												2005								
Tasks	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Project 1a - Batch Reactor Studies to Improve Kinetic Model																																								
1. Equipment Design/Modification/Automation	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦																														
2. Shake Down Tests											🟦	🟦	🟦	🟦	🟦																									
3. Parametric and Feedstock Studies																																								
- Using In-house Resids																3	4	4	4	1	2	5	3	3	3	6	4													
- Using Three New Resids																										1	3	4	🟥 5											
- Higher Pressure (80 to 100 psig)																													🟥 3	🟥 5	🟥 5									
- Recycle																													🟩 5	🟩 5	🟩 5									
4. Enhanced Kinetic Model Development																🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		
5. Final Report																																🟥	🟥						🟥	🟥
Project 1b - Process Optimization Studies																																								
1. Gas Injection Studies to Reduce Cracking (H_2)																																🟥 4	🟥 4	🟥 4						
2. Sulfur Removal Studies																																			🟥 4	🟥 4	🟥 4			
3. Kinetic Model Enhancements																																		🟥	🟥	🟥	🟥	🟥		
4. Final Report																																							🟥	🟥
Project 1c - Micro Coker Studies to Improve Screening Model																																								
1. Equipment Modification/Automation	🟦	🟦	🟦																																					
2. Shade Down Tests				7	8	8	4																																	
3. Parametric & Feedstock Studies																																								
- Using In-house Resids							2	12	10	12	17	11	11	8	3	1	3																							
- Using Three New Resids																					5	7	9	4	6	8														
- Recycle/blended resids																7	6	7	6	9	5	1																		
4. Enhanced Screening Model Development									🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦													
5. Final Report																												🟦												
Glass Coker Studies to better Understand Foaming																																								
1. Facility Design																											🟦	🟦												
2. Facility Construction																													🟥											
3. Shakedown Tests																														🟥										
4. Feedstock Studies																															🟥	🟥	🟥	🟥						
5. Final Report																																			🟥					

7. Activity Summary

The studies conducted with the small scale reactors are shown in the Gantt Chart presented in Table 1 while the studies conducted with the pilot unit are shown in the Gantt Chart presented as Table 2. The events colored in blue are complete while those in red are scheduled completions. The numbers in each cell tell you how many tests are planed or were completed that month.

During the last year, 79 micro reactor, 40 pilot unit and 48 batch reactor runs were made. The microreactor runs were to study the parametric effects. The pilot unit runs were conducted to study parametric effects as well as the effects of superficial velocity on foaming and morphology. Twenty-six of the batch reactor runs were with the six in house resids and eight with the three new resids. Coke morphology studies were begun on fifty samples selected from the nine resids. Over one hundred and fifty thermogravimetric tests were conducted to derive kinetic parameters for the kinetic model.

Analytical analyses were conducted by TU, Baker-Petrolite and GLC on all the coke and liquid products produced from the three facilities. The analyses conducted included the following: distillation, SimDis, Detailed Hydrocarbon Analysis, Metals, Sulfur, Ash, Volatiles, HGI, RON, CHN, Permeability, Porosity, and CT Scans.

Work continued on the optimization, kinetic and foaming models.

A. *MICROREACTOR STUDIES*

Sixty-five new tests and 14 repeat tests were conducted with the microreactor facility. Five runs were made with 100% recycle, ten runs were repeat parametric runs, thirty runs were made with 5 and 10% recycle, and the remaining runs were made with the three new resids, four using the heavy Canadian, two with Cerro Negro and seven with the Rose Pitch. The Suncor resid showed an increase in coke yield with increasing recycle (0 to 100%) at low temperature and high pressure whereas for Marathon, little change was observed. However, at a high temperature and low pressure, runs using Marathon recycle showed a decrease in coke yield with an increase in recycle. The effect of feedstock composition and operating conditions on product yields were successfully correlated for the nine resids used. When the new resids were added, a better correlation was found when asphaltenes were included. When the experimental data was compared to available correlations found in the literature, differences in the yield predictions varied by as much as 11%. This project is now complete. The results were documented and a user friendly GUI was added to the microcoker model for member utilization.

B. *BATCH REACTOR STUDIES*

Development of the first pass kinetic model was completed as was the first draft of the final report completed. The stirred-batch reactor model was developed using both the stirred-batch coker experiments and the thermogravimetric analysis (TGA) data. The model parameters, such as the activation energies and Arrenius factors, are found from the TGA while the stoichiometric coefficients are found from the stirred-batch coker. It predicts gas, gas components, liquid, liquid subproducts and coke yields fairly well. The model is currently undergoing Beta testing.

Work from the first phase of study showed that additional data is needed to enhance kinetic model predictions. This data is being obtained by taking additional liquid samples (8 to 12 per run) and by collecting larger samples to obtain the coke formation data. These objectives are being achieved by conducting additional runs using the modified batch reactor sampling system (12 liquid cuts) and by analyzing the resid samples extracted using SARA analysis to model the coke formation.

Forty-three batch reactor tests have been completed to date in the new facility. These tests were run using five of the nine available resids at pressures of 15, 40 and 60 psig. The higher pressure runs are producing significantly different data than the 15 or 40 psig runs. The components for building the apparatus for conducting the SARA analysis were assembled and testing begun.

C. ***PILOT UNIT STUDIES***

Fifteen pilot unit foaming runs were made using the Marathon and Suncor resid with different superficial velocities to gain an understanding of its impact on foaming and morphology change. The coke morphology produced from each run was described and the samples analyzed for metals content. The contents in the drum from all of the runs were quenched with water, some overhead and some via the feedline. The waters are being analyzed for trace metals. Nine tests with recycle were also conducted.

Seventeen pilot unit foaming runs were made using Cerro Negron and the Heavy Canadian resid using a range of operating conditions and different superficial velocities to gain an understanding of their impact on foaming and morphology change. The coke morphology produced from each run was described and the samples analyzed for metals content.

Tests with three resids were made to understand the effects of superficial velocity on morphology and foaming tendencies. One resid made shot, one sponge and the third a mixed morphology. Superficial velocity was changed by increasing the feed rate. Five feed rates, ranging from 1200 gm/hr to 6000 gm/hr, were used. Superficial velocities at 6000 gm/hr are at the low end of what is seen in commercial drums. For the resid that made sponge, foaming was not observed until a feed rate of 4800 gm/hr was used whereas for the resid that made shot foaming was observed at 2400 gm/hr. No change in morphology was seen for these resids.

Foam optimization studies were conducted that demonstrated that continuous injection of antifoam produced a coke with a more uniform density than injection on an as needed basis did. It was also shown that large volumes of antifoam are required to collapse foam if the injection is started late in the run rather than early in the run. Repeated constant volume antifoam injections showed that the time before the foam reappeared was increased when this injection strategy was used.

Development of a foam model that relates foaming tendencies to resid properties continued. The factors that affect foam development and possible foam heights were compared.

Parametric and superficial velocity tests were carried out using the Heavy Canadian and the Rose Pitch resids. A transition in morphology from agglomerated shot to transitional sponge was seen with an increase in superficial velocity for the Heavy Canadian resid. Foaming tendencies observed for the Rose Pitch runs were different than those observed for all the other runs. For the Rose Pitch resid, a shift in morphology from shot coke at 900 ^{O}F/15 psig to sponge coke at 930 ^{O}F/40 psig was observed.

Distillation and detailed hydrocarbon analysis (DHA) from pilot unit studies using the 6 foot drum were completed. Predictive correlations by cut for the various PIONA components were developed. These correlations are being incorporated into the optimization model for use by member companies.

Work on the sulfur analysis continued. Sulfur in the liquid fraction from the 3 foot and six foot drum runs were compared. The sulfur in each fraction is being summed and compared to the whole liquid cut. The analysis on the whole liquid cut analyzed by TU is being compared to the whole liquid cut analysis conducted by Baker-Petrolite.

Significant upgrades were made to the facilities. The 5880 GC was replaced with the refurbished 5890 GC shown in Figure 1. Chemstation software was added and this instrument will be used for both DHA and sim dis analysis. The modified lab area for the GC's is shown in Figure 2. The Foxboro operating system for the pilot unit (version 6.0) was replaced with the latest software package (version 7.1) and a new workstation computer. A hazop review was conducted with the aid of personnel from ChevronTexaco. As a result of the study, several modifications/enhancements were made to the facility. To minimize any potential exposure to H_2S from leaks, a 10,000cfm exhaust blower shown in Figure 3 was installed. This blower is connected to an H_2S monitor that automatically triggers the blower if the H_2S levels exceed 10 ppm. Manual intervention is required to shut off the blower. A new larger feed tank, shown in Figure 4, was added to the system. This tank is closed and was pressure tested to 300 psig at 500 ^{O}F. The closed system eliminates any vapor losses to the atmosphere as well as any potential fire hazards. The feed tank is equipped with a rupture disk that is connected to the blowdown tank, also shown in Figure 3, via a 1 inch heated line.

Figure 1 - 5890 GC

Figure 2 - GC Laboratory

Figure 3 - Exhaust Blower and Blow Down Tank

Figure 4 - Pressurized Feed Tank

D. *GLASS COKER STUDIES*

The design of a glass coker to study foaming was finalized and equipment components ordered. A second system is being sought from Great Lakes Carbon. Shakedown tests will begin next quarter. The results from this study will provide insight as to what effect resid properties have on foam bubble size, foam quality and foaming tendencies.

E. ***COIL FOULING STUDIES***

The coil fouling data base was updated with the results from the runs using the three new risids.. These resids have API's that are lower than the six resids used in the first phase of study. These tests have shown that the lower the API the higher the fouling. A trend in pressure is also seen, that is, the higher the pressure, the higher the fouling rate.

To put the data in a form that is more useable by the refinery operators, a fouling rate per unit surface area (gms/ft^2-hour) was calculated. The results for 900^0 F are shown in Figure 9. A trend line was imposed on the data points for utilization in the delayed coking optimization simulator.

Future studies will include examination of the pressure data to establish the pressure change per unit mass deposited as well as a temperature change on a per hour basis. Deposits will also be removed from the coils to try and determine an equivalent thickness per unit weight.

F. *MORPHOLOGY STUDIES*

Spreadsheets for 86 pilot unit runs to clearly denote the coke morphology of the coke and its variations in the top, middle and bottom of the bed were generated. This information will be used to develop better correlations for coke morphology as a function of feedstock properties and operating conditions. In addition to the CT scans, coke plug samples will be obtained for porosity and permeability measurements, which should lead to correlations for these properties as a function of operating conditions and perhaps a predictive relation between coke porosity and coke permeability. We will also be making some capillary pressure measurements using the mercury injection capillary pressure (MICP) technique. The data obtained give the pore volume distribution directly and with the aid of a pore physical model, permit a simple calculation of the dimensional distribution of pore sizes. We will also be able to get a series of capillary pressure curves as a function of permeability and drainage curves. This data will help with our quench model development, especially when overhead injection is used.

Correlations were developed to predict coke density when shot and sponge morphologies are produced. The three variables used in the correlation are pressure, temperature and mass accumulation. The degree of fit for this data is provided in Figure 5 and Figure 6.

Low overhead temperature was studied as one possible reason for carry over of a significant amount of resid during steam stripping. Equilon 7 and 8 runs were carried out at a temperature of 900 ^{o}F, a pressure of 15 psig and a feed rate of 3600 gm/hr. It was observed that during the striping process of this run, there was considerable loss of mass from the coke drum. Equilon 4 run was carried out under the same operating conditions of 900 ^{o}F, 15 psig and 3600 gm/hr. Figure 7 shows the overhead temperature comparison for Equilon 4, 7 and 8 runs. It can be seen that the overhead temperature for runs 7 and 8 was much lower compared to run 4. Figure 8 shows the steam strip plots for Equilon 7 and 8 runs. As can be seen, there is a considerable loss of mass during the stripping process. From this analysis, and from checking our records on thermocouple replacements, we noticed that TI 107 (fluid temperature) and TI 200 (furnace skin temperature of coil) were replaced after the Equilon 8 run. Even though the fluid temperature of the run was controlled at the set test conditions, the temperature was lower than what it was reading. It appears that these thermocouples degraded prior to the Equilon 7 run and that two runs Equilon 7 & 8 were made before it was replaced.

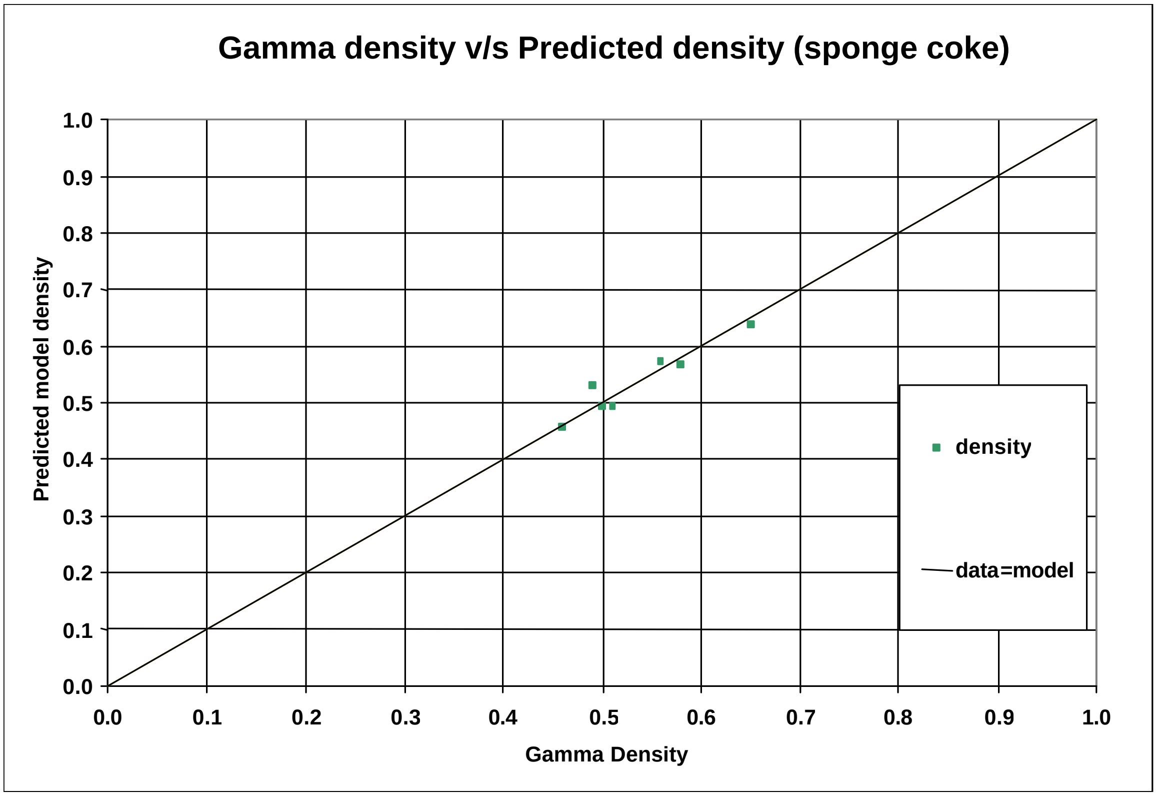


Figure 5 – Comparison of Gamma Density model Predicated Density for Sponge Coke

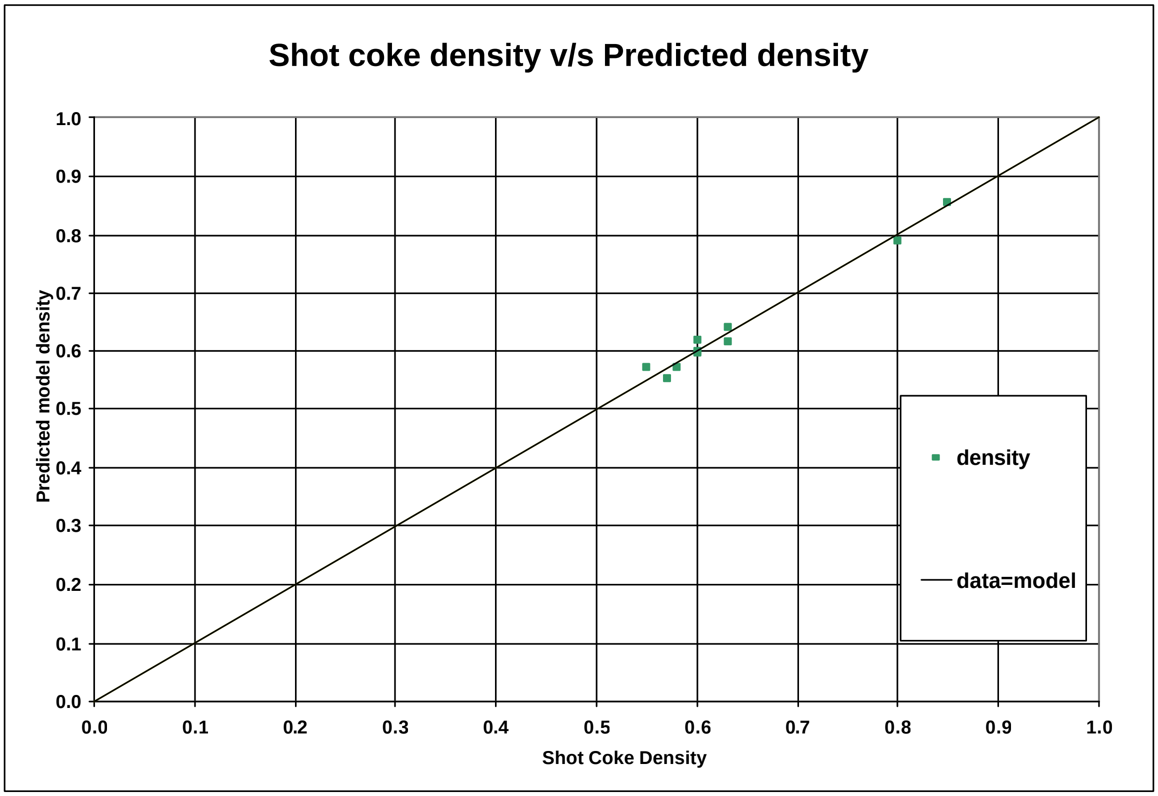


Figure 6 – Comparison of Gamma Density And Model Predicated Density for Shot Coke

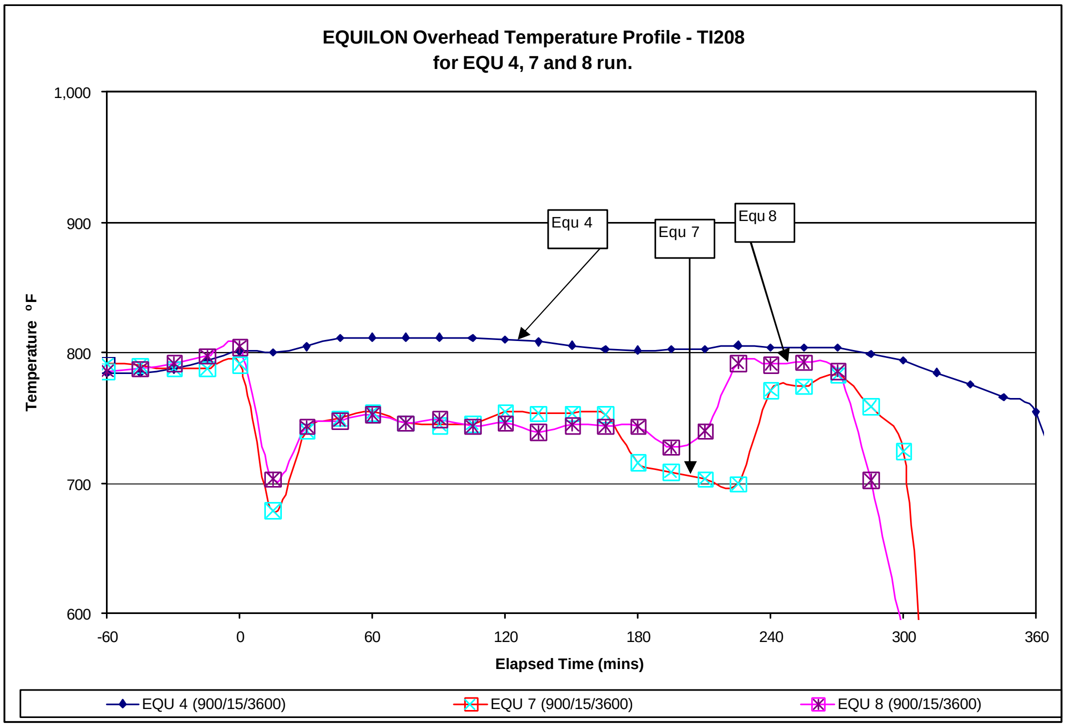


Figure 7 – Overhead temperature profile for Equilon runs

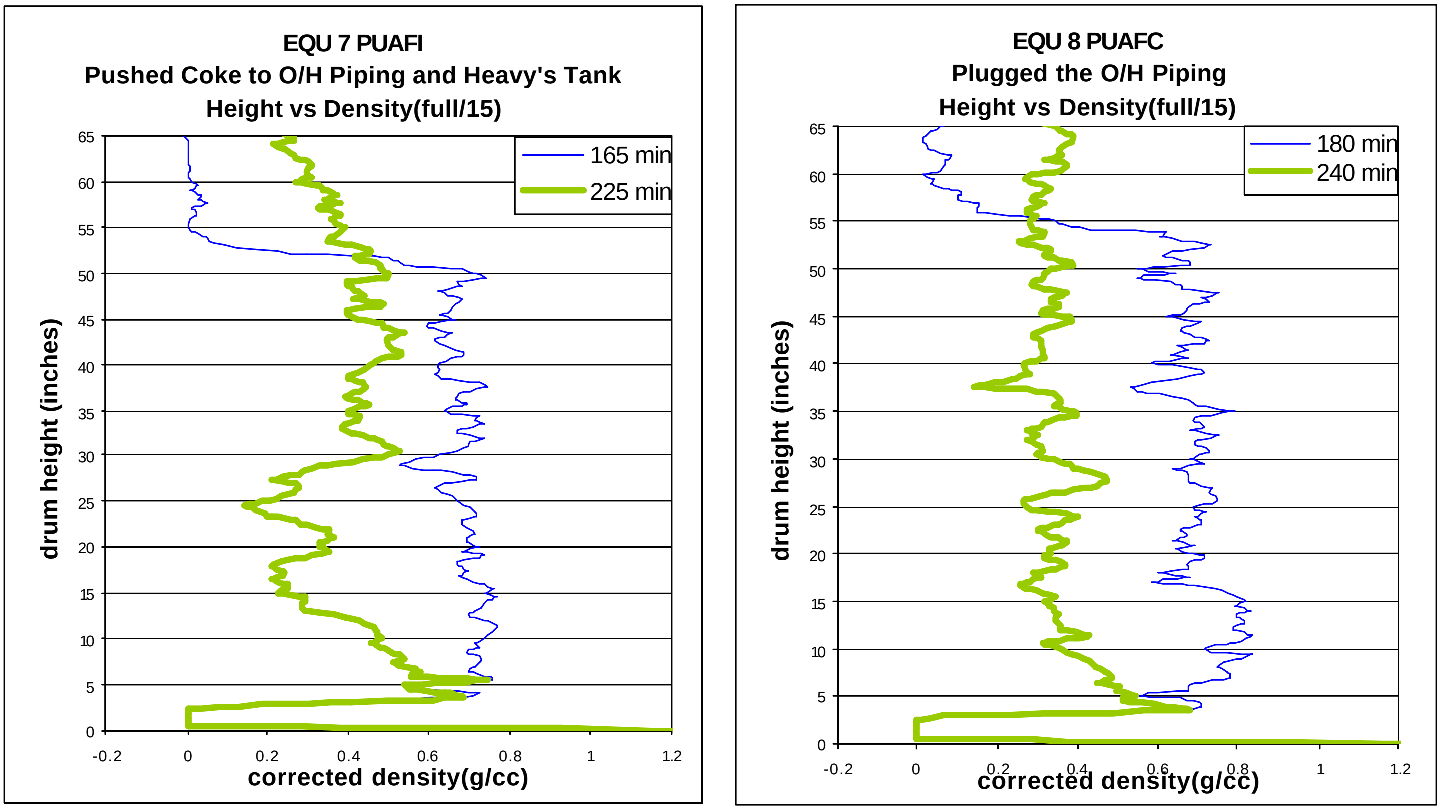


Figure 8 – Steam Strip plots Results

Coke morphology descriptions for the three new resids were added to the electronic database. The effect of pressure and temperature on morphology were quantified. Fifty plugs were drilled and permeability and porosity measurements made. A relationship between porosity and permeability as a function of morphology was observed. Thirty samples, one from each morphology group per resid, were picked for capillary pressure analysis. This data gives pore throat size distributions from .001 to 100 um and allows one to quantify the porosity as micro, meso and macro. For each sample, thin sections are being made and scanning electron photographs are being taken to provide visualization of the porosity and pore throat geometry. An example of the type of results being obtained is presented in Figure 9.

Coke morphology was seen to have an important effect on quenching. Hard dense sponge or agglomerated shot coke cooled very slowly, whereas the presence of loose shot or void spaces within the coke rum correspond to very fast cooling. Effort were begun to modify the existing quench model to account for varying porosity/permeability within the coke bed. The difference between uniform cooling and non uniform cooling due to morphology is shown in Figure 10 and Figure 11. Figure 10 shows a typical temperature profile plot for bottom quenching. In this case, it can be seen that the cooling proceeds uniformly from the bottom of the drum to the top.

Figure 11 shows the effect changing morphology in the drum has on cooling. Here zone 2 can be seen to cool faster than would normally be expected (as it is relatively close to the zone 1 curve) whereas zone 3 cools slower that expected (as it is relatively far from the zone 2 curve). This is due to coke morphology: the bottom 20 inches of the drum contained clusters of BB shot, whereas the next 20 inches contained very dense, hard agglomerated shot coke, followed by more clusters of BB shot in the top part of the drum. The clusters of BB shot cools slowly, apparently due to the permeability or low porosity of the coke.

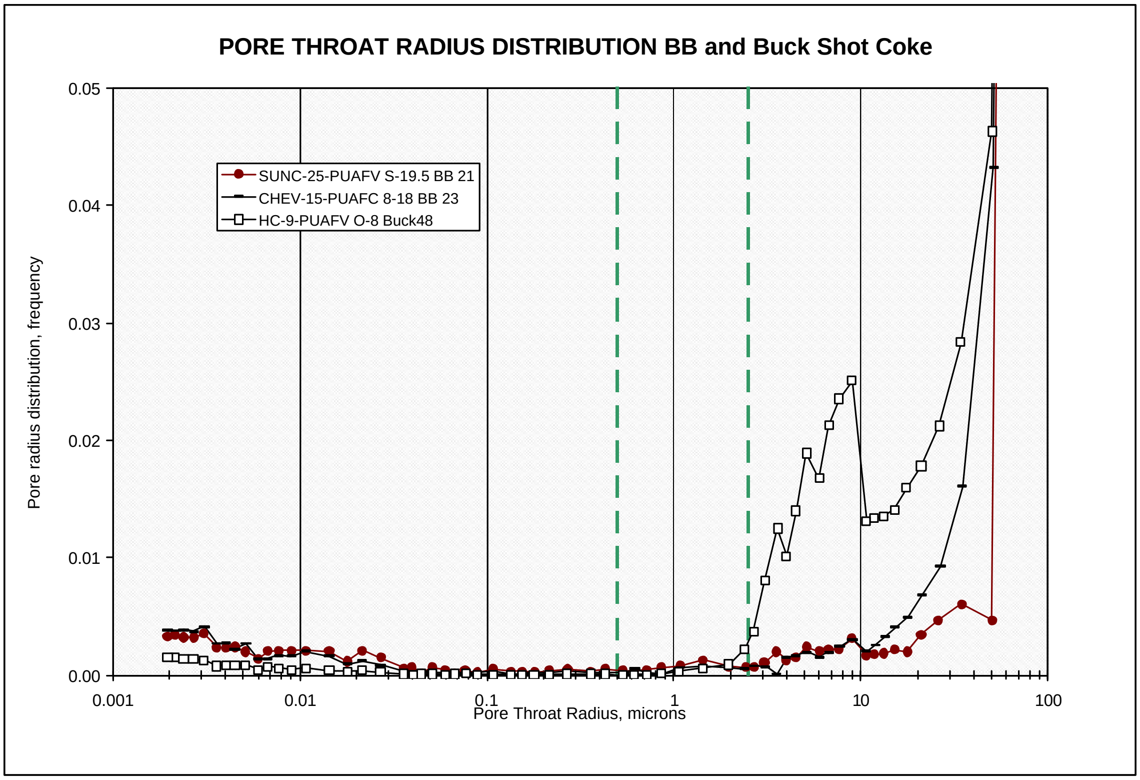


Figure 9 - Coke Morphology Experimental Data

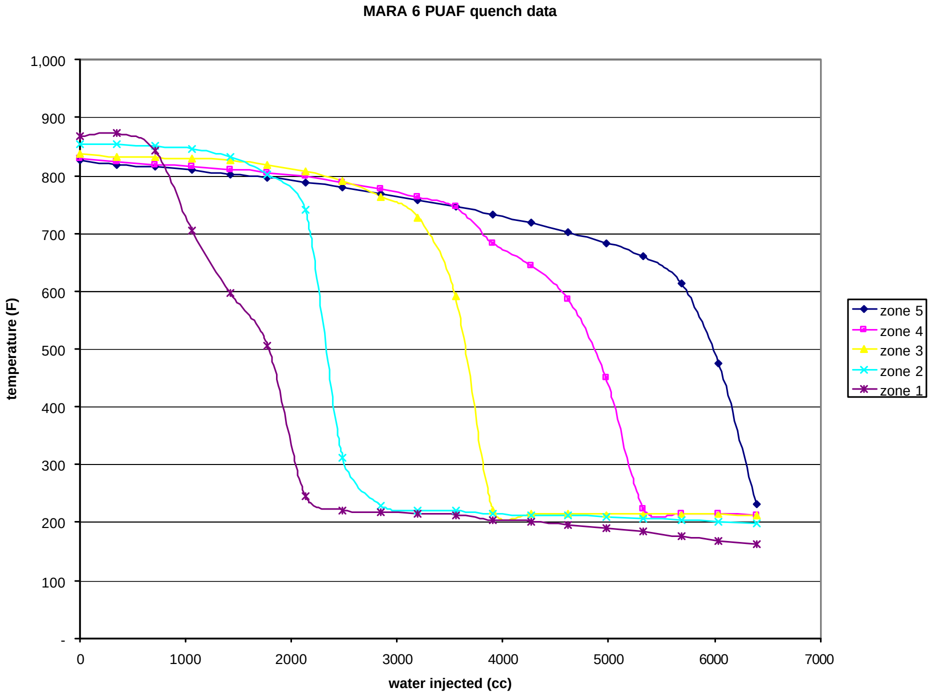


Figure 10 - Quench Results for Uniform Morphology

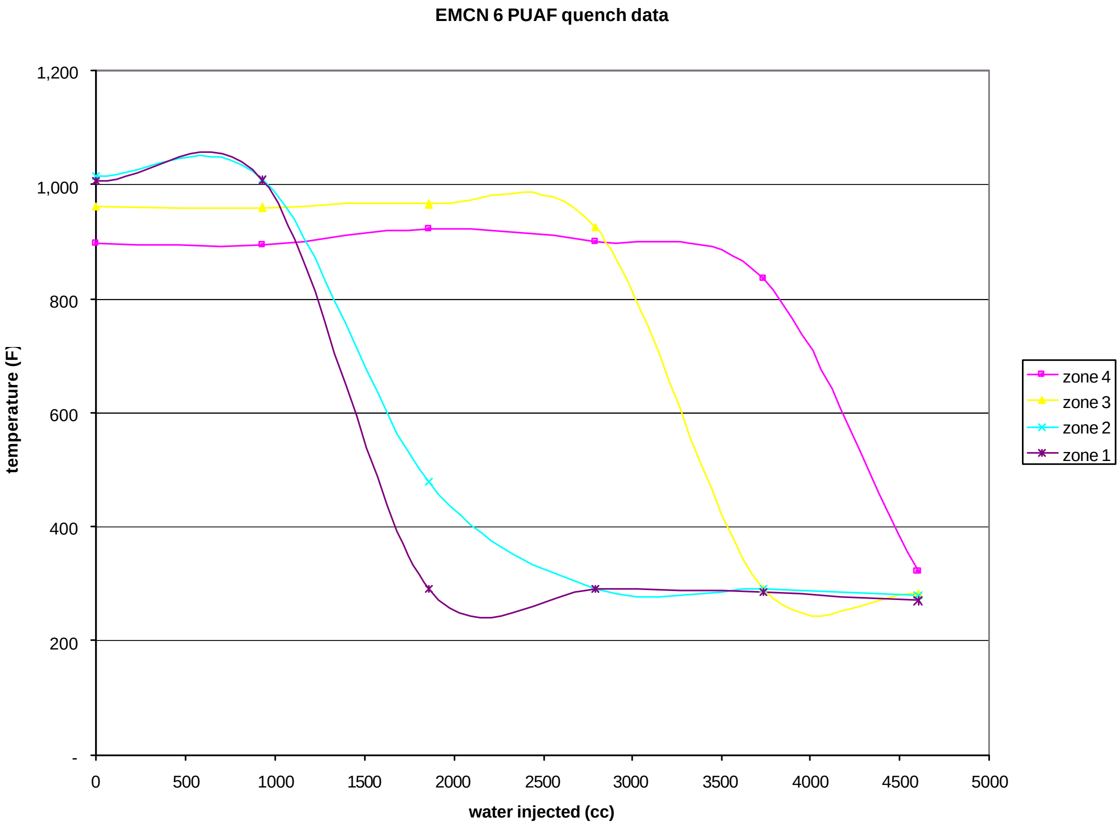


Figure 11 - Quench Results for Varying Morphology

G. SOFTWARE DEVELOPMENT

The overall structure for the delayed coker software was developed and is shown in Figure 12. The current model is mainly correlated data. In the long-run, it is proposed that we transition from correlated data to more mechanistic modeling of the delayed coking process.

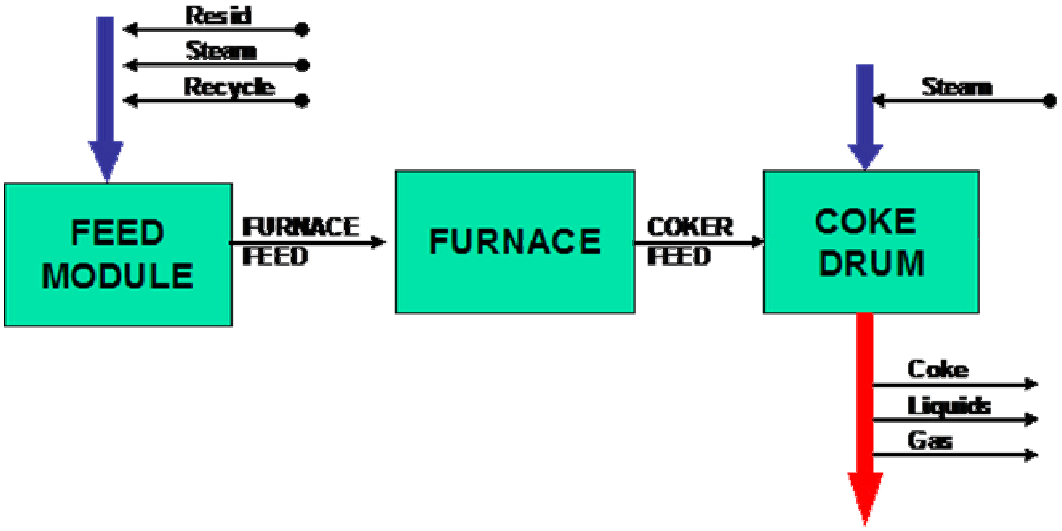


Figure 12 – Delayed Coking Optimization Simulator Structure

H. PROJECT STATUS/FUTURE EXPECTATIONS

The project is currently on target. During the upcoming year, testing will continue with the batch reactor at higher pressures. Beta testing of the kinetic model will continue and the model will be enhanced with detailed liquid data and the SARA analysis. Tests to determine the parametric effects and the effects of superficial velocity on foaming and morphology changes will continue with the pilot unit with the three new resids. Work on the delayed coking optimization simulator will continue.

8. Facilities

The coking test facilities consist of 3 reactors or cokers and eleven utilities. The 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, that utilizes a 3 foot drum, was obtained from Equilon in exchange for membership. The University expanded this facility to a six foot drum with a gamma densitometer to study foaming. 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 Reactor*

The micro-reactor is shown in Figure 13. 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-reactor as described and shown. Higher pressure is desirable to match refinery-operating conditions. Also foaming occurred in the pilot-coker coke drum when processing Equilon 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. In this modified set-up the glass traps were removed and replaced by a single piece of metal tubing.

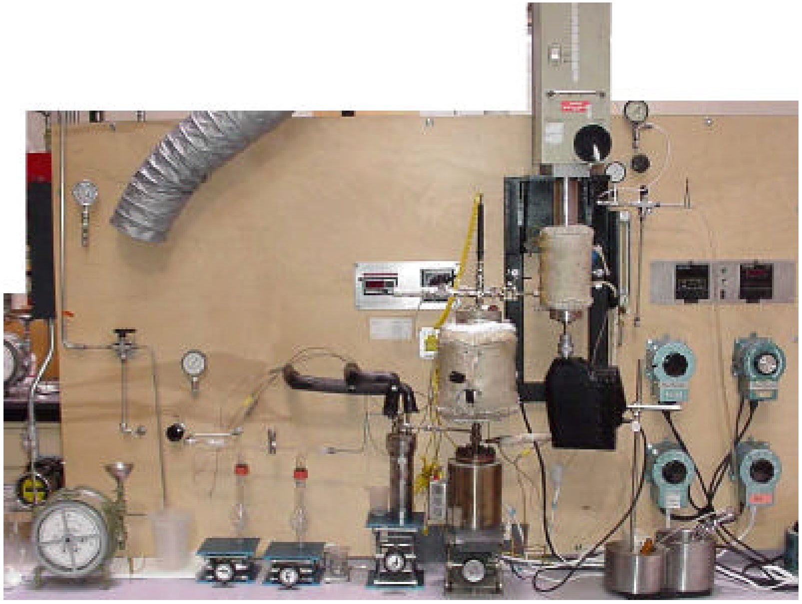


Figure 13 – Picture of Micro-Coker

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.

1. *Micro Reactor Upgrades*

To better monitor the micro-reactor and improve its functionality, upgrades to the system were made. These upgrades improved the assembly/disassembly time as well as the amount of data acquired and the process in which it is gathered. A picture of the modified micro-coker is shown in Figure 14.

During the first facility-testing phase of the micro-reactor, it was found that the gas recoveries were excessively high compared to pilot runs. The cause is considered in three phases. The vapor line pressure gauge was giving false (high) readings; this resulted in a high-standardized volume of gas. The absence of a carrier gas caused the vapors to become virtually stagnant at the beginning and end of each run, resulting in over cracking. The micro-reactor operating temperature was the furnace temperature, instead of an internal liquid temperature used in the pilot unit. This meant that the internal liquid temperature was lower. The lower internal temperature allows the liquids that are produced to sit in the reactor longer, extending cracking time. In response to these problems, a pressure transducer and digital pressure gauge was installed to measure the gas pressure more precisely, carrier gas flow is maintained even during the run to push off the stagnant vapors out of the reactor, and the run temperature is now controlled by an internal thermocouple at the bottom of the reactor. All the upgrades implemented are listed below:

1. New syringe pump housing is used to eliminate the stirrer. There were no apparent benefits to keeping the stirrer while its presence extends clean-up time and adds error to the mass balance due to the feed leaking around the seals-multiple housings has improved turn around time,
2. Temperature control- Four new Eurotherm temperature controllers were installed to control the reactor heater, pre-heater, mantle and the heat tape before the pre-heater-this upgrade eliminated the fluctuations in the temperature profiles from run to run,
3. A pressure transducer and digital pressure gauge was installed to measure the gas pressure more precisely. Helium is being injected into the top of the reactor to increase the flow rate of the hydrocarbon vapors out of the reactor. Pre-run helium flow data is recorded and an average flow rate is backed out of the final wet test meter reading. It has since been determined that the helium carrier which was left running over night was causing the evaporation of some of the liquids in the primary trap. The helium is now turned off at the end of each run and the system is being isolated to prohibit this evaporation. As a result the gas yields made a sizable decrease and were more consistent and comparable to the gas yields seen in the pilot unit.
4. Thermocouples- to improve correlations and comparisons to pilot unit data.
    a) Thermocouple well was installed in reactor head to hold thermocouple that reads top, middle and bottom reactor temperature,
    b) Thermocouple was installed to read temperature of the vapors leaving the reactor,
    c) Thermocouple was installed to read temperature of the vapors leaving the primary liquid trap,

    A typical temperature profile inside the drum for the new runs using modified micro-coker equipment is shown in Figure 15.

5. Pulse meter installed on wet test meter for computer data acquisition, and
6. Labview software for system controls and data acquisition (T's, P's and flows).

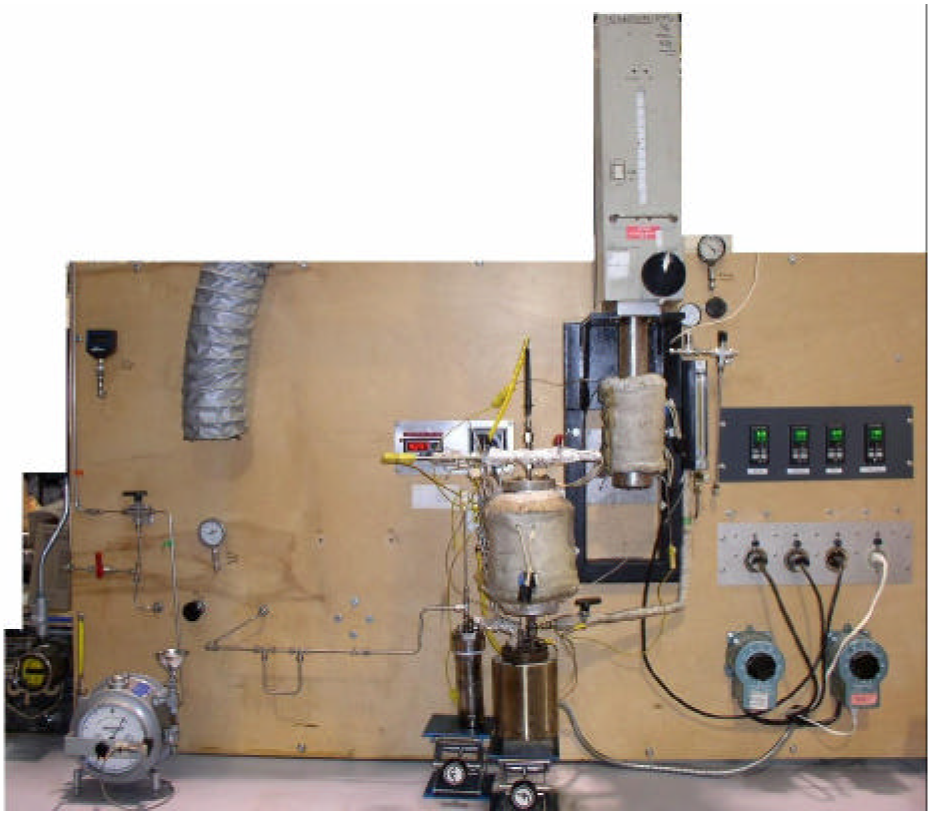


Figure 14 – Picture of Modified Micro-Coker

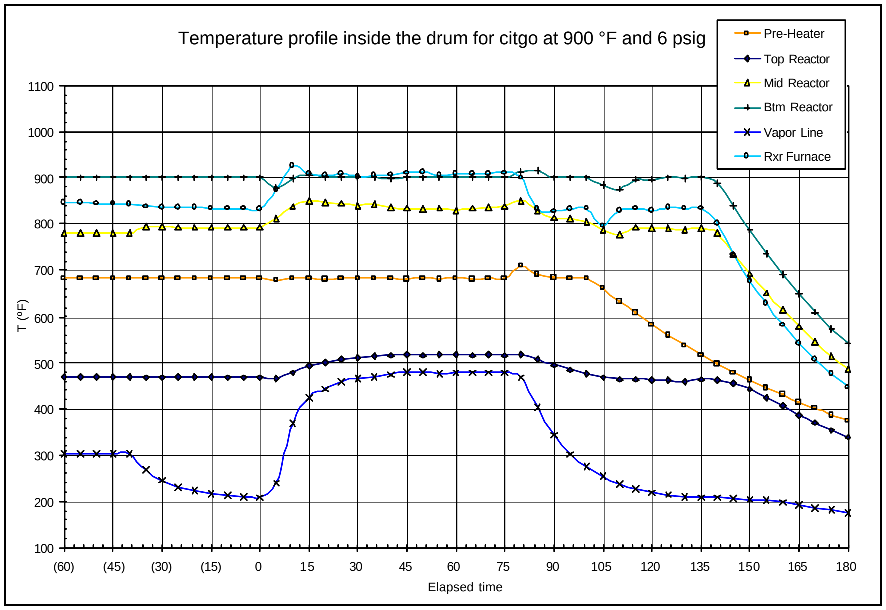


Figure 15 – Temperature profiles inside the drum

B. *Stirred Batch Reactor*

The stirred batch reactor unit is shown in Figure 16. 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.

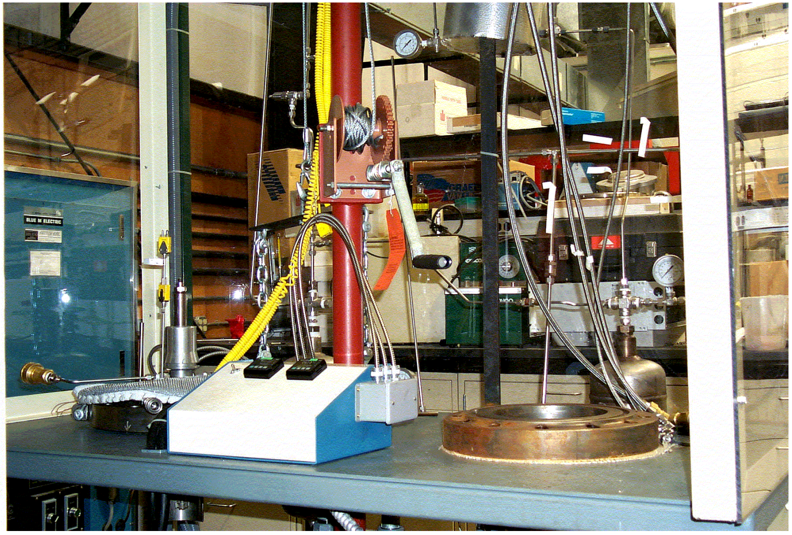


Figure 16 – Stirred Batch Reactor Unit

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 are analyzed using the high temperature gas chromatograph (HTGC) that can cover up to n-C100-n-C110 (~1330 °F).

Figure 17 – Liquid collection system with Hoke cylinders and quick disconnect valves

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 eliminated the need to close the 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 17.

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.

1. *Stirred Batch Reactor Upgrades – Quarter 4, 2002 & Quarter 1, 2003*

Upgrades to the batch reactor were made. The upgrades were focused on removing operator error in system functions and data acquisition and improving the system functionality. Limiting operator involvement will improve data reproducibility as well as increase time available for liquid sampling. The revised list of upgrades and the status of each upgrade is listed below.

1. The band heaters used in the old runs were run at the upper limits of voltage input causing early failure and limiting control. A new 11 kW ceramic heater was installed to eliminate this problem, see Figure 18,
2. The reactor was machined down from a 1.2 inch wall thickness to a 0.6 inch wall thickness to improve temperature control,
3. Thermocouples – see Figure 19
    a. A thermocouple was installed to read temperature of vapors leaving reactor,
    b. Thermocouples were installed to monitor reactor process temperature,
    c. Thermocouples were installed to monitor furnace element temperature for the purpose of a high temperature shutoff,
    d. Four thermocouples were installed in the reactor head at various heights from the bottom of the reactor. This gives a temperature profile inside the drum.
4. The hydrocarbon liquid collections system was automated, see Figure 20
    a. The light and heavy hydrocarbon liquids are split into 12 tanks each (increased from 4 each)
    b. The heavy tanks were fitted with dip tubes that allow a pressure differential indicator to measure the height of the liquid in the drums.
    c. Labview software is used to control two separate solenoid/pilot actuated manifold systems that step through the series of tanks as they fill. The tank stepping is controlled by the

height of the liquids in the heavies tanks, the temperature of the resid in the reactor and time elapsed,

5. A computer bypass switching system was installed for emergency and cleaning purposes, see Figure 21,
6. A pressure transducer was installed to measure the vapor line pressure for improving gas yield calculations,
7. A pulse meter was installed on the wet test meter for acquisition of gas volume, see Figure 22,
8. Labview software that is used for system controls and data acquisition(T's, P's and flows), see Figure 23 and Figure 24

The Labview tank switching controls and data acquisition functions are in working order. The three variables for switching - time, temperature and liquid level - have all been tested. Each variable was tested individually by adjusting the set points for each tank and visually verifying that the next tank in sequence was activated. All three variables were then turned on simultaneously to verify that any of the three variables reaching its set point would cause a tank switch. For the case where an inadvertent switch occurs during operation, a tank increment and decrement switch was installed on the tank switching page in Labview, see Figure 24. For emergency and cleaning purposes a computer bypass switching system was installed. This switching system allows the operator to manually step through the series of tanks, see Figure 21 and Figure 25.

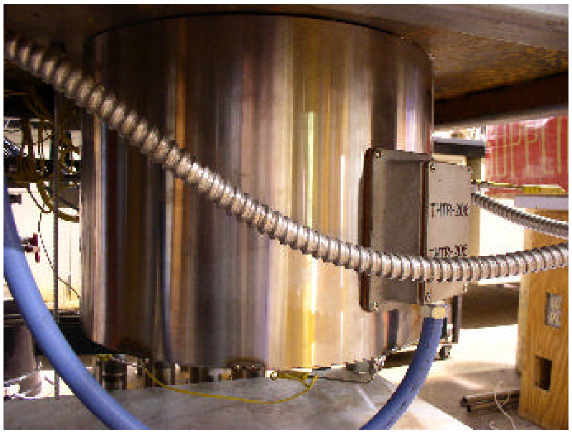


Figure 18 – Batch Reactor Furnace

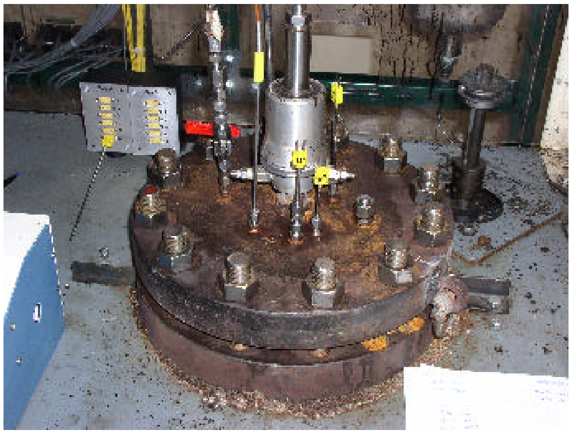


Figure 19 – Batch Reactor Head

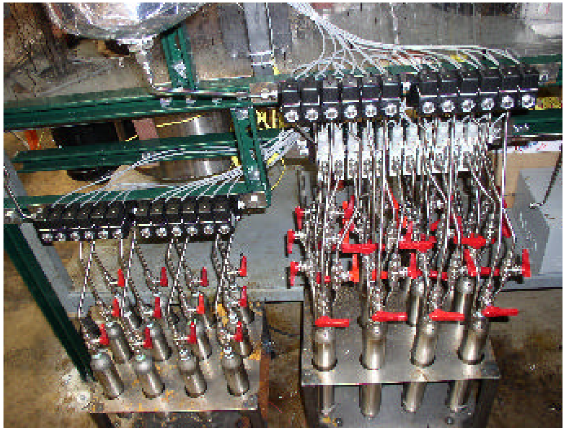


Figure 20 – Batch Reactor Manifold

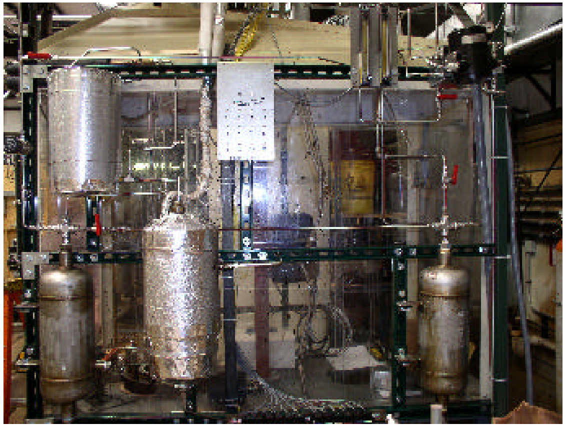


Figure 21 – Batch Reactor Tanks and Bypass Switching System

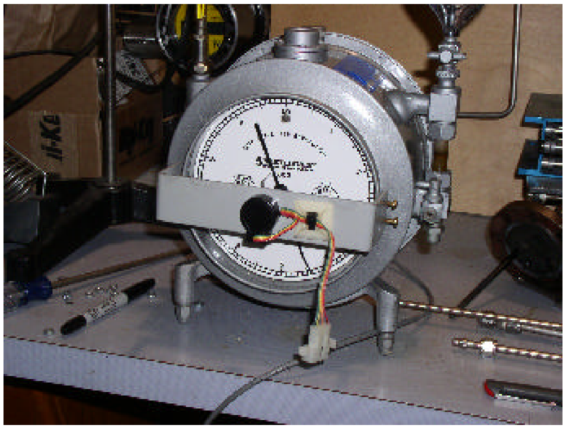


Figure 22 – Batch Reactor Wet Test Meter

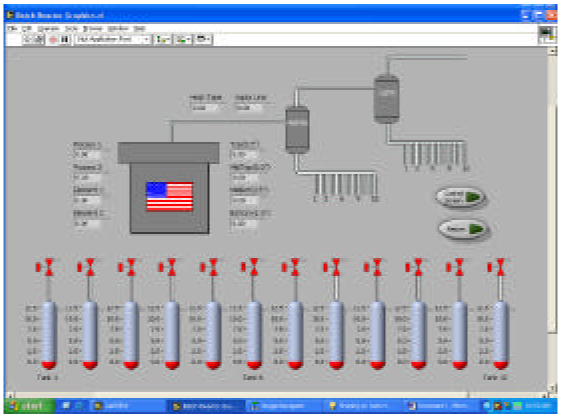


Figure 23 – Batch Reactor Labview

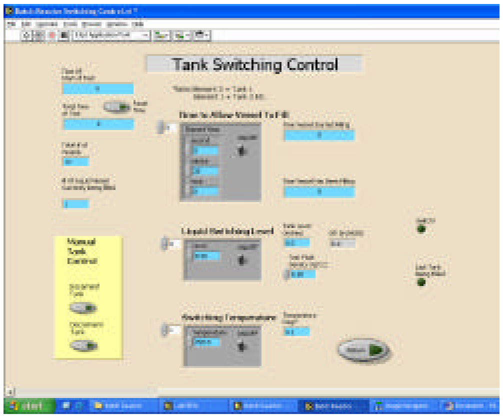


Figure 24 – Batch Reactor Labview

Figure 25 – Batch Reactor Back Side View

Sample Tube Upgrades

The old sampling tube was very cumbersome. It required many valves, attached nitrogen lines to purge resid from inserted tube and time to take each sample. The old sample tube can be seen in Figure 26. The new sample tube consists of a ½" diameter compression chamber between two valves and a collection tube that is inserted into the reactor, see Figure 27. The sample tube uses the pressure in the system to force the feed into the sample tube, compressing the gases above. The size of the compression chamber was calculated using a desired sample size of 30 mL. The pressure of most of the batch runs will be approximately 3.72 atmospheres (40 psig). The gases in the compression chamber before the bottom valve on the sample tube is opened are assumed to be one atmosphere. Thus, the compression chamber volume must be approximately 1.27 times the desired sample volume.

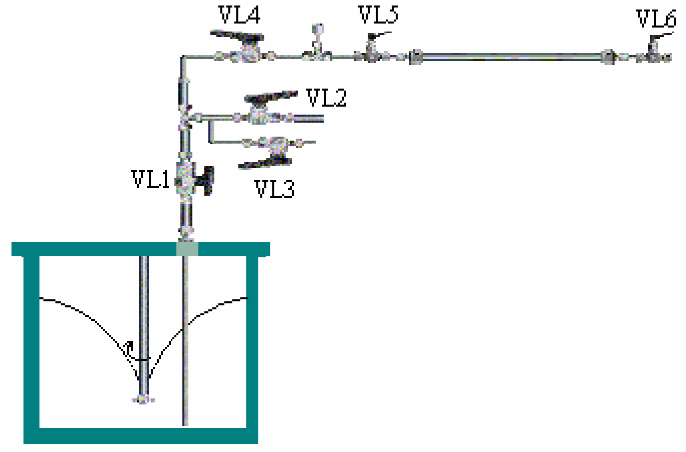


Figure 26 – Old Batch Sample Tube Assembly

The collection tube was designed in two pieces. The bottom portion is ¼" tubing and the top portion is 3/8" tubing. The two piece design was used because the 3/8" tubing holds more sample, minimizing the length of the assembly. The collection tube was oversized to allow a small head space between the sample and the bottom valve. Thus, the losses from each tube are limited to approximately $10 worth of tubing and ferrules.

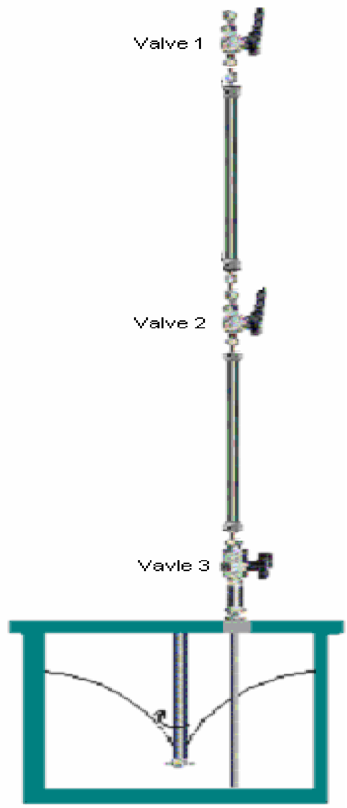


Figure 27 – New Batch Sample Tube Assembly

The new sample tube assembly was first tested with ambient water and hot oil. The tubes consistently drew 25-30 ml of sample, over a series of eight attempts. A vent line has since been added to the new sample tube assembly above the valve at the bottom of the compression chamber. It was added to prevent any compressed gases above the sample from forcing the sample out of the tube after it is removed from the reactor. The new sample assembly has since been tested in the Marathon recycle facility testing runs. In a series of three facility testing runs, 20+ grams of sample was taken in each attempt.

C. *PILOT UNIT EQUIPMENT*

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 28. 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 29) 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.

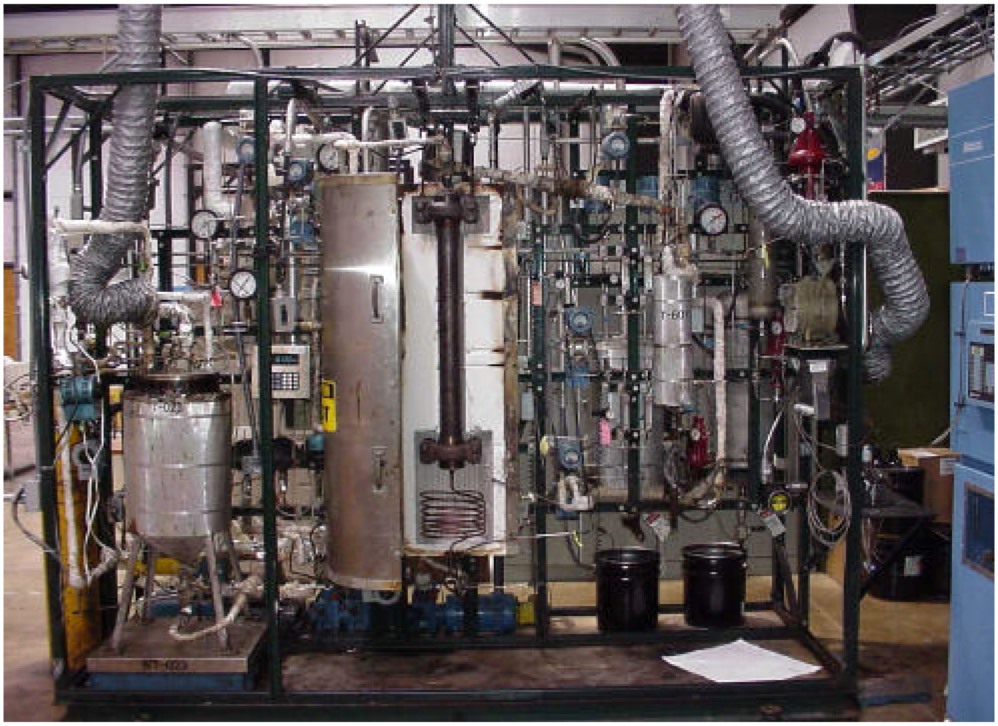


Figure 28 – Picture of Pilot-Coker Unit

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 is the workhorse in this Joint Industry Project (JIP) experimental investigation.

2. *Control System Description*

The control system includes 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 30 & Figure 31). 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.

Figure 29 – Zenith pump for pilot-coker

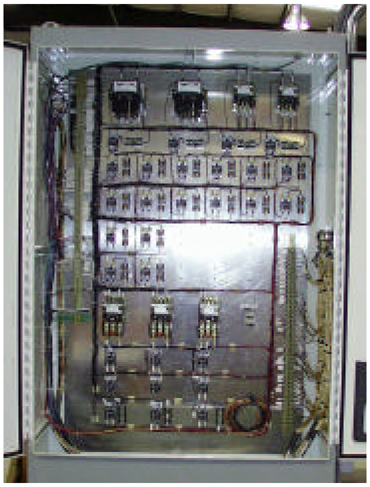


Figure 30 – Electrical control box

Figure 31 – Foxboro field bus module cabinet and a Foxboro ?-IA controller mounted on the bottom

D. *FOAMING STUDIES APPARATUS*

As shown in Figure 32, 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 was 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 32 – New foaming studies apparatus

1. *Facilities to inject carrier fluids and antifoaming agent*

As shown in Figure 33, the carrier fluid and antifoam are stored in a calibrated burette to measure the amount of fluid being feed to the antifoam pump. The system is manifolded with a valving system such that the antifoam can be injected overhead or into the feed line. The pump can inject the antifoam/carrier mixture from very low rates to a rate of 600 cc/hr.

Figure 33 – Injection Antifoam

The objectives of this system are:

1. Quantify foam heights for model development,
2. Compare overhead injection of antifoam versus injection with feed,
3. Determine how antifoam partitions in the products,
4. Establish whether injection of antifoam in the feed alters the coke density, and
5. Longer coking runs (10 to 15 hours at feed rates used in the prior JIP).

2. *Quench Water Injection Facilities*

Figure 34 – Water Injection Facilities

E. ***UTILITIES***

The utilities include an on-line gas chromatograph and caustic scrubber from Equilon, 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.

9. Feedstock Analysis

Feedstock analysis was conducted by Baker Petrolite on the Cerro Negro, Heavy Candian and Rose Pitch resids. Analyses were also conducted on the new shipments of the Marathon, Petrobras and Suncor resids, to check against the properties for the previous shipments of these resids.

For the Marathon, Petrobras and Suncor resids, the new results were compared to properties measured for the original shipment of feedstocks. The largest discrepancy appeared to be in the % asphaltenes, which varied considerably from the old analysis. The elemental analyses, including sulfur, carbon and hydrogen, generally match very well, as does the NMR % saturates/aromatics. The rest of the SARA analysis (asphaltic resins and filterable solids) and the acid number are in fair agreement. The discrepancy in the % asphaltene measurements may be due to sampling problems (i.e., obtaining a uniform sample of the resid for measurement), or there may be some differences in the technique of performing the SARA analysis. Based on the other measurements, however, it appears that the properties of the new shipments of resid match reasonably closely to thos of the old shipments.

10. Micro Reactor Studies

Tests using two recycle ratios on the Marathon resid were conducted in the upgraded Micro-Coker equipment at temperatures of 900°F, 930°F and 950°F and pressures 6 psig, 15 psig and 40 psig. The test matrix of completed recycle test runs along with the new Cerro Negro resid is listed in Table 3. The Suncor recycle and new resid were tested at temperatures of 900°F and 930°F and pressures 6 psig, 15 psig and 40 psig.

Table 3 – Test Matrix Completed for Recycle Resids and New Resids

Resid	% Recycle	900°F			930°F			950°F		Total
		6 psig	15 psig	40 psig	6 psig	15 psig	40 psig	15 psig	40 psig	
Marathon Recycle	5	1	1	1	1	1	1	1	1	8
	10	1	1	1	1	1	1	1	1	8
	100			1		1				2
Suncor Recycle	5	1	1	1	1	1	1			6
	10	1	1	1	1	1	1			6
	100	1		1		1				3
Cerro Negro	0	1	1	1	1	1	1			6
Total		6	5	7	5	7	5	2	2	39

A summary of un-normalized product recoveries for the runs completed for Marathon and Suncor along with new resids are listed in Table 4. The liquid sub-product yields are calculated in terms of both the weight percent of liquids and the weight percent of feed. The weight percent of feed is considered for data analysis.

Table 4 – Un-normalized recovery for Marathon and Suncor Resids

		CONDITIONS			
Test Number	Date	Bottom T(ºF)	Middle T(ºF)	P P(psig)	Feed rate (g/min)
MARMR-16	1/13/2003	900	860	6	2.02
MARMR-17	1/16/2003	900	865	15	2.18
MARMR-19	1/23/2003	900	864	15	1.97
MARMR-20	1/24/2003	900	861	15	1.99
MARMR-21	1/28/2003	930	874	6	1.85
MARMR-22	1/30/2003	930	872	15	2.15
MARMR-31	6/4/2003	900	841	40	2.17
MARMR-33	6/13/2003	950	895	15	2.09
MARMR-52	10/2/2003	950	933	40	1.89
MARMR-53	10/3/2003	930	890	40	2.21
MARMR-38 (5% rec)	8/13/2003	900	839	6	2.24
MARMR-39 (5% rec)	8/21/2003	930	866	6	2.21
MARMR-40 (5% rec)	8/25/2003	900	835	15	1.86
MARMR-41 (5% rec)	8/26/2003	930	866	15	2.22
MARMR-42 (5% rec)	8/27/2003	900	858	40	2.27
MARMR-43 (5% rec)	9/2/2003	930	878	40	2.22
MARMR-44 (5% rec)	9/3/2003	950	893	15	2.19
MARMR-62 (5% rec)	11/17/2003	950	913	40	2.02
MARMR-49 (10% rec)	9/18/2003	900	865	15	2.06
MARMR-51 (10% rec)	9/24/2003	930	885	6	2.09
MARMR-54 (10% rec)	10/20/2003	930	907	15	2.2
MARMR-58 (10% rec)	11/3/2003	930	911	40	2.16
MARMR-59 (10% rec)	11/5/2003	950	919	15	2.19
MARMR-63 (10% rec)	11/19/2003	900	863	6	2.21
MARMR-64 (10% rec)	11/20/2003	950	926	40	2.07
MARMR-65 (10% rec)	11/24/2003	900	886	40	2.11
MARMR-67 (100% rec)	12/2/2003	930	895	15	2.11
MARMR-68 (100% rec)	12/3/2003	900	882	40	1.87
SUNMR-34	7/24/2003	900	831	6	2.22
SUNMR-25	4/30/2003	900	842	15	2.19
SUNMR-26	5/1/2003	900	848	40	2.23
SUNMR-27	5/5/2003	930	849	6	2.16
SUNMR-29	5/8/2003	930	882	40	2.05
SUNMR-31	5/15/2003	930	884	15	2.19
SUNMR-32	6/25/2003	950	860	15	2.06
SUNMR-33	6/26/2003	950	900	40	1.93
SUNMR-39 (5% rec)	12/16/2003	900	830	6	2.11
SUNMR-40 (5% rec)	12/17/2003	900	839	15	2.19
SUNMR-41 (5% rec)	1/5/2004	900	850	40	2.09
SUNMR-44 (5% rec)	1/12/2004	930	873	40	2.35
SUNMR-51 (5% rec)	2/3/2004	930	872	6	2.41
SUNMR-52 (5% rec)	2/5/2004	930	886	15	2.29
SUNMR-45 (10% rec)	1/14/2004	900	835	6	2.38
SUNMR-46 (10% rec)	1/19/2004	900	817	15	2.48
SUNMR-47 (10% rec)	1/22/2004	900	835	40	1.94
SUNMR-48 (10% rec)	1/27/2004	930	860	6	2.25
SUNMR-49 (10% rec)	1/28/2004	930	879	15	2.3
SUNMR-50 (10% rec)	2/2/2004	930	870	40	2.2
SUNMR-37 (100% rec)	12/4/2003	930	899.0	15	2.02
SUNMR-38 (100% rec)	12/11/2003	900	836.0	40	1.98
EMCNMR-1	3/1/2004	900	875.0	6	1.96
EMCNMR-2	3/8/2004	900	853.1	15	2.01
EMCNMR-3	3/10/2004	900	836.0	40	1.91
EMCNMR-4	3/15/2004	930	856.6	6	2.13
EMCNMR-6	3/22/2004	930	843.4	15	1.96
EMCNMR-7	3/25/2004	930	830.4	40	1.95

Table 5 – Average error with the micro-coker unit in predicting the product yields

	Coke%	Liquids%	Gases%	Gasoline%	Diesel%	Gas Oils%
Average Error (plus or minus)	0.8%	0.8%	0.7%	0.5%	0.9%	1.4%

Table 6 – Average error for the micro-coker unit in predicting the gas composition (mol %)

Average Error In Terms of mole%									
Gas Composition	Hydrogen	H2S	Methane	Ethane	Propane	C4' s	C5' s	Hexane	Olefins
Average Error (plus or minus)	2.21%	0.21%	1.45%	0.68%	0.24%	0.11%	0.08%	0.19%	0.64%

Table 7 - Average error with the micro-coker unit in predicting the gas composition

Average Error In Terms of no. of moles/gm of amount fed									
Gas Composition	Hydrogen	H2S	Methane	Ethane	Propane	C4' s	C5' s	Hexane	Olefins
Average Error (plus or minus)	0.0003059	0.0000210	0.0001975	0.0000713	0.0000307	0.0000118	0.0000052	0.0000138	0.0000717

A. *Effect of Recycle on Product Yields for Marathon*

Comparisons of main products and liquid sub-product yields at 0%, 5% and 10% recycle were completed for Marathon resid at same temperature and pressure. The main products showed a variation of 0 to 2% in yields for the Marathon test runs at 0%, 5% and 10% recycle. The main product yields can be predicted within plus or minus 0.8% accuracy using the Micro-Coker Model. Hence the recycle effects at 5% and 10% recycle for Marathon resids were difficult to conclude due to small variations in the main products.

Though the variations in main product yields are small for Marathon recycle, it has been observed that the yields are affected by the variation in the temperature profiles. The temperature profiles inside the drum for recycle and non-recycle test runs for Marathon resid are shown in Table 8. The top reactor temperatures for the five percent recycle test runs stayed lower than the non-recycle and ten percent recycle test runs. Five percent recycle test runs showed average low top reactor temperatures that were 76°F lower than the ones from the non-recycle test runs and 55°F lower when compared to the ten percent recycle test runs. The middle reactor temperatures for the five percent recycle test runs were 10°F to 26°F lower than those from the zero and ten percent recycle test runs respectively. This could the reason why the coke yields stayed high and liquid yields stayed low for the five percent recycle when compared to zero and ten percent recycle test runs. Coming to liquid sub-product yields, gasoline yields stayed high and the gas oil yields stayed low for five percent recycles when compared to zero and ten percent recycle test runs. The effect on main and liquid sub-product yields due to the difference in temperature profiles is significant for 40 psig test runs.

Table 8 – Temperature profile comparison inside the reactor for Marathon recycles and non-recycles

Test		Bottom	Top	Middle	Vapor line	P	Feed rate
Number	Date	T(ºF)	T(ºF)	T(ºF)	T(ºF)	P(psig)	(g/min)
MARMR-16	1/13/2003	900	605	860	413	6	2.02
MARMR-38 (5% Recycle)	8/13/2003	900	549	839	472	6	2.24
MARMR-63 (10% Recycle)	11/19/2003	900	696	863	484	6	2.21
MARMR-17	1/16/2003	900	613	865	402	15	2.18
MARMR-40 (5% Recycle)	8/25/2003	900	551	835	492	15	1.86
MARMR-49 (10% Recycle)	9/18/2003	900	687	865	489	15	2.06
MARMR-31	6/4/2003	900	637	841	448	40	2.17
MARMR-42 (5% Recycle)	8/27/2003	900	558	858	466	40	2.27
MARMR-65 (10% Recycle)	11/24/2003	900	718	886	491	40	2.11
MARMR-21	1/28/2003	930	620	874	464	6	1.85
MARMR-39 (5% Recycle)	8/21/2003	930	567	866	384	6	2.21
MARMR-51 (10% Recycle)	9/24/2003	930	697	885	465	6	2.09
MARMR-22	1/30/2003	930	621	872	474	15	2.15
MARMR-41 (5% Recycle)	8/26/2003	930	547	866	497	15	2.22
MARMR-54 (10% Recycle)	10/20/2003	930	711	907	469	15	2.2
MARMR-53	10/3/2003	930	696	890	423	40	2.21
MARMR-43 (5% Recycle)	9/2/2003	930	551	878	474	40	2.22
MARMR-58 (10% Recycle)	11/3/2003	930	709	911	455	40	2.16
MARMR-33	6/13/2003	950	669	895	455	15	2.09
MARMR-44 (5% Recycle)	9/3/2003	950	575	893	412	15	2.19
MARMR-59 (10% Recycle)	11/5/2003	950	734	919	499	15	2.19
MARMR-52	10/2/2003	950	743	933	457	40	1.89
MARMR-62 (5% Recycle)	11/17/2003	950	699	913	419	40	2.02
MARMR-64 (10% Recycle)	11/20/2003	950	736	926	469	40	2..07

B. *EFFECT OF RECYCLE ON PRODUCT YIELDS FOR SUNCOR*

Test conditions for the Suncor resid with recyles were at temperatures of 900°F and 930°F and pressures of 6, 15 and 40 psig. The coke yield increased by an average of 3% and the liquid yield decreased by an average of 1.2% when the recycle is increased from zero percent to five percent. When the recycle is further increased from five percent to ten percent, the coke yields increased by an average of 1.6% where as the liquid yields decreased by an average of 2.45%. The gas yields did not show any definite variation with an increase in recycle. From the plots it has been observed that the variation in recycle is large at 900°F when compared to the variation in yields at 930°F.

Coming to the liquid sub-product yield comparisons, the gasoline and the diesels did not show much variation in yields but the gas oils followed similar trends as the liquid yields. About 5% decrease in yields was observed with an increase in recycle from zero to five percent. The decrease in gas oils was within the error bars when the recycle was increased from five to ten percent recycle.

Table 9 – Temperature profile comparison inside the reactor for Marathon recycles and non-recycles

Test		Bottom	Top	Middle	Vapor line	P	Feed rate
Number	Date	T(ºF)	T(ºF)	T(ºF)	T(ºF)	P(psig)	(g/min)
SUNMR-34	7/24/2003	900	522	829	403	6	2.22
SUNMR-39 (5% rec)	12/16/2003	900	657	830	410	6	2.11
SUNMR-45 (10% rec)	1/14/2004	900	666	835	414	6	2.38
SUNMR-25	4/30/2003	900	642	842	425	15	2.19
SUNMR-40 (5% rec)	12/17/2003	900	676	839	434	15	2.19
SUNMR-46 (10% rec)	1/19/2004	900	645	817	386	15	2.48
SUNMR-26	5/1/2003	900	623	848	386	40	2.23
SUNMR-41 (5% rec)	1/5/2004	900	681	850	417	40	2.09
SUNMR-47 (10% rec)	1/22/2004	900	654	835	372	40	1.94
SUNMR-27	5/5/2003	930	641	849	405	6	2.16
SUNMR-51 (5% rec)	2/3/2004	930	676	872	331	6	2.41
SUNMR-48 (10% rec)	1/27/2004	930	701	860	430	6	2.25
SUNMR-31	5/15/2003	930	679	884	511	15	2.19
SUNMR-52 (5% rec)	2/5/2004	930	689	886	376	15	2.29
SUNMR-49 (10% rec)	1/28/2004	930	698	879	393	15	2.3
SUNMR-29	5/8/2003	930	685	882	427	40	2.05
SUNMR-44 (5% rec)	1/12/2004	930	690	873	414	40	2.35
SUNMR-50 (10% rec)	2/2/2004	930	685	870	376	40	2.2

C. STRAIGHT RECYCLE TESTS

Marathon and Suncor recyle were tested at to see the variation in product yields. Two micro tests were completed for Marathon at 930°F, 15psig and 900°F, 40psig. An overall increase in liquids and a decrease in coke have been observed with increase in recycle for Marathon resid. At 930°F and 15psig, the coke yields decreased by thirteen percent and liquids increased by eighteen percent when straight recycle test runs were compared with the non-recycle test runs for the Marathon resid. At 900°F and 40psig, when the 100% recycle test run is compared with the non-recycle test run, the coke yields decreased by three percent and liquid yields increased by five percent.

The effect of recycle on the product yields at 930°F and 15psig was greater when compared to the product yields at 900°F and 40psig. At low temperature and high pressure, the coke yields maximize and this resulted in high coke yields for 900°F-40psig test run compared to the test run at 930°F-15psig, for 100% recycles. Temperature and pressure had a large impact on the product yields when Marathon recycle was used.

When the liquid sub-product yields were compared, the gasolines decreased by nine percent for the 100% Marathon recycle runs. The gas oils were dominating in the liquid sub-products for 930°F-15psig test run whereas for 900°F-40psig test run the diesels were dominating. At low temperature and high pressure there will be less vaporization and more cracking of heavy gas oils. This resulted in low gas oils for the recycle test run at 900°F and 40psig.

Two micro tests were completed for Suncor at run conditions of 930°F-15psig and 900°F-40psig. At 930°F and 15psig, the coke yield showed a fourteen percent increase and the liquid yield showed a twelve percent decrease when the 100% recycle test run was compared to the non-recycle test run. At 900°F and 40psig, the coke yields increased by seventeen percent and liquid yields decreased by seventeen percent when the recycle was increased from zero to 100% recycle. The gas yields showed no variation. When the liquid sub-product yields were compared, the gasoline and the gas oils showed six and eight percent decrease in yields respectively with an increase in recycle from zero to one hundred percent. No significant variations were seen for the diesel cut.

The variation in product yields between the non-recycle and the straight recycle test runs for the Marathon resid and Suncor resids were due to the large difference in their feedstock properties. The Suncor resid behaved differently for 100% recycle compared to Marathon resid at 100% recycle. There was an increase in coke yields and a decrease in liquid yields with an increase in recycle for Suncor whereas for Marathon an opposite trend was observed. The discrepancy can be explained by comparing the feedstock property- Asphaltic resins and %Sat/Arom. Though CCR and asphaltenes percent were high for the Suncor resid when compared with the Suncor recycle, the coke yields were lower for the non-recycle test runs than the recycle test runs. The reason could be because the %Asphaltic resins and %Sat/Arom for Suncor resid was 51.3 and 2.5 respectively whereas for Suncor recycle the %Asphaltic resins and %Sat/Arom was 87.6 and 0.9 respectively. High %Asphaltic resins and low %Sat/arom produces high coke yields and low liquid yields. The Marathon resid has high Asphaltic resins compared to Marathon recycle. Hence the non-recycle test runs for Marathon showed a higher coke yield than the recycle test run. The effect of feedstock properties on the recycle resids is discussed in more detail in a separate section.

D. *GAS ANALYSIS*

The effects of recycle on gas composition were determined for Marathon and Suncor resids. The gas composition was analyzed using the number of moles per gram of amount fed of each component that is passed through the Gas Chromatograph (GC). To simplify the gas composition comparisons, n-butane and isobutane are grouped as C4's; n-pentane and iso-pentane are grouped as C5's; and ethylene, propylene, isobutylene, trans 2-butene, cis 2-butene, 3-methyl 1-butene, 2-methyl 1-butene, 2-methyl 2-butene, 1-pentene, trans 2-pentene, cis 2-pentene are grouped as olefins. Hydrogen, methane and olefins occupy eighty percent of the total gas composition and the remaining twenty percent gas composition contains hydrogen sulfide, ethane, propane, C4's, C5's and hexanes.

The hydrogen yields were high for 5% Marathon recycles due to overcracking caused by low temperatures at the top and middle reactor as discussed earlier. There was an overall decrease in hydrogen and methane yields with increase in recycles for the Marathon resid. Coming to the effect of recycle on the gas composition for the Suncor resid, the variation was within the error bars for the 0%, 5% and 10% recycle tests. At 900ºF and 40 psig the 100% recycle gas composition decreased significantly but at 930ºF and 15 psig there was no change in the gas composition. The variation in gas composition was not consistent with the increase in recycle for the Suncor resid. More test runs at 100% recycle would be helpful in drawing definite conclusions on the effect of recycle on gas composition.

E. *MICRO-SCREENING MODEL PREDICTION FOR RECYCLE RESIDS*

A material balance was done using 100% recycle and 0% recycle test runs to predict the yields at 5% recycle and 10% recycle. The fresh feed and the recycle resid were assumed to not interact with each other during cracking. A comparison was made of the predicted yields to the experimental yields. The differences in predicted and experimental yields are small for Marathon 5 and 10 percent recycles at 930°F and 15psig. At 900°F and 40psig, the 5% recycle for Marathon resid showed 2% low coke and 2% high liquid yields for the predicted yields. In the liquid sub-products, 4% low gasoline and diesels, and 9% high gas oils were predicted. The 10% recycle for Marathon resid showed little variation in coke and liquid yields. When the liquid sub-products were compared, 3 to 4% low gasoline and diesels and 5% high gas oils have been observed. The yields predicted using the non-recycle test runs and 100% recycle test runs for Marathon resid worked fairly well for the main product yields.

The model prediction for Suncor recycle worked well for 930°F test runs when compared to 900°F test runs. The coke yields were 3 to 4% high and the liquid yields were 3% low when the experimental yields are compared with the predicted yields. There was a large variation for the Suncor resid when the recycle ratio was increased to five and ten percent at 900°F as shown previously. This resulted in large differences in the predicted and experimental yields for the Suncor resid at 900°F.

The comparison between the Micro-Screening Model developed by Tomas Zambrano and the experimental yields for Marathon and Suncor straight recycles are shown in Table 10. The parameters used in the Zambrano Micro-Screening model were CCR, temperature and pressure. At 930°F and 15psig, the model predicted 0.5% low coke yields and 2% high liquid yields for Marathon recycle. Coming to the liquid sub-products, the model predicted 16% high gasoline yields, 3% high diesels and 16% low gas oils. At 900°F and 40psig, the deviation from the experimental yields further increased. Large differences in predicted vs. experimental yields have been observed for Suncor recycles. The model gives high coke yields with high CCR% but the Suncor recycle which has 9% CCR produced more coke than the Suncor resid which has 20.2% CCR. This shows that CCR does not work well as a parameter to predict the yields when recycle is used. Other feedstock properties like asphaltenes, asphaltic resins and %Sat/Aromatics might be helpful in predicting the yields more accurately.

Table 10 Tomas Model Prediction vs. Experimental Yields for Straight Recycles

Test Number	Date	T(ºF)	P(psig)	F(g/min)	CCR	Coke%	Liquids%	Gases%	Gasoline%	Diesel%	Gas Oils%
Tomas Model Prediction						8.73%	84.75%	6.51%	24.35%	25.70%	34.70%
MARMR-67	12/2/2003	930	15	2.11	0.8	9.25%	82.79%	7.96%	9.11%	22.35%	51.33%
Tomas Model Prediction						14.38%	76.25%	9.34%	27.87%	25.51%	22.87%
MARMR-68	12/3/2003	900	40	1.87	0.8	22.21%	67.09%	10.70%	13.42%	44.28%	9.39%
Tomas Model Prediction						22.09%	67.12%	10.76%	25.34%	22.77%	19.01%
SUNMR-38	12/11/2003	900	40	1.98	9	47.27%	39.72%	13.01%	14.30%	18.67%	6.75%
Tomas Model Prediction						16.44%	75.62%	7.92%	21.82%	22.96%	30.84%
SUNMR-37	12/4/2003	930	15	2.02	9	40.25%	48.65%	11.10%	20.43%	11.19%	17.03%

F. *Pilot vs. Micro Unit Comparisons for Marathon and Suncor Resids*

Pilot vs. Micro data comparisons were made for Marathon and Suncor resids at the same temperature and pressure. The test run data compared for the Marathon and Suncor resids are shown in Table 11 and Table 12 respectively. The major difference in the coker tests was that the pilot unit had liquid temperature controlling and the Micro unit had bottom reactor temperature controlling. The Micro-Coker test runs showed 1 to 3% more coke and 2 to 5% less liquid when compared to the Pilot unit test runs for the Marathon resid. When the temperature profiles inside the drum were compared, the top reactor temperature for the Pilot unit was higher when compared to the Micro unit. This resulted in higher liquid yields for the Pilot unit. The gas yields for the Micro unit were higher when compared to the Pilot unit because the vapors overcrack in the Micro unit due to the longer residence times. The 930°F-40psig non-recycle test run for the Marathon resid was the one exception where an opposite trend was observed.

When the Pilot vs. Micro test run data were compared for the Suncor resid, the non-recycle test runs showed high coke yields (2%) and low liquid yields (2 to 4%) for the Micro unit. When the recycle test runs were compared, higher coke yields (8 to 10%) and lower liquid yields (6 to 10%) were observed for the Micro unit. There was a large difference in product yields between the Micro and Pilot unit when the Suncor recycles were compared. When the liquid sub-product yields are compared between the Micro unit and Pilot unit runs, the Micro unit made more gasoline and more diesel. The heavy hydrocarbon vapors are staying inside the reactor for longer time in Micro unit, which caused the vapors to overcrack resulted in more gasoline and diesel product. The gas oil yields were lower for the micro unit when compared to the Pilot unit because of low vaporization resulting in more cracking.

The 100% recycle runs for the Pilot unit and the Micro unit were run at different temperatures and pressures. There were no common grounds to compare the yields for the Micro and Pilot unit test runs.

Table 11 Pilot vs. Micro Comparison for Marathon Resid

				CONDITIONS					Liquid Sub-Products			
		Test				Feed rate			In terms of wt% of feed			
RUN	RECYCLE	Number	Date	T(ºF)	P(psig)		Coke%	Liquids%	Gases%	Gasoline%	Diesel%	Gas Oils%
MICRO	NO-REC	MARMR-22	1/30/2003	930	15	2.15	22.57%	64.87%	12.56%	18.81%	22.71%	22.06%
PILOT	NO-REC	MARA 4 PUAF	10/18/2002	930	15	4800	20.16%	71.35%	8.49%	13.56%	17.84%	39.95%

Effect of Recycle on Pilot Unit for Marathon and Suncor resids:

The effect of recycle on the product yields for Marathon and Suncor resids were determined in the Pilot Unit. The coke yield decreased by 2% when the recycle was increased from 0 to 10% for the Marathon resid at test conditions of 900°F and 15psig. The same trend was seen for the Micro-Unit where the coke yields decreased with an increase in the recycle from 0 to 100%. At 900°F-15psig and 940°F-40psig, the coke yields for the Suncor resid showed an increase with increase in recycle to 100%. A similar trend was observed for Suncor recycle test runs in the Micro Unit.

G. EFFECT OF TEMPERATURE AND PRESSURE ON MAIN AND LIQUID SUB-PRODUCT YIELDS

The effect of temperature were determined on product yields at constant pressures of 6, 15 and 40 psig for Marathon with recycle and without recycle. The coke yields showed an overall decrease and the liquid yields showed an increase with an increase in temperature**.** The gas yields do not follow a definite trend. For the liquid sub-products, only a slight variation in gasoline yields was observed with an increase in temperature. The diesels and gas oils do not follow a definite trend with temperature.

The effect of pressure on product yields for the Marathon resid at 900ºF, 930ºF and 950ºF were also determined. At constant temperature, the coke yields decreased consistently with an increase in pressure from 6 psig to 40 psig and the liquid yields decreased with an increase in pressure following the expected trend. An increase in gas yields was observed when the pressure was increased. When the liquid sub-product yields were compared, the gasoline yields increased and the gas oil yields decreased with pressure. There was no definite trend for diesel.

Similar trends were observed for the product yields for the effect of temperature and pressure on the main and liquid sub-product yields for the Suncor recycles and the Cerro Negro resid.

H. EFFECT OF TEMPERATURE AND PRESSURE ON AVERAGE MOLECULAR WEIGHT OF GAS COMPOSITION

The effects of temperature and pressure on the average molecular weight of gas composition were determined for the six resids. Only a slight variation in average molecular weight was observed with a change in temperature. The variation in mole percent of the gas composition was not significant with temperature and hence the average molecular weight was not affected by an increase in temperature.

The trends in mole percent of hydrogen, methane and olefins with temperature and pressure for the six resids were established. With an increase in pressure, the average molecular weight showed a significant decrease. This is due to the decrease in mole percent of methane, ethane and olefins with an increase in pressure. The average molecular weight is contributed largely by this group in the gas composition. Even though there was a large increase in mole percent of hydrogen at higher pressures, this had little effect on the average molecular weight of the gas composition.

I. ***EFFECT OF FEEDSTOCK PROPERTIES***

The feedstock properties were analyzed to see the effect on product yields as shown in Table 13. Since asphaltic resins convert to ashpaltenes during the coking process, the combined effects of asphaltenes and asphaltic resins on the product yields were analyzed.

Table 13 Feedstock Properties

	Carbon Residue wt%	Asphaltenes %	Asphaltic Resins %	Asphaltenes%+ Asphaltic resins%
Chevron	19	17.6	53	70.6
Citgo	24.3	34.2	54.7	88.9
Equilon	28.5	39.2	41.6	80.8
Marathon	15.6	12.1	48.1	60.2
Marathon Recycle	0.8	0.2	21.2	21.4
Petrobras	20.7	24.3	49.8	74.1
Suncor	20.2	25.2	51.3	76.5
Suncor Recycle	9	8	87.6	95.6

The trend line along with the R^2 value was calculated for each data series to reveal how closely the estimated values correspond to the actual data. The coke yields are predicted well using the MCR having R^2 values of 0.94, 0.99 and 0.98 for 6, 15 and 40 psig pressures respectively. The coke yields showed a linear relationship with MCR. The liquids are predicted as good as the coke using MCR for 15 and 40 psig pressures having R^2 values 0.98 and 0.96 respectively. The trend line showed a negative slope for liquids. The gas yields did not show a definite trend with MCR and the R^2 values are worse. The liquid sub-product yield predictions using MCR is not as good as the predictions for the combined liquids. The trend line showed a negative slope for the liquid sub product yields similar to the trend observed in liquid yields.

The effect of asphaltenes on the main and liquid sub-product yields were analyzed at a temperature 930ºF and pressures of 6, 15 and 40 psig. The coke and liquid yields are predicted reasonably well using asphaltenes. The change in asphaltene percent from one resid to another resid stay close to trend followed by the MCR percent. This resulted in similar patterns of trend lines for MCR and asphaltenes in the prediction of product yields. When the product yield predictions for MCR and asphaltenes were compared, the MCR showed better predictions than the asphaltenes.

The combined effects of asphaltenes and asphaltic resins on coke and liquid yields were analyzed at 930ºF for six resids (Chevron, Citgo, Equilon, Marathon, Petrobras and Suncor). The R^2 values are 0.5 to 0.6 for coke and liquid yield predictions. The Equilon resid showed exceptionally high coke and low liquid yields when compared to the remaining five resids. When the Equilon resid was removed from the data series, the R^2 values for coke and liquid yields significantly improved.

The percent of asphaltic resins stayed higher than the asphaltenes by twenty to thirty-five percent for the five resids where as for the Equilon resid there was only a two percent difference. Equilon resid has high coke yields when compared to the remaining five resids. The prediction worked well using MCR and asphaltenes because the increase in these feedstock properties showed a consistent increase in coke yields. The increase in the percent of asphaltic resins did not show a consistent increase in coke yields. For the Equilon resid, the other feedstock properties like MCR and asphaltenes might have affected the coke yields dominating the effect incurred by asphaltic resins.

The combined effect of asphaltenes and asphaltic resins on product yields at 930ºF-15psig and 900ºF-40psig for six resids and two recycles (Chevron, Citgo, Equilon, Marathon, Marathon Recycle, Petrobras, Suncor and Suncor Recycle) were determined. The predictions are good at 930ºF-15psig test conditions having R^2 values of 0.9 and 0.92 for coke and liquids respectively. Whereas at 900ºF-40psig the R^2 values for the coke and liquid yields are 0.6 and 0.65. At 900ºF-40psig, the prediction was not good because the data points of Marathon recycle, Equilon and Suncor recycle were high when compared to the remaining five resids. More straight recycles will be helpful to see the combined effect of asphaltenes and asphaltic resins on product yields.

1. *Micro-coker correlations*

Correlations were developed for the micro-coker product yields for the six in-houe resids (Chevron, Citgo, Equilon, Marathon, Petrobras, and Suncor) including mixed (Marathon + Marathon Recycle, Suncor + Suncor Recycle), pure recycle as feed (Marathon and Suncor Recycles) and three new resids (Cerro Negro, Heavy Canadian and Rose Pitch). The three new resids along with the recycle resids did not correlate well with the feedstock Micro Carbon Residue (MCR), as previous studies with the micro-coker had indicated. Moreover, Asphaltenes did not show good correlation for the recycle resids. An overall model could not be developed using MCR or Asphaltenes as a feedstock parameter. Therefore, the overall model was developed using Asphaltenes plus Asphaltic Resins which showed good correlation for the three new resids and recycle resids when compared with MCR and Asphaltenes alone. These correlations were developed for all the six resids including mixed, recycle and three new resids. Good adjusted R^2 values (about 0.82) were seen for the coke and liquid yields when compared to the liquid sub-product yields. The sign of the coefficients showed the expected trends for the operating conditions: temperature and pressure.

2. *Relation between micro-coker model and pilot unit/refinery results*

The purpose of the micro-coker experimental program is to develop a screening tool that can predict coker yields for industry-scale conditions with a short, simple test. In order to do this, the micro-coker results need to be scaled up or correlated with the pilot unit results, which already have been shown in our previous work to match well with refinery conditions.

The micro-coker results correlated best with the middle reactor temperature. For refinery applications, however, a correlation with overhead temperature would be most practical, since this temperature is frequently the only coke drum temperature that is accurately known. Unfortunately, the micro-coker overhead temperature does not correspond to the overhead temperature seen in the pilot unit or the refinery. It reads much lower, for the same feed temperature, than the pilot overhead temperature does due to the purge stream of helium that was introduced at the top of the micro-coker.

To match the model prediction to the pilot yields, correction factors were introduced as previously discusseed in the thesis by Tomas Zambrano. The coke and liquid yields were adjusted by multiplying the results by constant factors and the gas yields by remaining percent left in overall material balance.

The constant factors multiplied to the results of the correlations were calculated by using the slope of trend line with zero intercept for predicted vs. experimental data. Figure 35 shows a comparison between predicted yields by adjusted correlations and experimental yields for the pilot unit.

A similar method was used to adjust the predicted yields of the micro correlations for predicting pilot unit yields. The equations were corrected such that the summation of liquid sub-products gives the adjusted liquid yields.

The comparison between predicted yields by adjusted correlations and experimental yields for pilot unit are shown in Figure 36. The data points for the model prediction using corrected new screening model for the pilot unit were more close to the model=data line when compared to the prediction used by the Zambrano model.

The micro-correlations now predict product yields that are more meaningful to the pilot unit and hence to the industrial yields. The experimental yields for the pilot unit were run at the feed temperatures of 900°F and 930°F. The adjusted correlations should therefore be used between these feed temperatures.

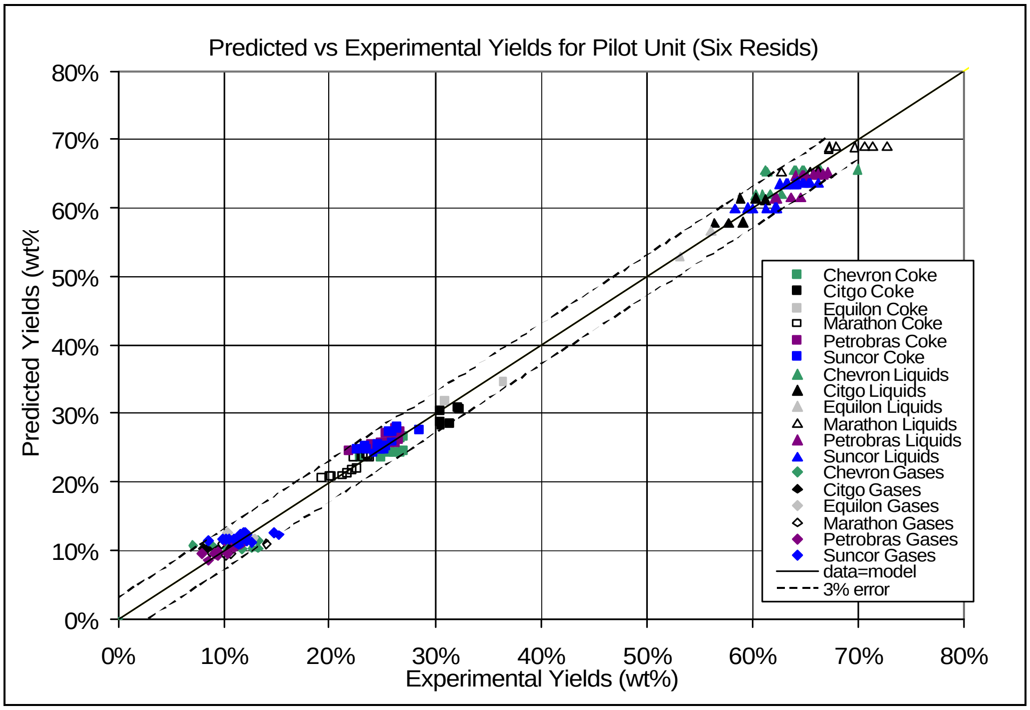


Figure 35 Predicted vs. Experimental yields for Pilot Unit after Correction

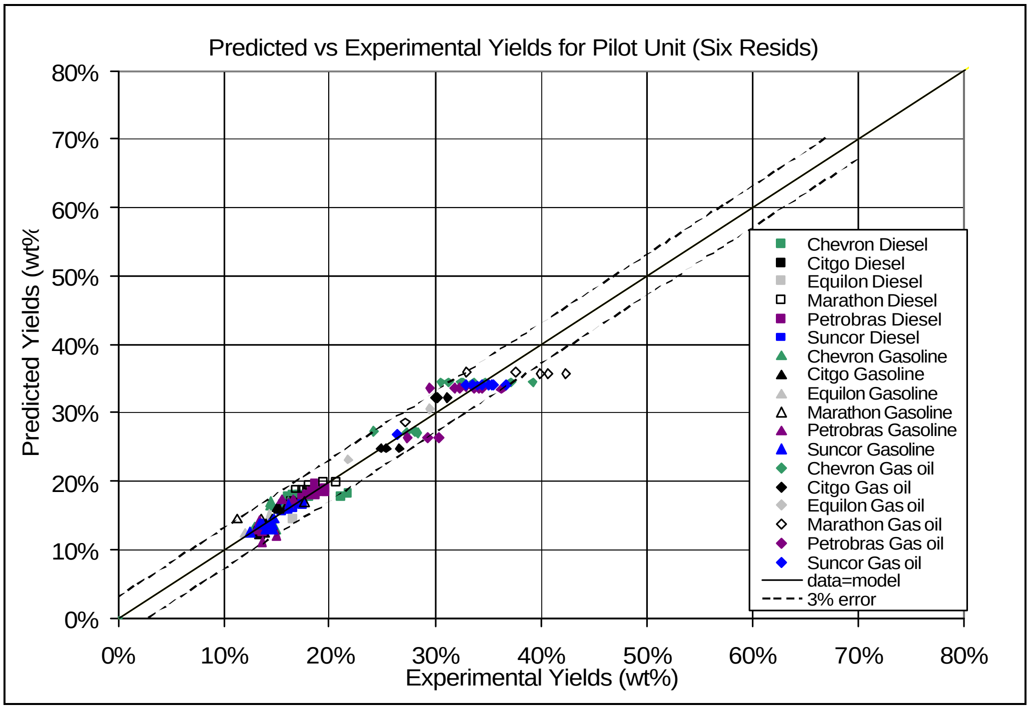


Figure 36 Predicted vs. Experimental yields for Pilot Unit after Correction

11. Batch Reactor Studies

A. *Parametric Tests*

Forty-eight batch reactor tests have been completed to date in the new facility using all resids. Operating conditions include 1400ºF(medium heating) and 1700ºF(high heating) element temperatures and 15, 40 and 60 psig reactor pressures. Runs operated with an element temperature of 1400ºF generally have a 2-4ºF/min increase in the internal temperature at one-inch from the bottom. Runs operated with an element temperature of 1700ºF generally have a 4+ºF/min increase. The un-normalized yields for the batch reactor tests are listed in Table 14. The operating conditions and heating rates can also be found in both tables. The heating rate is calculated as the time it takes to increase the one-inch internal temperature from 775ºF to 930ºF.

Table 14 - Batch Reactor - Un-normalized Yields with Internal Sample Weights

		CONDITIONS			
Test Number	**Date**	**Element (ºF)**	**P (psig)**	**Heat Rate (ºF/min)**	**% Total%**
CHVBR-1	4/5/2004	1700	40	7.0	96.36%
CHVBR-2	4/12/2004	1700	40	6.0	99.73%
CHVBR-3	6/14/2004	1700	15	7.8	96.39%
CITBR-1	9/17/2004	1700	60	5.5	97.03%
CITBR-2	9/20/2004	1700	40	3.4	94.93%
EQBR-2	6/16/2004	1700	15	5.5	102.74%
EQBR-3	6/21/2004	1700	40	5.7	99.25%
PETBR-1-SD	10/15/2003	1400	40	2.3	99.48%
PETBR-2-SD	10/17/2003	1400	40	3.1	101.97%
PETBR-3-SD	11/3/2003	1400	40	1.6	101.59%
PETBR-6-SD	12/17/2003	1700	40	4.7	100.47%
PETBR-7-SD	12/22/2003	1700	40	5.5	101.24%
PETBR-8-SD	1/7/2004	1700	40	4.6	100.68%
PETBR-9	2/19/2004	1400	15	3.3	98.60%
PETBR-10	2/27/2004	1700	15	5.5	98.34%
SUNBR-1	3/3/2004	1400	15	2.5	97.07%
SUNBR-2	3/8/2004	1700	15	6.5	97.91%
SUNBR-3	3/10/2004	1400	40	3.2	102.23%
SUNBR-4	3/15/2004	1700	40	6.2	102.63%
EMHCBR-1	8/4/2004	1700	15	9.7	97.11%
EMHCBR-2	8/6/2004	1400	15	4.2	98.92%
EMHCBR-3	8/9/2004	1400	40	5.0	99.10%
EMHCBR-4	8/11/2004	1700	40	7.4	100.40%
EMHCBR-5	8/23/2004	1400	60	3.4	99.59%
EMHCBR-6	8/25/2004	1700	60	7.8	95.84%
RPBR-1	8/13/2004	1400	40	2.7	100.04%
RPBR-2	8/16/2004	1700	40	6.5	97.40%
RPBR-3	8/18/2004	1400	15	3.7	99.41%
RPBR-4	8/19/2004	1700	15	7.4	95.62%
RPBR-5	9/1/2004	1700	60	5.2	98.94%
RPBR-6	9/3/2004	1400	60	3.2	100.59%

B. HEATING RATES

All runs are classified by operating pressure and heating rate. The three classifications of runs by heating rate are low, medium and high. The heating rates are calculated by determining the time it takes for the internal temperature at one-inch from the bottom of the liner to increase from 775ºF to 930ºF. The low heating rate runs are those run in the old facility. They generally saw an increase of the internal temperature at a rate of less than 2ºF/min. The new facility runs are classified by the element temperature set point. The two setting used are 1400ºF and 1700ºF. The 1400ºF element temperature runs, depending on the resid, normally saw an increase in the temperature at a rate of 2-4ºF/min. The number of runs outside this range are limited but one case saw the temperature rise at a rate as fast as 5ºF/min(EMHCBR-3). The 1700ºF element runs had heating rates in excess of 4ºF/min. The maximum heating rate for a high heating rate run was a 15 psig, Heavy Canadian run(EMHCBR-1).

The fluctuations in yields have been calculated in Table 15. The values have been separated by operating pressure for each resid and show the direction of the fluctuation as the temperature of the heating elements was changed from 1400ºF to 1700ºF. In most cases, as the temperature was increased, the coke yields decreased and the liquid yields increased. The gas yield fluctuations were resid dependent.

Table 15 – Batch Reactor – Yield Fluctuations Due to Heating Rate

	Pressure	15 psig			40 psig			60 psig		
		Coke	Liq	Gas	Coke	Liq	Gas	Coke	Liq	Gas
Chevron (No 1400's)	1400 to 1700	*****	*****	*****	*****	*****	*****	*****	*****	*****
Citgo (No 1400's)	1400 to 1700	*****	*****	*****	*****	*****	*****	*****	*****	*****
Equilon (No 1400's)	1400 to 1700	*****	*****	*****	*****	*****	*****	*****	*****	*****
Petrobras	1400 to 1700	-1.90%	-0.73%	2.63%	-3.57%	3.89%	-0.32%	*****	*****	*****
Suncor	1400 to 1700	-1.53%	-0.16%	1.69%	-3.20%	0.83%	2.37%	*****	*****	*****
Heavy Can.	1400 to 1700	-2.69%	1.51%	1.18%	-3.67%	2.61%	1.06%	-0.62%	0.13%	0.50%
Rose Pitch	1400 to 1700	-3.85%	6.24%	-2.38%	-3.78%	5.77%	-1.99%	-1.96%	2.60%	-0.64%
*** No runs for comparison										

The minimum, maximum and average heating rates have been calculated for each resid at each of the two element set points and are listed in Table 16 and Table 17. Table 16 includes all resids by combining all operating pressures and for the 15 psig runs. Table 17 includes all resid runs at 40 and 60 psig. Under all operating pressures and heater element settings, Heavy Canadian was the fastest heating resid.

Table 16 - Batch Reactor Testing – Heating Rate Effects(All & 15 psig)

All Runs			Low Rate (1400ºF)	High Rate (1700ºF)
	Chevron (3 runs)	max	*****	7.8
		min	*****	6.0
		avg	*****	6.9
	Citgo (3 runs)	max	*****	5.7
		min	*****	3.4
		avg	*****	4.9
	Equilon (2 runs)	max	3.2	5.7
		min	3.2	5.5
		avg	3.2	5.6
	Petrobras (8 runs)	max	3.3	5.5
		min	1.6	4.6
		avg	2.6	5.1
	Suncor (4 runs)	max	3.2	6.5
		min	2.5	6.2
		avg	2.8	6.3
	Heavy Can. (6 runs)	max	5.0	9.7
		min	3.4	7.4
		avg	4.2	8.3
	Rose Pitch (6 runs)	max	3.7	7.4
		min	2.7	5.2
		avg	3.2	6.3
	* No runs made			

15 psig			Low Rate (1400ºF)	High Rate (1700ºF)
	Chevron (1 run)	max	*****	7.8
		min	*****	7.8
		avg	*****	7.8
	Citgo (1 run)	max	*****	5.7
		min	*****	5.7
		avg	*****	5.7
	Equilon (1 run)	max	*****	5.5
		min	*****	5.5
		avg	*****	5.5
	Petrobras (2 runs)	max	3.3	5.5
		min	3.3	5.5
		avg	3.3	5.5
	Suncor (2 runs)	max	2.5	6.5
		min	2.5	6.5
		avg	2.5	6.5
	Heavy Can. (2 runs)	max	4.2	9.7
		min	4.2	9.7
		avg	4.2	9.7
	Rose Pitch (2 runs)	max	3.7	7.4
		min	3.7	7.4
		avg	3.7	7.4
	* No runs made			

Table 17 - Batch Reactor Testing – Heating Rate Effects(40 & 60 psig)

40 psig			Low Rate (1400ºF)	High Rate (1700ºF)
	Chevron (1 run)	max	*****	7.0
		min	*****	6.0
		avg	*****	6.5
	Citgo (1 run)	max	*****	3.4
		min	*****	3.4
		avg	*****	3.4
	Equilon (1 run)	max	*****	5.7
		min	*****	5.7
		avg	*****	5.7
	Petrobras (2 runs)	max	3.1	5.5
		min	1.6	4.6
		avg	2.3	4.9
	Suncor (2 runs)	max	3.2	6.2
		min	3.2	6.2
		avg	3.2	6.2
	Heavy Can. (2 runs)	max	5.0	7.4
		min	5.0	7.4
		avg	5.0	7.4
	Rose Pitch (2 runs)	max	2.7	6.5
		min	2.7	6.5
		avg	2.7	6.5
	* No runs made			

60 psig			Low Rate (1400ºF)	High Rate (1700ºF)
	Chevron (0 runs)	max	*****	*****
		min	*****	*****
		avg	*****	*****
	Citgo (1 run)	max	*****	5.5
		min	*****	5.5
		avg	*****	5.5
	Equilon (0 runs)	max	*****	*****
		min	*****	*****
		avg	*****	*****
	Petrobras (0 runs)	max	*****	*****
		min	*****	*****
		avg	*****	*****
	Suncor (0 runs)	max	*****	*****
		min	*****	*****
		avg	*****	*****
	Heavy Can. (2 runs)	max	3.4	7.8
		min	3.4	7.8
		avg	3.4	7.8
	Rose Pitch (2 runs)	max	3.2	5.2
		min	3.2	5.2
		avg	3.2	5.2
	* No runs made			

C. PRESSURE EFFECTS

Three operating pressures have been used to date – 15, 40 and 60 psig. The fluctuations due to pressure of each of the yields are organized by resid and heating rate in Table 18. In nearly every case, as the pressure in increased from 15 to 40 psig or 40 to 60 psig for a set element temperature set point, the coke yields increased, the liquid yields decreased and the gas yields increased. In the cases where these trends were not followed, the changes can be explained by analyzing the temperature profiles differences between the runs. The most dramatic changes in yields were when the pressure was increased from 15 to 40 psig. In the majority of the resids, the coke yields increased from 2 to 4 percent and the liquids decreased from 3 to 5 percent. The fluctuations as the pressure was increased from 40 to 60 psig were not as dramatic. This is not the trend for all resids, the Heavy Canadian resid saw an increase in the coke yields of 3.5 percent and a decrease in the liquid yields of 3.2 percent for the 40 to 60 psig increase.

Table 18 - Yield Fluctuations Due to Pressure

	Pressure	1400			1700		
		Coke	Liq	Gas	Coke	Liq	Gas
Chevron	15 to 40	*****	*****	*****	3.73%	-6.55%	2.82%
Citgo	15 to 40	*****	*****	*****	*****	*****	*****
	40 to 60	*****	*****	*****	-0.31%	-2.91%	3.22%
Equilon	15 to 40	*****	*****	*****	3.82%	-5.88%	2.07%
Petrobras	15 to 40	4.01%	-5.09%	1.08%	2.35%	-0.47%	-1.87%
Suncor	15 to 40	2.44%	-5.60%	3.16%	0.76%	-4.61%	3.84%
Heavy Can.	15 to 40	2.37%	-2.91%	0.54%	1.40%	-1.81%	0.41%
	40 to 60	0.52%	-0.73%	0.21%	3.56%	-3.21%	-0.35%
Rose Pitch	15 to 40	3.20%	-3.37%	0.16%	3.28%	-3.83%	0.56%
	40 to 60	-0.48%	-0.40%	0.88%	1.33%	-3.56%	2.23%

*** No runs for comparison

D. FUTURE WORK

Future tests to be completed are all runs listed in Table 19 and Table 20 that are shaded in gray. Any runs that do not have acceptable data at this time may be added to the future test matrix as re-runs. Future runs may also include higher pressure runs, 80 psig or higher – this is dependent on the maximum rated working pressure of the reactor.

A more in-depth look at the liquid production with respect to time and temperature will need to be done. This will give much greater detail to the effects of the heating rate and operating pressure on the system. This evaluation will include boiling point distributions for each of the heavy and light liquid cuts.

Analysis of the internal reactor samples will also need to be completed. The C7, Toluene and Quinoline insolubles and the SARA analysis have been started. They will take a few months of work to complete the entire matrix of samples to be analyzed. This data will be reviewed for correlating coke development and deposition versus temperature and time.

Table 19 - Batch Test Matix - Original Resids

Resid	Pressure									Total
	15			40			60			
	*Heating Rate			*Heating Rate			*Heating Rate			
	Low	Med	High	Low	Med	High	Low	Med	High	
Chevron			1	2		2			1	6
Citgo			1	1		1			1	4
Equilon			1	4		1			1	7
Marathon			1	11		1			1	14
Petrobras		1	1	7	3	3		1	1	17
Suncor		1	1	4	1	1		1	1	10
Total										58
Remaining										15

	Low	Med	High
*Element Temp. Setting(ºF) - New Runs	1200	1400	1700
Heating Rate Range(ºF/min)	0 to 2	2 to 4	4+

Table 20 - Batch Test Matix - New Resids

Resid	Pressure									Total
	15			40			60			
	*Heating Rate			*Heating Rate			*Heating Rate			
	Low	Med	High	Low	Med	High	Low	Med	High	
Cerro Negro		2	1		1	1		1	1	7
Canadian		1	1		1	1		1	1	6
Rose Pitch		1	1		1	1		1	1	6
Recycle 1										0
Recycle 2										0
Recycle 3										0
Remaining										19

	Low	Med	High
*Element Temp. Setting(ºF) - New Runs	1200	1400	1700
Heating Rate Range(ºF/min)	0 to 2	2 to 4	4+

12. Pilot Unit Studies

A. FOAMING STUDIES

1. *Recycle runs with Suncor and Marathon resids*

Table 21 gives the pilot unit foaming studies data for Suncor runs with recycle. Suncor 6, 14, 15 (5% RC), 16 (10% RC) runs were carried out at a temperature of 900 ^{o}F, a pressure of 15 psig and a feed rate of 2400 gm/hr. Suncor 17 (15 % RC) was run at industry conditions, at a temperature of 928 ^{o}F, a pressure of 38 psig and a feed rate of 2400 gm/hr. Figure 37 shows the comparison of furnace skin temperatures for these runs. It is observed that with an increase in recycle, the heat input required increased. It is observed that with an increase in the amount of recycle the density of the coke formed decreases. Suncor 18 (15 % RC) and 19 (5% RC) runs were carried out at industry conditions, at a temperature of 928 ^{o}F, a pressure of 38 psig and a feed rate of 3600 gm/hr. At these conditions recycle appears to have little effect on density. Suncor 28 (100% RC) was run at a temperature of 930 ^{o}F, a pressure of 40 psig and a feed rate of 2400 gm/hr. Suncor runs with and without recycle made shot coke irrespective of operating conditions. The coke yields were in the range of 24.5 – 27%, the liquid yields were in the range of 61.5 – 63%, and the gases were in the range of 10 to 12%. There was not much difference observed in the overall SimDis data with the increase in recycle at 900 ^{o}F and 15 psig. For the higher pressure and temperature run, Suncor 17, an increase in gasoline and a decrease in gas oil was seen. There was around 6% increase in coke and 6% decrease in liquid with 100% recycle for Suncor run 28.

Table 21 – Pilot unit foaming studies data for Suncor runs

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (cc)	Actual AF used	# of inj	First Foam	Re-appearance	?T	Steam Strip
		^{0}F	psig	gm/hr			Defoamer(AF+D)	(cc)		Front(min	of Foam(min)	min	Behaviour
SUNC 14	9/11/2003	900	15	2400	100,000 cSt (0.3 AF/ 70 D)	0	112	0.49	11	25.5	36	11	Average/Void
SUNC 15 (5%RC)	9/17/2003	900	15	2400	100,000 cSt (0.3 AF/ 70 D)	0	80	0.35	8	42	78	36	Good
SUNC 16(10% RC)	9/25/2003	900	15	2400	100,000 cSt (0.3 AF/ 70 D)	0	90	0.39	9	31.5	66	35	Good
SUNC 17 (15 % RC)	10/1/2003	928	38	2400	100,000 cSt (0.3 AF/ 70 D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
SUNC 18 (15% RC)	10/6/2003	928	38	3600	100,000 cSt (0.3 AF/ 70 D)	0	60	0.26	5	15	30	15	Good
SUNC 19 (5% RC)	11/11/2003	928	38	3600	100,000 cSt (0.3 AF/ 70 D)	0	20	19.91	2	22.5	37.5	15	Good
SUNC 28 (100% RC)	3/24/2004	930	40	2400	100,000 cSt (0.3 AF/ 70 D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good

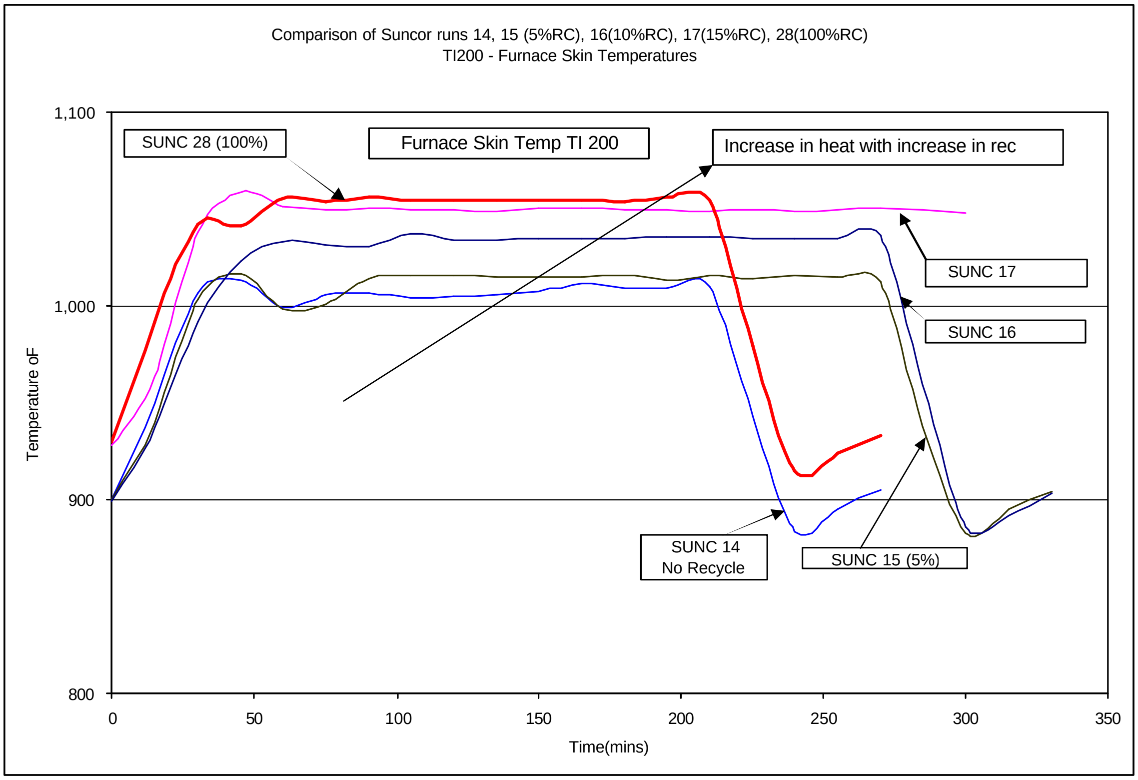


Figure 37 – Furnace Skin temperature comparisons for Suncor runs

The second phase of the Marathon runs were carried out during the last quarter of 2003 and continued into the first quarter of 2004. Table 22 shows the foaming studies data for the Marathon runs. Marathon 8, 9 (5%RC) and 10 (10%RC) runs were carried at a temperature of 900 ^{o}F, a pressure of 15 psig and a feed rate of 2400 gm/hr. During these runs, foam was not observed and hence antifoam was not injected. Figure 38 shows the temperature profile for these runs. It is observed that with the addition of recycle in the feed, the amount of heat required to attain the desired run temperature increases. The runs with recycle produced a coke with a slightly lower density compared to runs with no recycle, although for all practical purposes not much change was seen. For the 3600 gm/hr runs little change in density with an increase in recycle was observed as well. It was noted that the mass of bed was lifted during the steam strip process. The coke yields were in the range of 20 – 22%, the liquid yields were in the range of 68–70%, and the gases were in the range of 9 to 11%. With an increase in recycle concentration, an increase in gasoline was seen. There was not much difference observed in diesel and gas oils. Marathon 17 (100%RC) was run at a temperature of 930 ^{o}F, a pressure of 40 psig and a feed rate of 2400 gm/hr. With 100% recycle and at higher temperature and pressure, it is observed that Marathon has the highest liquid yields and lowest coke yields. The 100% recycle for the Marathon resid produced more liquids whereas with the Suncor resid at 100% recycle more coke was produced. This can be attributed to higher asphaltene content property of the resid. The Suncor resid has almost twice the asphaltene content as the Marathon resid.

Table 22 – Pilot unit foaming studies data for Marathon runs

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (cc)	Actual AF used	# of inj	First Foam	Re-appearance	?T	Steam Strip
		°F	psig	gm/hr			Defoamer(AF+D)	(cc)		Front(min	of Foam(min)	min	Behaviour
MARA 8 PUAFI	11/18/2003	900	15	2400	100,000 cSt (0.3 ml AF/ 70 ml D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 9 (5%RC)	11/21/2003	900	15	2400	100,000 cSt (0.3 ml AF/ 70 ml D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 10 (10%RC)	12/2/2003	900	15	2400	100,000 cSt (0.3 ml AF/ 70 ml D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 11 (5%RC)	12/19/2003	900	15	3600	100,000 cSt (0.3 ml AF/ 70 ml D)	O+F	155	0.68	5	169	180	11	Average
MARA 12 (10%RC)	1/8/2004	900	15	3600	100,000 cSt (0.3 ml AF/ 70 ml D)	0	205	0.89	17	8	18	10	Average
MARA 17 (100% RC)	3/26/2004	930	40	2400	100,000 cSt (3 ml AF/ 70 ml D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good

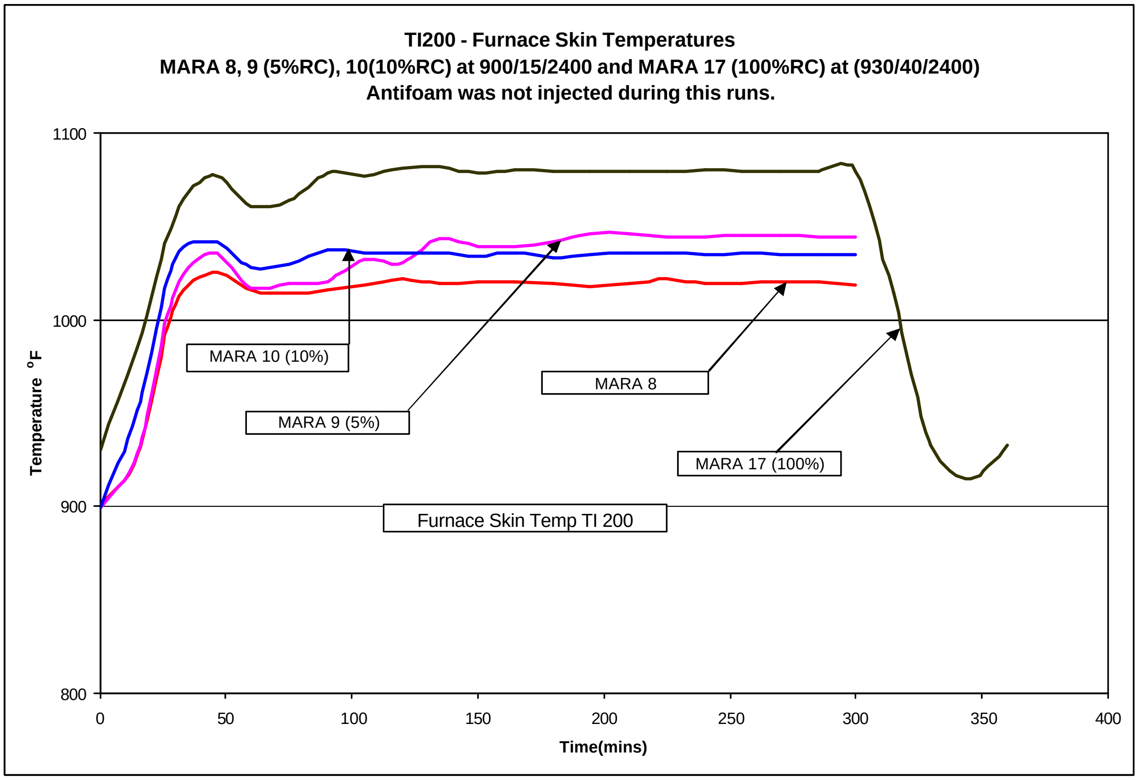


Figure 38 – Temperature Profile for Marathon 8, 9 (5%RC) and 10 (10%RC) runs

2. *Foaming Tendencies for Suncor Recycle Runs*

Not much foaming was observed with 5% recycle. At a drum height of 30 inches, some collapse of foam was observed. It was observed in that after several antifoam injections, the time for re-appearance of foam is longer compared to the initial appearance time. In other words, the time of foam suppression after antifoam injection was 1, 3, 7, 10 and 10 minutes, thereby increasing with each injection. Less foaming was observed with 15% recycle hence a total of 5 injections were made of low concentration antifoam. Suncor run 28 with 100% recycle was carried out at a temperature of 930 °F, a pressure of 15 psig and a feed rate of 2400 gm/hr. Foaming was not observed during this run and hence antifoam was not injected. In general the time to rise of foam for the Suncor recycle runs is usually in the range 12 – 15 minutes. The time of collapse of foam at different drum heights is usually in the range of 35 – 40 minutes. Hence it can be said that Suncor resid with recycle mixed in the feed shows little to moderate foaming tendencies.

3. *Foaming Tendencies for Marathon Recycle Runs*

The Marathon runs 8, 9(5% RC) and 10(10%RC) were carried out at a temperature of 900 ^oF, a pressure of 15 psig and a feed rate of 2400 gm/hr. Under these operating conditions, the Marathon resid did not foam and hence antifoam was not injected. Foam was not observed during these runs. The Marathon 11 (5%RC) and 12 (10%RC) runs were carried out at a temperature of 900 ^oF, a pressure of 15 psig and a feed rate of 3600 gm/hr. During these runs, foam was observed and hence 100,000 cSt antifoam with a (0.3/70) concentration was injected through the overhead on an as needed basis. For these runs, little change in density was seen with the addition of recycle. It can be observed that once the foam rose beyond the 2/3rd level in the coke drum, it became very difficult to control. Note that with continuous injection of antifoam during the end of the Marathon 11(5%RC) run, the foam rose and collapsed through out the injection period. It is interesting to note that during run 11, antifoam was not injected during the first 3 hours of the run and hence the density continued to decrease from bottom to top of the drum. There is no clear indication of coke density and the bubbly liquid and foam layers until the 225 minute mark when the antifoam injection collapsed the bubbly liquid layer. The Marathon 12 run used continuous antifoam injection. A total amount of 205 cc was injected. The density versus time plot for the last 2 hours of the run shows the density through out the drum was approximately 0.6 gm/cc. This antifoam injection procedure made a much more uniform coke bed than what was made in Marathon run 11. It is also interesting to note that during the Marathon 11 run, there was foam at the 50 inch height level inside the drum, which is approximately at the 2/3rd's level in the drum. Although antifoam was injected late into the run, a sustained injection of antifoam made the run progress 70 more minutes, thereby increasing the volume of coke bed produced by as much as 30% at the end of the run. Marathon run 17 with 100% recycle was carried out at a temperature of 930 ^oF, a pressure of 15 psig and a feed rate of 2400 gm/hr. Foaming did not occur during this run and hence antifoam was not injected. Marathon resid at low feed rates of 2400 gm/hr with or without recycle did not show any foaming tendencies. Table 23 gives the foaming tendencies data for the Marathon runs. It shows the time to rise and collapse of foam during antifoam injection times at different heights in the coke drum. Among all the resids the Marathon resid foams the least and makes sponge coke irrespective of operating conditions. Table 24 gives a summary of recycle runs for thr Marathon and Suncor resids.

Table 23 – Foaming tendencies data for Marathon runs

Run #	Feed Rate	Drum Height	Time to Rise	Time to Collapse	Re-appearance of Foam	?T
	gm/hr	inches	mins into the run	mins into the run	mins into the run	min
MARA 8	2400	No foam was observed and hence antifoam was not injected.				
MARA 9(5%RC)	2400	No foam was observed and hence antifoam was not injected.				
MARA 10(10%RC)	2400	No foam was observed and hence antifoam was not injected.				
MARA 11(5%RC)	3600	50	169.5	228		58.5
		55	181	183	184.5	2
		60	180	184.5	195	4.5
MARA 12(10%RC)	3600	20	15	57	61.5	42
		25	18	20	36	2
		30	21	28	30	7
		35	160.5	165		4.5
MARA 17 (100% RC)	2400	No foam was observed and hence antifoam was not injected.				

Table 24 – Summary of recycle runs for Marathon and Suncor resids

Summary of Recyle Runs			
Marathon Resid		Suncor Resid	
Morphology	Produced sponge coke, not much difference in coke densities with increase in recycle concetration. coke density usually in the range 0.58-0.61 gms/cc	Morphology	Produced shot coke, with increase in recycle concetration we observed that the density of the coke formed decreases unlike Marathon resid.
Furnace Effects	With increase in recycle concetration, it required more heat input.	Furnace Effects	With increase in recycle concetration, it required more heat input.
Foaming Tendencies	At 2400 gms/hr along with recycle, foaming was not observed in Marathon runs. But at higher feed rate of 3600 gms/hr, Marathon runs with 5 and 10% recycle foamed badly and did require lot of antifoam to control it.	Foaming Tendencies	Not much difference in foaming tendencies when recycle is used. The foam height was around 25 to 30 inches of drum height for most of the recycle runs. Generally it has shown medium foaming tendencies.
Steam Strip	Usually good, but at 3600 gms/hr along with recycle, a lift of coke bed was observed.	Steam Strip	Good steam strip behaviour with tendency to make voids.
Suggestions	Running a 100% recycle at 3600 gms/hr to observe foaming tendencies. Using continuous injection of antifoam to control foaming.	Suggestions	Comparing the recycle yields with Micro coker to obtain a correlation. Using a feedline injection technique for future Suncor recycle runs to observe the effect on morphology.

4. *Superficial Velocity Studies*

These tests were conducted to understand the effects of superficial velocity on morphology and foaming tendencies. Three resids were used for these tests namely Marathon, Suncor and Chevron.

5. *Suncor Superficial Velocity Runs*

The Suncor resid makes shot coke irrespective of operating conditions. It has shown moderate foaming tendencies compared to other resids. Suncor test runs were carried out at different feed rates to analyze the foaming tendencies and to study the morphology of the coke formed. Table 25 gives the foaming studies data for the Suncor superficial velocity tests.

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (cc)	Actual AF used	# of inj	First Foam	Re-appearance	?T	Steam Strip
		^{0}F	psig	gm/hr			Defoamer(AF+D)	(cc)		Front(min	of Foam(min)	min	Behaviour
SUNC 1 PUAFI	2/25/2002	930	15	2400	100,000 cSt(5% AF in sun diesel)	0	18	0.9	3	30	60	30	Good
SUNC 20 PUAFV	2/5/2004	930	15	1200	100,000 cSt (0.3 AF/ 70 D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
SUNC 10 PUAFC	7/17/2002	930	15	3600	100,000 cSt (30 AF/ 70 D)	0	48.2	14.46	C	24	38	14	Good
SUNC 25 PUAFV	3/4/2004	930	15	4800	100,000 cSt (0.3 AF/ 70 D)	0	280	1.22	6	15	25	10	Good
					100,000 cSt (30 AF/ 70 D)	0	20	0.84	1				
SUNC 14 PUAFI	9/11/2003	900	15	2400	100,000 cSt (0.3 AF/ 70 D)	0	112	0.49	11	25.5	36	11	Average/Void
SUNC 22 PUAFV	2/17/2004	900	15	3600	100,000 cSt (0.3 AF/ 70 D)	0	205	0.89	9	10	18	8	Good
SUNC 7 PUAFI	5/23/2002	900	40	2400	100,000 cSt (0.3 AF/ 70 D)	0	No Foam was observed during this run, hence antifoam was not injected.						Good
SUNC 23 PUAFV	2/20/2004	900	40	3600	100,000 cSt (0.3 AF/ 70 D)	0	200	0.87	6	19.5	32	13	Good
SUNC 26 PUAFV	3/16/2004	930	40	4800	100,000 cSt (3 AF/ 70 D)	0	70	2.94	7	10.5	30	20	Good
SUNC 27 PUAFV	3/19/2004	930	40	6000	100,000 cSt (3 AF/ 70 D)	0	173	7.26	4	19.5	29	9.5	Good

Table 25: Suncor superficial velocity runs data.

Suncor runs 14 and 22 were carried out at a temperature of 900 ^{o}F, a pressure of 15 psig and at feed rates of 2400 gms/hr and 3600 gms/hr respectively. The Suncor resid starts foaming with a tall column of mass inside the drum and gradually increases in density with time. Also the formation of a void was seen at the end of the run. Little foaming was observed at a feed rate of 2400 gms/hr for Suncor resid. It was observed that at a higher feed rate of 3600 gms/hr, more foaming was seen compared to runs at lower feed rates. During the first hour, antifoam was injected in heavy doses and we see a rise and collapse of foam from 15 to 35 inches of drum height. Figure 39 shows the steam strip plots for these runs. It can be seen that run 14 made a void of 5 inches from 24 to 29 inches inside the drum and had a coke density of approximately 0.42 gm/cc. Suncor run 22 had a coke density of around 0.48 to 0.52 gm/cc at drum height of 20 inches. Above that drum height the coke was very dense with a density near to 0.95 gm/cc. The coke transformed to bonded shot.

Suncor runs 7 and 23 were carried out at a temperature of 900 ^{o}F, a pressure of 40 psig and at feed rates of 2400 gms/hr and 3600 gms/hr respectively. Suncor 7 was a five hour run whereas during Suncor run 23 due to high differential pressure, the run was stopped after 3.5 hours. Increasing the run pressure from 15 psig to 40 psig, resulted in no substantial increase in coke density. Antifoam was not injected in Suncor run 7 whereas a total amount of 200 cc of antifoam was injected overhead for Suncor run 23. No foam was observed during the Suncor 7 run. Heavy injections of antifoam were made during the first hour to collapse the foam. Continuous rise and collapse of foam was seen during this period.

Suncor runs 1, 10, 20 and 25 were carried out at a temperature of 930 °F, a pressure of 15 psig. The feed rate for each of these runs was different to understand the effect of superficial velocity. At a low feed rate of 1200 gms/hr, foaming did not occur and hence antifoam was not injected in Suncor run 20. The Suncor resid tends to make a very dense coke usually from 20 to 40 inches inside the drum. With increasing feed rate, we observe that the dense coke is formed higher in the drum. For a feed rate of 2400 gms/hr, little foaming was observed and hence antifoam was only injected 3 times overhead on an as needed basis. Suncor run 10 used continuous overhead injection of 100,000 cSt with a (30/70) concentration antifoam. The antifoam was injected at a rate of 0.2 ml/min throughout the run. The density of the coke formed was highest at 25 inches inside the drum. At 4800 gms/hr Suncor run 25 foamed badly during the first hour of the run. As needed overhead injection of the 100,000 cSt antifoam with a (0.3/70) concentration was used. A total of 280 cc of antifoam was injected during the first hour to control foaming. It can be seen that foam was observed as high as 55 inches inside the drum. This can be attributed to the higher feed rate, as at lower feed rates we observe foam usually at the 25 to 30 inches during the first hour. It continued to foam and hence to control foaming the antifoam concentration was increased to (3/70). Only one injection of 20 cc was made with this ten times higher concentration of antifoam. This injection controlled the foaming and no foam was observed later in the run. It has been observed that Suncor runs at higher feed rates of 3600 – 4800 gms/hr tend to develop a differential pressure inside the drum. Due to this build up of differential pressure, the runs were stopped well before five hours.

Suncor runs 26 and 27 were carried out at a temperature of 930 °F and a pressure of 40 psig. Run 26 was run at a feed rate of 4800 gm/hr and run 27 was run at a feed rate of 6000 gm/hr. The foaming studies data is shown in Table 25 for these runs. Run 26 produced a very dense coke from a drum height of 15 inches to 40 inches whereas run 27 produced the dense coke over the drum height of 20 to 45 inches. Run 27 also made a void of 5 inches at a drum height of 15 to 20 inches. Both runs used 100,000 cSt (3/70) concentration antifoam with as needed overhead injection. During run 27 at 6000 gm/hr, 173 ml of total antifoam with carrier was injected during the four injections. Run 26 used a total of 70 ml in its seven injections. It can be seen that run 27 foamed badly during the first hour compared to run 26. It was observed that these runs foamed badly during the transient phase. Injecting antifoam overhead usually controlled foaming. After the first 70 to 90 minutes, no foam was observed. Figure 40 and Figure 41 show the coke, bubbly liquid, and foam layers for these runs. As can be seen, foaming occurred during the transient phase only.

6. *Marathon Superficial Velocity Runs*

The Marathon resid makes sponge coke irrespective of operating conditions. It has shown minimal foaming tendencies compared to other resids. Marathon runs 2, 3, 4 and 13 were carried out at a temperature of 930 °F, a pressure of 15 psig and the feed rate was different for each run. During the runs with a feed rate of 1200, 2400 and 3600 gms/hr, no foam was observed and hence antifoam was not injected. During the Marathon 4 run with a feed rate of 4800 gms/hr, foaming was observed and antifoam with a higher concentration of 100,000 cSt (30/70) was injected through the feedline. A total amount of 17.7 cc antifoam was injected during this run. Due to the higher feed rate, i.e., higher superficial velocity, foaming occurred during this run and it foamed over thereby clogging the overhead lines. A total of 144.5 grams of coke was collected from the overhead lines. No foam was observed during the Marathon 13 run. At drum heights of 5 and 10 inches only, we saw a density of around 0.7 gms/hr. Due to the higher feed rate, foaming was observed during this run and the density at different drum heights fluctuated with time. During this run a 100,000 cSt antifoam with a (30/70) concentration was injected through the feedline on an as needed basis. Marathon runs 14, 7, 15 and 16 were carried out at a temperature of 930 °F, a pressure of 40 psig with different feed rates.

Table 26: Marathon superficial velocity runs data.

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (cc	Actual AF used	# of inj	First Foam	Re-appearance	?T	Steam Strip
		oF	psig	gm/hr			Defoamer(AF+D)	(cc)		Front(min	of Foam(min)	min	Behaviour
MARA 13 PUAFI-V	1/14/2004	930	15	1200	100,000 cSt (0.3 ml AF/ 70 ml D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 3 PUAFI-V	10/16/2002	930	15	2400	100,000 cSt (0.3 ml AF/ 70 ml D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 2 PUAFI-V	10/11/2002	930	15	3600	100,000 cSt (0.3 ml AF/ 70 ml D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 4 PUAFI-V	10/18/2002	930	15	4800	100,000 cSt (30 ml AF/ 70 ml D)	F	17.67	5.31	4	12	94.5	83	Good
MARA 14 PUAFI-V	1/21/2004	930	40	1200	100,000 cSt (0.3 ml AF/ 70 ml D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
MARA 7 PUAFI-V	11/12/2002	930	40	2400	100,000 cSt (0.3 ml AF/ 70 ml D)	O	No Foam was observed during this run, hence antifoam was not injected.						Average/Good
MARA 15 PUAFI-V	1/27/2004	930	40	3600	100,000 cSt (0.3 ml AF/ 70 ml D)	O	300	1.31	18	22.5	45	23	Good
MARA 16 PUAFI-V	1/30/2004	930	40	4800	100,000 cSt (0.3 ml AF/ 70 ml D)	O	199	0.87	5	15	20	5	Good

Marathon 15 and 16 runs were carried at a temperature of 930 ^{o}F, a pressure of 40 psig and at feed rates of 3600 gms/hr and 4800 gms/hr respectively. During these runs, foam was observed and hence 100,000 cSt antifoam with a (0.3/70) concentration was injected overhead on an as needed basis. Figure 42 shows the furnace skin temperature profile for the Marathon runs at a temperature of 930 ^{o}F and a pressure of 40 psig. As can be seen, with increasing feed rate, the heat input to the furnace increased. A total of 18 antifoam injections were made during the Marathon 15 run. 300 cc's of antifoam was injected overhead. Due to regular antifoam injections, the density was approximately 0.65 – 0.7 gm/cc throughout the drum. In Marathon run 16, a total of 199 cc's of antifoam was injected through overhead. During this run antifoam was injected in heavy doses during the first hour. A heavy dose of 110 cc's of antifoam was injected continuously which collapsed the foam completely. Although this run was at a higher feed rate of 4800 gms/hr, due to heavy injection of antifoam within the first hour, no foam was observed later in the run. A very dense coke was formed during the Marathon 10 run. The density of the coke at the 25 inches of height was higher compared to those observed at other drum heights. Hence it was very difficult to remove the coke from the drum.

7. *Yields comparison for Suncor and Marathon Superficial runs*

The highest liquid yields for both resids were obtained at operating conditions of 930 ^{o}F, a pressure of 15 psig and a feed rate of 2400 gm/hr. The Marathon resid produced more liquids whereas the Suncor resid produced more coke. The highest coke yield for the Suncor resid was obtained at operating conditions of 900 ^{o}F, a pressure of 40 psig and a feed rate of 2400 gm/hr. The Marathon resid produced the highest coke yield at operating conditions of 930 ^{o}F, a pressure of 40 psig and a feed rate of 3600 gm/hr. The simulated distillation data will be analyzed to observe the yields of diesel, gasoline and gas oils for these resids.

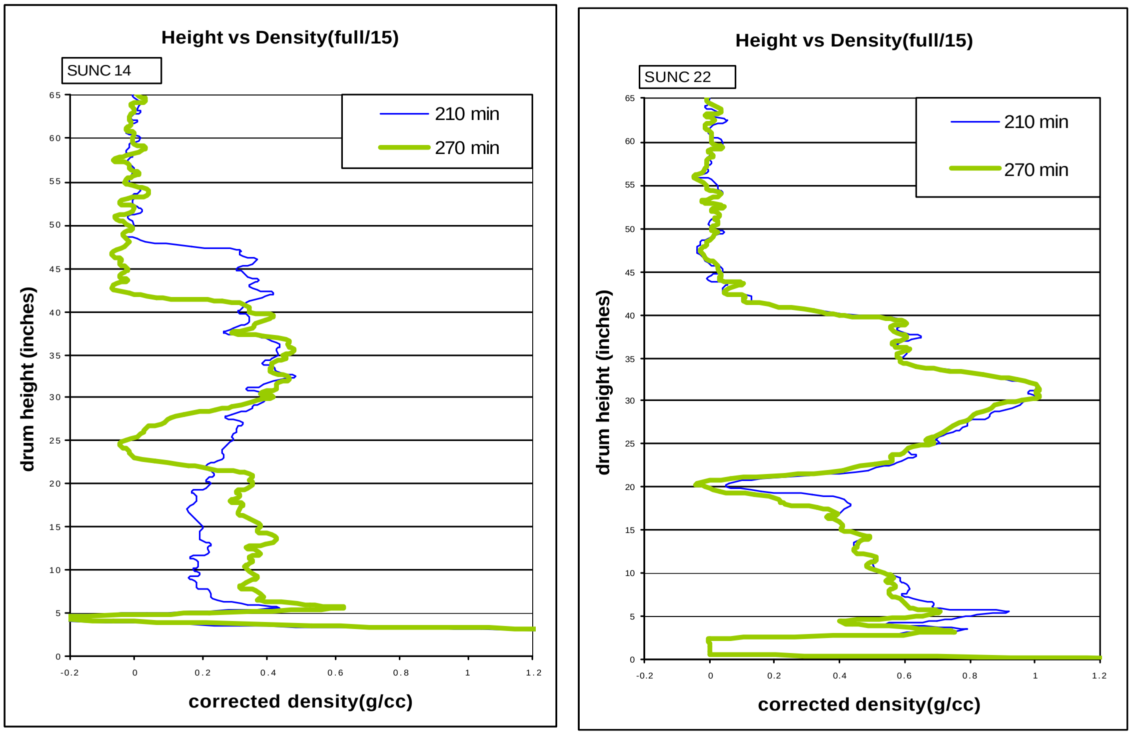


Figure 39 – Steam strip plots for Suncor runs 14 and 22

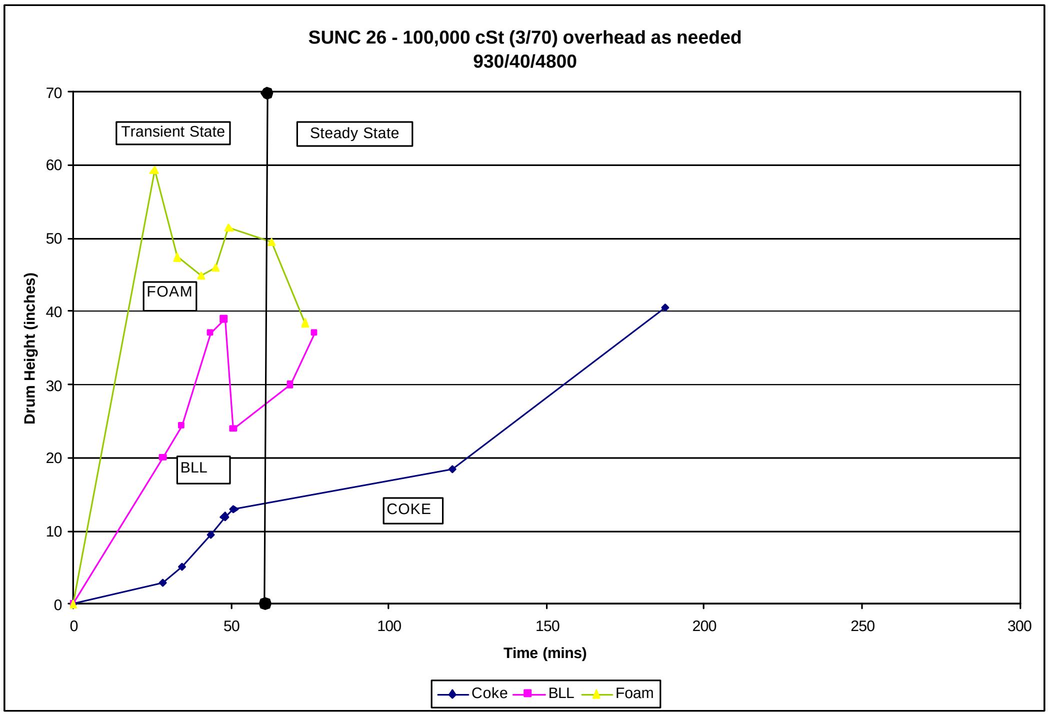


Figure 40 – Coke, BLL and Foam layer for Suncor run 26

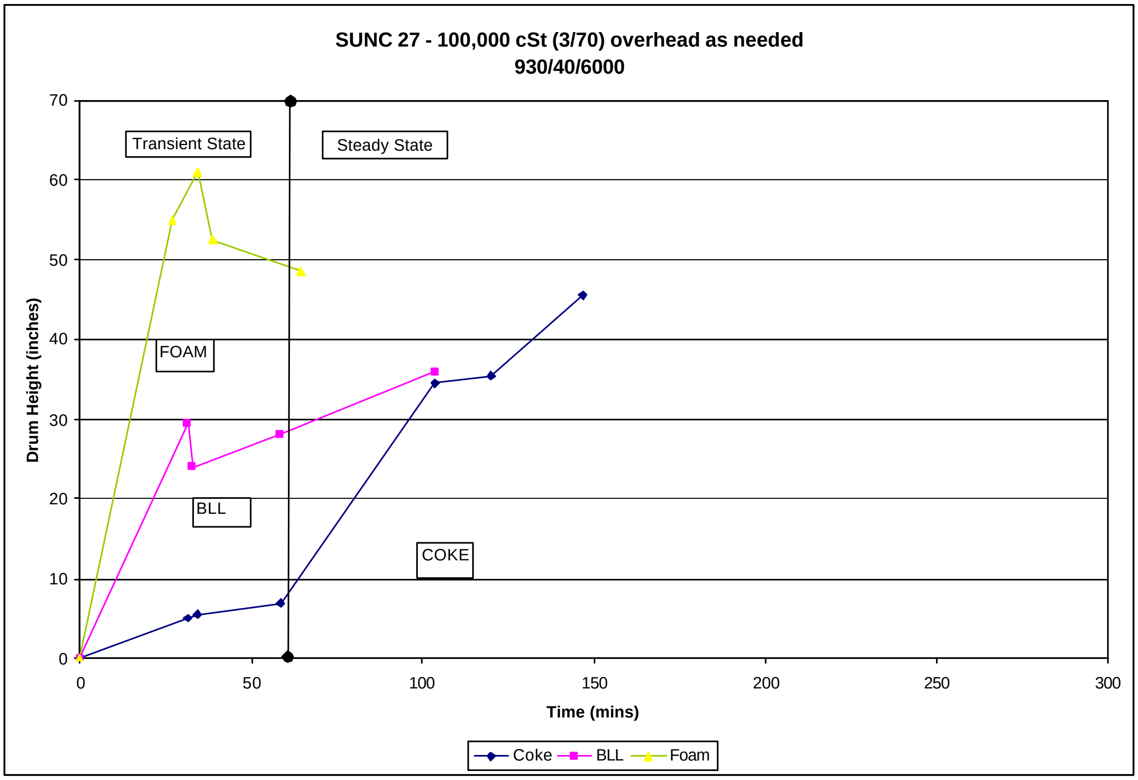


Figure 41 – Coke, BLL and Foam layer for Suncor run 27

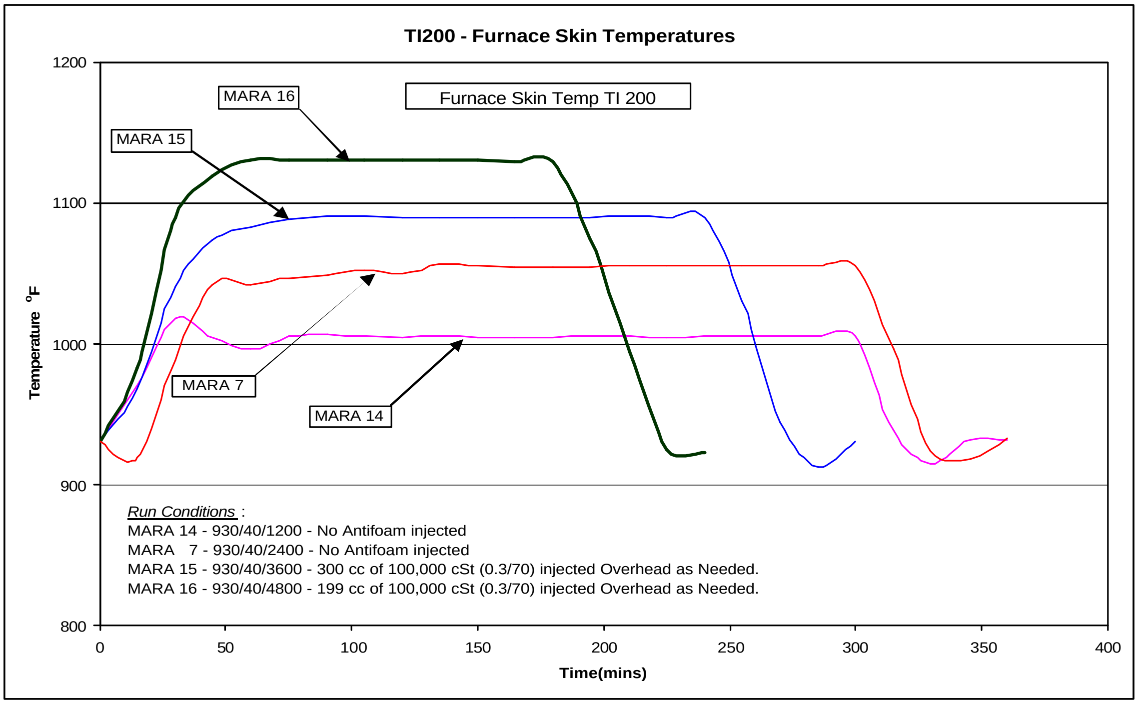


Figure 42 – Furnace skin temperature profile for Marathon runs

Table 27 – Summary of superficial velocity runs

Summary of Superficial Velocity Runs			
Marathon Resid		Suncor Resid	
Morphology	Marathon resid produces sponge coke irrespective of operating conditions. Coke density in the range of 0.57-0.62 gms/cc	Morphology	Suncor resid produces shot coke irrespective of operating conditions. Fat coke bed at 20 - 25 inches in the drum.Coke density in the range of 0.6-0.9gms/cc
Foaming Tendencies	Higher feed rate continuous injection of antifoam gives better control of foaming for Marathon resid Overall it has shown medium to least foaming tendecy Does not foam at lower feed rates of 1200-2400 gms/hr.	Foaming Tendencies	Foaming increased at higher feed rates. Usually foaming occurs during the transient phase only.A heavy dose of antifoam injected during the first hour controls foaming. Overall medium foaming tendencies.
Yields	Highest Coke yields at 930-40-3600, around 24%. Highest Liquid yields at 930-15-2400, around 72.70%.	Yields	Highest Coke yields at 900-40-2400, around 28.5%. Highest Liquid yields at 930-15-2400, around 67%.
Steam Strip	Good steam strip behavior, no loss of mass	Steam Strip	Average steam strip behavior tendency to make voids.
Suggestions	Future runs to include more higher feed rate. Continuous injection of antifoam gives better control Using recycle at higher feed rates.	Suggestions	Future runs to include more higher feed rate. Using a higher viscosity antifoam to observe control over foaming. Using recycle at higher feed rates.

8. *Parametric tests for EMCN (Exxon Mobil Cerro Negro) Resid*

The Cerro Negro resid was obtained from Exxon Mobil during the month of March, 2004. The first phase of EMCN (Exxon Mobil Cerro Negro) runs was carried out in April, to observe the effect of pressure on density, foaming and morphology of the coke formed. Table 29 shows the pilot unit foaming studies data for EMCN runs. Runs 1 to 4 were carried out at a temperature of 900 ^{o}F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig to 45 psig with an increment of 10 psig for each run.

At 15 psig there was a tall column of shot coke inside the drum at the end of the run. Also a loss of mass occurred during the steam strip process from 45 to 55 inches of drum height. A drum full of light BB shot coke was produced during run EMCN 1. With EMCN run 2, the pressure was increased from 15 psig to 25 psig and a dense layer of coke was formed from a drum height of 20 to 42 inches. The morphology changed from BB coke to dense agglomerated (bonded) shot coke at that drum height. EMCN 3 was carried out at a pressure of 35 psig and the dense layer of coke was formed at drum height of 20 to 43.5 inches. This run produced shot coke with a solid agglomerated outer wall 0.5 inches thick over the bottom 8 inches of the drum. The morphology changed from clusters of BB to loose BB's to a dense hard agglomerated coke in the top 20 inches of the drum. During EMCN run 4 the pressure was increased to 45 psig and a dense layer of coke was produced at drum height of 25 to 36.5 inches. The morphology of coke produced was BB shot coke mixed with loose BB's and dense agglomerated shot coke at the top of the drum. In runs 2 and 3, it was observed that after around 180 minutes of run time, a differential pressure started to build up inside the drum. This differential pressure keeps increasing with time resulting in a termination of run. The same was observed with run 4 after around 150 minutes into the run. It has been observed that resids that are high in asphaltene content and that produce dense shot coke tend to develop a differential pressure inside the drum thereby abruptly terminating the run. The bonded shot coke in runs 2 and 3 was very dense while run 4 was brittle and fairly easy to remove. The foaming tendencies during these runs are discussed in the next section.

EMCN runs 5 and 6 were carried out at a higher temperature of 930 ^{o}F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig for run EMCN run 5 to 45 psig for run EMCN run 6. The foaming studies data for these runs is shown in Table 28. EMCN run 5 lasted for 225 minutes and then it was switched to steam strip process due to the build up of differential pressure inside the drum. Run 6 was a five hour run. The EMCN run 5 continued to make a dense layer of coke like those in runs 2, 3 and 4. The thick layer of coke was formed at drum height of 17 to 37 inches. The density for this layer was greater than 0.8 gm/cc. It required a lot of effort (5 hours) to take the coke out of the drum, as the coke produced was very hard and dense. The morphology of coke produced changed from clusters of BB shot coke from 20 inches to very hard dense agglomerated shot coke at 39.5 inches of drum height. The temperature and feed rate were the same and the pressure was increased to 45 psig for EMCN run 6. EMCN run 6 lasted for 300 minutes without the build up of differential pressure. Run 6 produced more coke that was dense throughout the drum. It was observed during the run that with time the shot coke started filling towards the bottom of the drum as well and hence we don't see a dense layer at the top of the drum. The shot coke produced during this run was very hard and dense. There was considerable difficulty in breaking the coke out of the drum.

Table 28 – Foaming studies data for Exxon Mobil Cerro Negro runs

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (cc)	Actual AF used	# of inj	First Foam	Re-appearance	?T	Steam Strip
		^{0}F	psig	gm/hr			Defoamer(AF+D)	(cc)		Front(min	of Foam(min)	min	Behaviour
EMCN 1 PUAF	4/1/2004	900	15	3600	100,000 cSt (3 AF/ 70 D)	0	46	1.93	9	6	21	15	Average
EMCN 2 PUAF	4/6/2004	900	25	3600	100,000 cSt (3 AF/ 70 D)	0	126	5.29	11	4.5	27	23	Good
EMCN 3 PUAF	4/8/2004	900	35	3600	100,000 cSt (3 AF/ 70 D)	0	45	1.89	7	12	16.5	4.5	Good
EMCN 4 PUAF	4/13/2004	900	45	3600	100,000 cSt (3 AF/ 70 D)	0	50	2.1	5	9	25	16	Good
EMCN 5 PUAF	4/15/2004	930	15	3600	100,000 cSt (3 AF/ 70 D)	0	20	0.84	3	12	21	9	Good
EMCN 6 PUAF	4/20/2004	930	45	3600	100,000 cSt (3 AF/ 70 D)	0	20	0.84	3	13.5	25.5	12	Good

9. *Foaming tendencies for EMCN parametric tests*

The EMCN 1 run was carried out at a pressure of 15 psig. The foam was at a drum height of 35 to 40 inches and the rise and collapse of foam at antifoam injection times was seen. During the first hour four antifoam injections did not control foaming for EMCN Run 2. Hence 6 more antifoam injections were made during the second hour. Severe foaming continued to occur and we see continuous rise and collapse of foam at drum heights of 34 to 45 inches. It was observed that the Cerro Negro resid foamed severely during the first 70 to 90 minutes of run time. An average of 60 ml of 100,000 cSt (3/70) concentration antifoam when injected through overhead controls foaming. Later into the run, during the steady state period, this resid tends to make a dense layer of coke at average drum heights of 20 to 45 inches. Once this dense layer is produced, foaming does not occur. Hence it is our preliminary conclusion that the reduction in superficial vapor velocity (interstitial velocity) might be the reason for foaming not to occur. Some foaming occurred during the EMCN 1 during the last hour of the run, but as we increased the pressure from 15 psig to 45 psig during runs EMCN 2, 3 and 4, foaming was not observed after the transient phase. Figure 43 shows the coke, bubbly liquid and foam layer for each of the EMCN runs. It can be seen that the foaming occurs during the transient phase only and then we see a growing coke layer with time.

At higher temperature of 930 ^oF, EMCN runs 5 and 6 showed least foaming tendencies compared to runs at low temperature. A total of 20 ml's of antifoam was injected for each of these runs. The foaming occurred during the first hour, i.e., the transient phase only. No foam was observed after the transient phase and hence antifoam was not injected during this period. For run 5, there is a rise and collapse in densities at different drum heights whereas for run 6, the densities at different drum heights are rising towards the coke density.

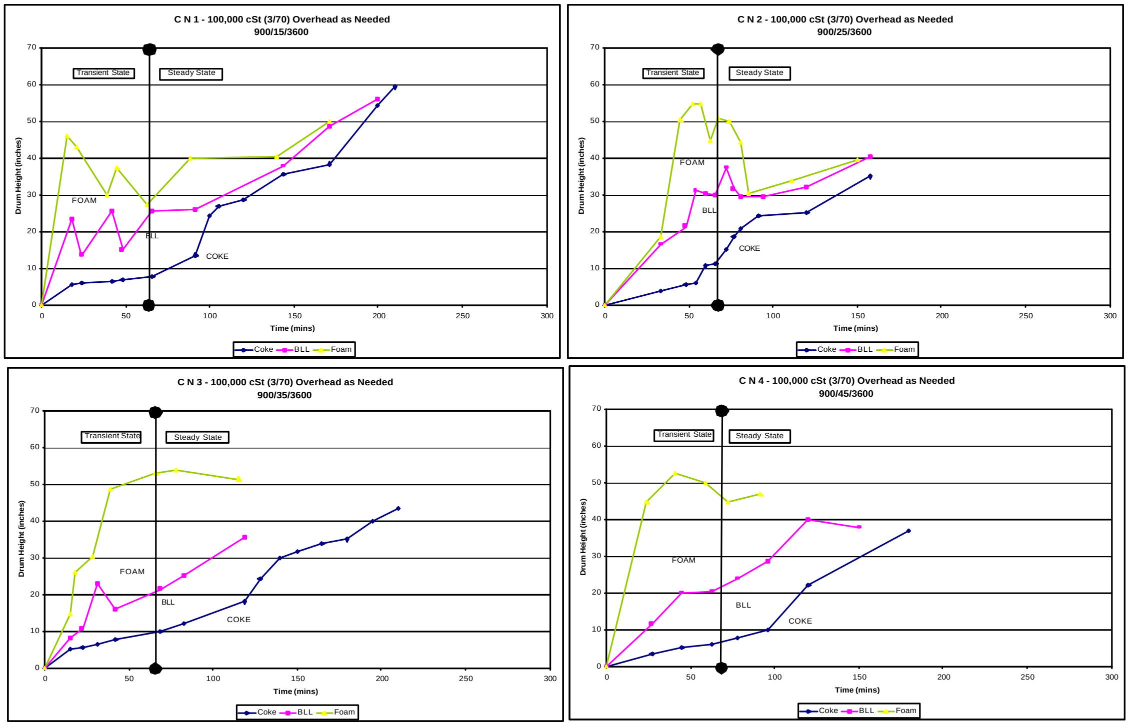


Figure 43 – Drum height of foam, bubbly liquid and coke layers with time for EMCN runs 1 to 4

10. *Parametric tests of Exxon Mobil Medium Heavy Canadian (EMHC)*

The Heavy Canadian resid was obtained from Exxon Mobil during the month of March, 2004. Runs were carried out to observe the effect of pressure on density, foaming and morphology of the coke formed. Table 29 shows the pilot unit foaming studies data for EMHC runs.

Pilot Unit Foaming Studies Data

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (c	Actual AF use	# of inj.	First Foar	Re-appearanc	?T	Steam Strip
		^{o}F	psig	gm/hr			Defoamer(AF+D	(cc)		Front(min	of Foam(min)	min	Behaviour
EMHC 1 PUAFV	4/22/2004	900	15	3600	100,000 cSt (3 AF/ 70 D)	O	20	0.84	3	12	32	20	Good
EMHC 2 PUAFV	4/28/2004	900	25	3600	100,000 cSt (0.3 AF/ 70 D)	O	85	0.37	4	13.5	24	10.5	Good
EMHC 3 PUAFV	5/4/2004	900	35	3600	100,000 cSt (0.3 AF/ 70 D)	O	90	0.39	4	21	40	19	Good
EMHC 4 PUAFV	5/6/2004	900	45	3600	100,000 cSt (0.3 AF/ 70 D)	O	60	0.26	4	20	32	12	Good
EMHC 5 PUAFV	6/8/2004	930	15	3600	100,000 cSt (0.3 AF/ 70 D)	O	30	0.13	2	7.5	34	26.5	Good
EMHC 6 PUAFV	6/10/2004	930	45	3600	100,000 cSt (0.3 AF/ 70 D)	O	10	0.04	1	18	45	27	Good
EMHC 7 PUAFV	6/15/2004	900	35	2400	100,000 cSt (0.3 AF/ 70 D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
EMHC 8 PUAFV	6/17/2004	900	35	4800	100,000 cSt (0.3 AF/ 70 D)	O	100	0.44	6	22.5	30	7.5	Good
EMHC 9 PUAFV	6/23/2004	900	35	6000	100,000 cSt (3 AF/ 70 D)	O	90	3.78	8	18	28	10	Bad
EMHC 10 PUAFV	6/29/2004	930	35	2400	100,000 cSt (0.3 AF/ 70 D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good

Table 29: Foaming studies data for Exxon Mobil Heavy Canadian runs.

Runs 1 to 4 were carried out at a temperature of 900 ^{o}F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig to 45 psig with an increment of 10 psig for each run. As can be seen, the density profile of the coke formed is the same with increasing pressure. Although at 45 psig run the coke yield was higher compared to other runs. As a result of that the density of coke formed is lesser in the region of 20 to 40 inches of drum height as compared to other runs. The morphology of coke formed changed from bonded BB shot and buck shot coke to sponge coke for EMHC run 1. Runs 2 to 4 produced sponge with a transition to hard dense bonded sponge coke at the top of the drum. EMHC runs 1 to 3 experienced a build up of differential pressure (around 20 to 35 psi) after 180 minutes into the run. The same was not observed during run 4 at 45 psig.

EMHC runs 5 and 6 were carried out at a temperature of 930 ^{o}F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig for run 5 to 45 psig for run 6. The density profile of the coke formed is the same for these runs. These runs produced bonded sponge coke which has a solid outer wall at the bottom and high in pitch at the top of the drum. Run 5 had a large range of operational differential pressure with first hour range being (1.84-16.5 psi), second hour (5.7-52.0) and so on. Run 6 too observed a high differential pressure due to a restriction in the feed line through out the run.

EMHC runs 3, 7, 8 and 9 were carried out at a temperature of 900 ^{o}F and 35 psig of run pressure. The feed rate was increased from 2400 gm/hr to 6000 gm/hr with an increment of 1200 gm/hr for each run. EMHC run 7 was carried out at 2400 gm/hr, this run produced sponge coke with solid agglomerated outer wall. Run 8 was carried out at a feed rate of 4800 gm/hr. The coke produced during this run changed the morphology from clusters of agglomerated shot coke surrounded by a solid wall at the bottom of the drum to clusters of sponge coke high in pitch towards the top of the drum. The coke produced during this run was dense and hence was difficult to remove from the drum. Run 9 was carried out at a higher feed rate of 6000 gm/hr. Due to the higher superficial velocity during this run, the drum was filled with coke within two hours of the run and had to be stopped due to the height of coke inside the drum. A loss of mass was encountered during the steam strip process which can be attributed to unreactive mass of bed inside the drum. Thus the steam strip process was stopped after 10 minutes and the drum was allowed to cook for 40-45 minutes. The stripping process was resumed after that for the remaining period of time. **Error! Reference source not found.** shows the loss of mass during the steam strip process for EMHC run 9. This run produced 72.5 inches of coke. The morphology of coke produced changed from grape clusters of buck shot coke lodged in the center at the bottom of the drum to clusters of sponge coke in the middle and dense sponge coke high in pitch towards the top of the drum.

a) Foaming Tendencies for EMHC Runs

The antifoam injection data is shown in Table 29 for EMHC runs. All runs used as needed overhead injection of antifoam. Runs 1 and 9 used a higher concentration of (3/70) antifoam whereas all the other runs used a lower concentration of (0.3/70) antifoam. Diesel is used as the carrier for the antifoam. Runs 1 to 4 were carried out at a temperature of 900 ^oF and a feed rate of 3600 gm/hr with a 10 psig increase in pressure with each run. During these runs an average of four antifoam injections were made. Usually foaming occurred during the transient phase of around 60-80 minutes into the run. Foaming was not observed during the steady state period for these runs.

EMHC runs 5 and 6 were carried out at a higher temperature of 930 ^oF and a feed rate of 3600 gm/hr. A decrease in foaming was observed for these runs at 930 ^oF compared to runs at 900 ^oF. Irrespective of temperature, at lower feed rates of 2400 gm/hr during EMHC runs 7 and 10, foaming did not occur and hence antifoam was not injected during these runs.

During EMHC run 8 at 4800 gm/hr, a total amount of 100 cc of antifoam was injected through the overhead. Foaming was observed during the first two hours of the run. Run 9 at higher superficial velocity (6000 gm/hr of feed rate) used 10 times higher concentration of (3/70) antifoam injected overhead with as needed injection technique. During this run, the mass of bed inside the drum was highly unreacted indicating a large bubbly liquid layer. Hence some loss of mass was encountered during the steam strip process.

Usually foaming occurred during the transient phase for EMHC runs. Antifoam of 100,000 cSt (0.3/70) concentration is injected through overhead once the foam height reaches the 2/3rd level of drum height. The injection of antifoam collapses the foam and quantifies the bubbly liquid layer (BLL) determined by an increase in density. Based on this information, the heights of foam, bubbly liquid layer and the growth of coke layer with time are determined.

Figure 44 shows the collapse of foam during EMHC run 8 at 4800 gm/hr. It depicts the drum height of the three layers of delayed coking, the foam, the bubbly liquid layer (BLL) and the coke. Figure 45 shows the collapse of foam and drum height of foam, liquid and the coke layer during EMHC run 9 and 6000 gm/hr.

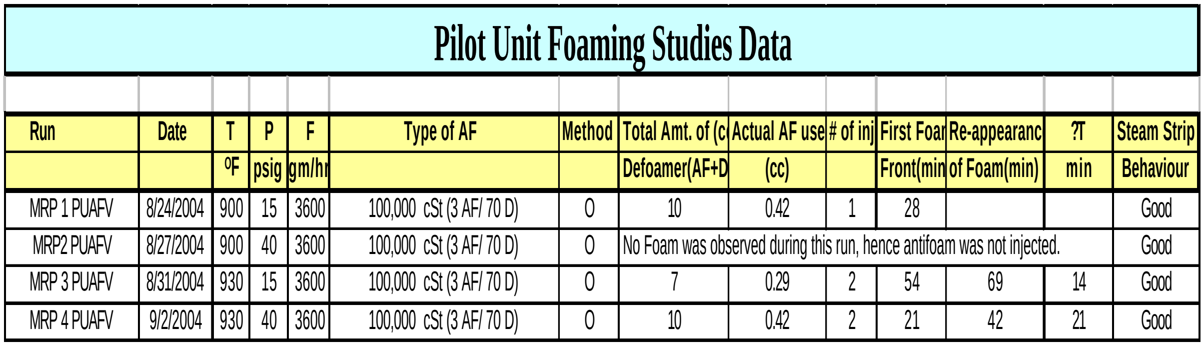
b) Conclusion

Superficial velocity tests were carried out using the Medium Heavy Canadian resid. At a run temperature of 900 ^oF and a feed rate of 3600 gm/hr, with increase in pressure with each run, the density profile of the coke formed was generally the same. A morphology change for the coke produced was observed for this resid. The morphology changed from bonded shot coke to a transitional coke and finally to a dense bonded sponge coke. At a higher run temperature of 930 ^oF, the EMHC runs 5 and 6 developed an operational differential pressure inside the drum. These runs produced sponge coke in the center with solid agglomerated outer wall at the bottom of the drum and bonded sponge coke mixed with pitch at the top of the drum. At higher feed rates of 4800 gm/hr and 6000 gm/hr, due to the higher vapor superficial velocity, the morphology of the coke produced transitioned from agglomerated shot coke to a transitional sponge coke and finally into a dense sponge mixed with pitch at the top of the drum. The EMHC run 9, at 6000 gm/hr of feed rate observed a loss of mass during the steam strip process due to the build up of unreacted mass of bed inside the drum.

Usually foaming occurred during the transient phase for EMHC runs at a run temperature of 900 °F. At a higher run temperature of 930 °F, EMHC runs 5 and 6 showed least foaming tendencies. Irrespective of run temperature, runs 7 and 10, at a low feed rate of 2400 gm/hr foaming was not observed. Hence antifoam was not injected during these runs. At higher feed rates of 4800 gm/hr and 6000 gm/hr, larger quantities of antifoam were needed to control foaming. At these feed rates foaming occurred during the first 120 minutes of the run. It should be noted that the higher feed rate runs only lasted 2 to 3 hours. At 6000 gm/hr run, it is speculated that it had a larger bubbly liquid layer compared to the foam layer. Generally once the steady state is attained, foaming is not observed for the Medium Heavy Canadian resid.

11. *Parametric tests of Marathon Rose Pitch (MRP)*

The Rose Pitch resid was obtained and tests were conducted to observe the effect of pressure on density, foaming and morphology of the coke formed. Table 30 shows the pilot unit foaming studies data for MRP runs.



Pilot Unit Foaming Studies Data

Run	Date	T	P	F	Type of AF	Method	Total Amt. of (c	Actual AF use	# of inj	First Foar	Re-appearanc	?T	Steam Strip
		°F	psig	gm/hr			Defoamer(AF+D	(cc)		Front(min	of Foam(min)	min	Behaviour
MRP 1 PUAFV	8/24/2004	900	15	3600	100,000 cSt (3 AF/ 70 D)	O	10	0.42	1	28			Good
MRP2 PUAFV	8/27/2004	900	40	3600	100,000 cSt (3 AF/ 70 D)	O	No Foam was observed during this run, hence antifoam was not injected.						Good
MRP 3 PUAFV	8/31/2004	930	15	3600	100,000 cSt (3 AF/ 70 D)	O	7	0.29	2	54	69	14	Good
MRP 4 PUAFV	9/2/2004	930	40	3600	100,000 cSt (3 AF/ 70 D)	O	10	0.42	2	21	42	21	Good

Table 30: Pilot Unit foaming studies data for Marathon Rose Pitch runs.

MRP runs 1 and 2 were carried out at a temperature of 900 °F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig to 40 psig. The density profile of the coke formed was the same with increasing pressure. Run 1 produced 43 inches of shot coke. The morphology changed from Buck shot at the bottom to BB shot coke towards the top of the drum. Run 2 produced 40 inches of shot coke with the morphology changing from Buck shot coke at the bottom to a transitional shot coke in the middle of the drum and finally clusters of BB shot coke mixed with pitch towards the top of the drum.

MRP runs 3 and 4 were carried out at a temperature of 930 °F and a feed rate of 3600 gm/hr. The pressure was increased from 15 psig to 40 psig. Run 3 at 15 psig had less coke deposition compared to run 4 at 40 psig. Run 3 produced 27 inches of shot coke with morphology changing from Buck shot coke at bottom to clusters of BB shot coke and finally to bonded shot coke at the top of the drum. It was hard to remove the bonded (agglomerated) shot coke formed at the top of the drum. The first hour of the MRP 3 run saw a regular density profile. It is around the 90 minute mark that we saw the profile changing to a dense head in the middle of the drum. It continued to grow denser in that region until the end of the run.

The run was stopped due to the build up of differential pressure inside the drum. The temperature profile inside the drum is explained later in the report. Run 4 produced 45 inches of shot coke. Interesting morphology was observed during this run. The bottom part of the drum produced clusters of BB shot coke with the morphology changing to dense pitch like sponge in the middle section of the drum and finally into bonded (agglomerated) shot coke towards the top of the drum.

a) Foaming Tendencies for MRP Runs

The antifoam injection data is shown in Table 30 for MRP runs. All runs used as needed overhead injection of 100,000 cSt (3/70) concentration antifoam. Moderate foaming tendencies was observed with MRP runs.

For MRP Run 1 an increase in density is observed after the collapse of foam, quantifying the bubbly liquid layer. Only one antifoam injection was needed to control foaming during this run. Foam was not observed during MRP run 2 and hence antifoam was not injected.

A deposit of some kind was observed along the wall at drum height of 35-60 inches during MRP run 3. As a result of it a bulging density profile is observed in that region. Runs 3 and 4 at a higher feed temperature of 930 ^{o}F foamed more compared to runs 1 and 2 at a lower feed temperature of 900 ^{o}F.

b) Temperature Profile for MRP runs

Three thermocouples were added to the drum to measure the skin temperature of the drum. These were added to establish whether the drum is being operated adiabatically. As shown in Table 31, the drum is divided into six different zones along the height of the drum. The location of thermocouples in each zone is also shown in Table 31. The drum skin thermocouples are placed between the internal thermocouples on the outer skin of the drum.

Figure 46 through Figure 49 show the drum temperature profile for MRP runs 1 to 4. It can be observed from these plots that the drum skin temperature is approximately 20 – 40 degrees cooler compared to the drum internal temperature. Hence it can be deduced that the drum is not being operated under adiabatic conditions. This brings up the question whether the coke drum should be operated based on the drum skin temperature. If so, then what would be the optimum drum skin temperature, the drum should be operated during a run. This issue was discussed during the advisory board meeting held October 20th 2004.

		Thermocouple (TI)		
	Zone	Internal	Skin	zone
Top	6	208	306	206
	5	209	305	205
		210		
	4	211	304	204
		212		
	3	213	303	203
		214		
	2	215		202
Bottom	1			201

Table 31: Location of thermocouples.

c) Conclusion

Parametric tests were carried out using the Marathon Rose Pitch resid. At a run temperature of 900 ^{o}F and a feed rate of 3600 gm/hr, with increase in pressure (15 to 40 psig), the density profile of the coke formed was generally the same. The morphology of coke produced under these operating conditions was generally buck shot coke at the bottom to clusters of BB shot coke towards the top of the drum. At 930 ^{o}F, 15 psig and a feed rate of 3600 gm/hr, the density profile produced during MRP run 3 was different compared to other runs. It produced a dense head of shot coke at drum height of 15 to 30 inches. MRP run 4 produced a mixed morphology of coke. The morphology of coke changed from BB shot coke at the bottom to a dense sponge in the middle part of the drum and finally into a bonded (agglomerated) shot coke at the top of the drum. Overall Rose Pitch resid showed moderate foaming tendencies. The foaming tendencies increased at higher run temperature of 930 ^{o}F compared to lower temperature runs. Resids like Cerro Negro and Medium Heavy Canadian have shown rigorous transient state foaming tendencies, whereas worst foaming resids like Petrobras and Chevron foam all throughout the run. Comparatively Rose Pitch resid has shown a different foaming tendency as it usually tends to foam after the first hour of the run. Based on the drum temperature profile for MRP runs 1 to 4, it was determined that the drum is not being operated under adiabatic conditions. Hence further insight in this matter as to how to control the temperature during a coking run was sought during the advisory board meeting held October 20th 2004.

d) Future Work

Conduct tests with Rose Pitch resid at higher superficial velocities to observe the foaming tendencies and the morphology of coke produced. Analyze the simulated distillation data for the Cerro Negro, Medium Heavy Canadian and the Rose Pitch resid.

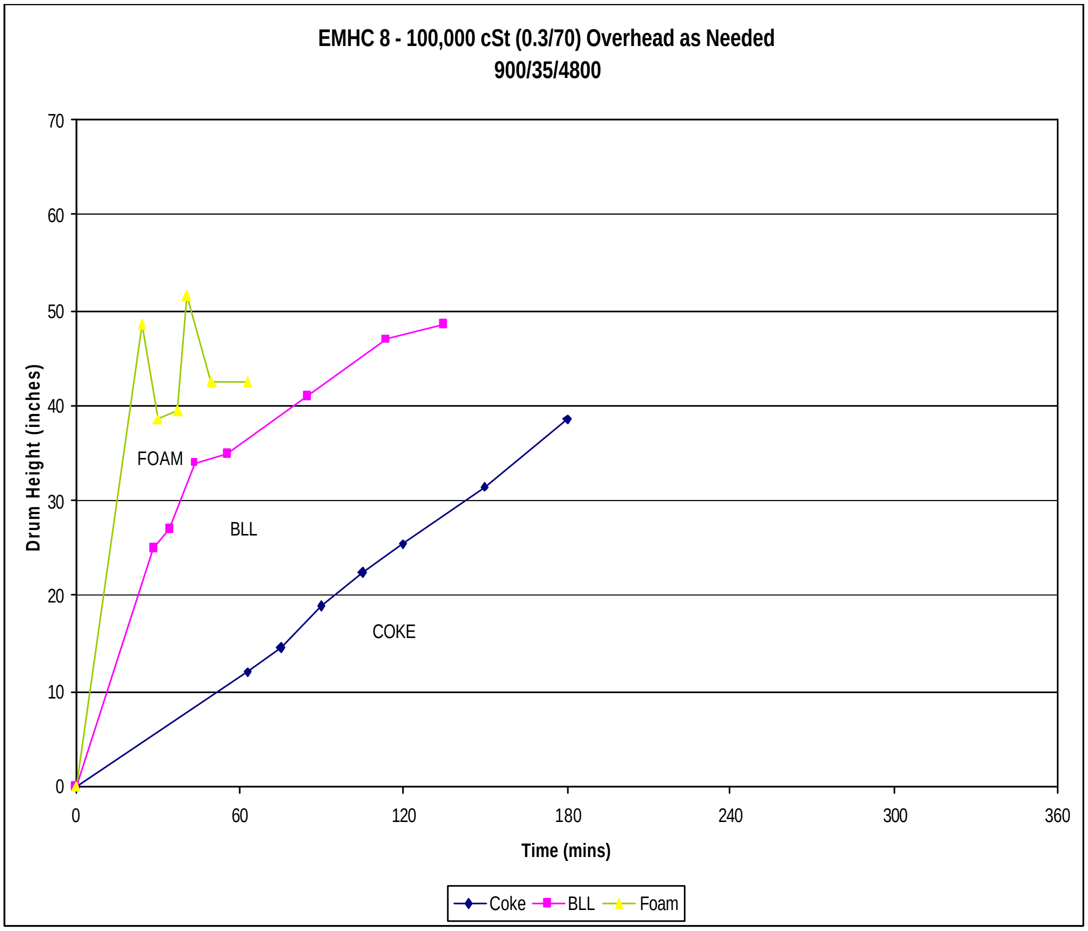


Figure 44: Drum height of foam, liquid and the coke layer during EMHC run 8.

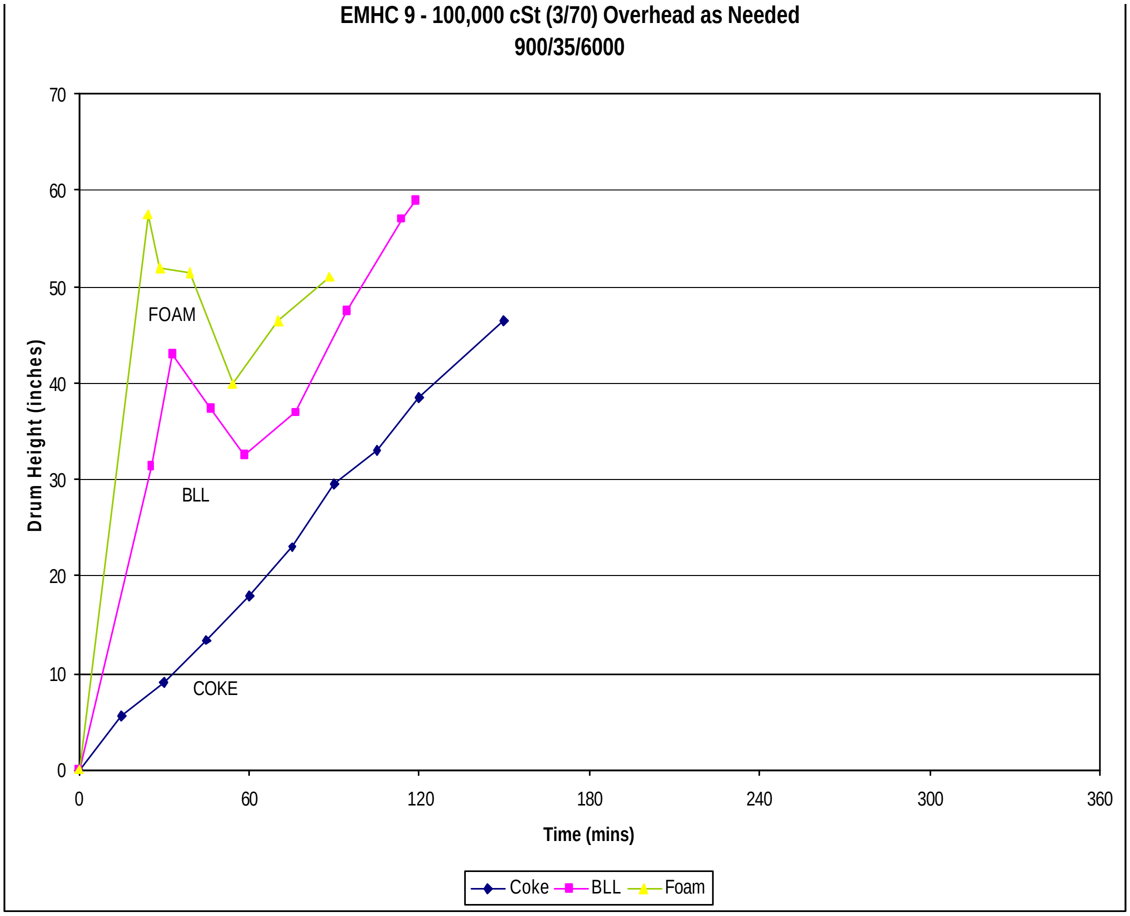


Figure 45: Drum height of foam, liquid and the coke layer during EMHC run 9.

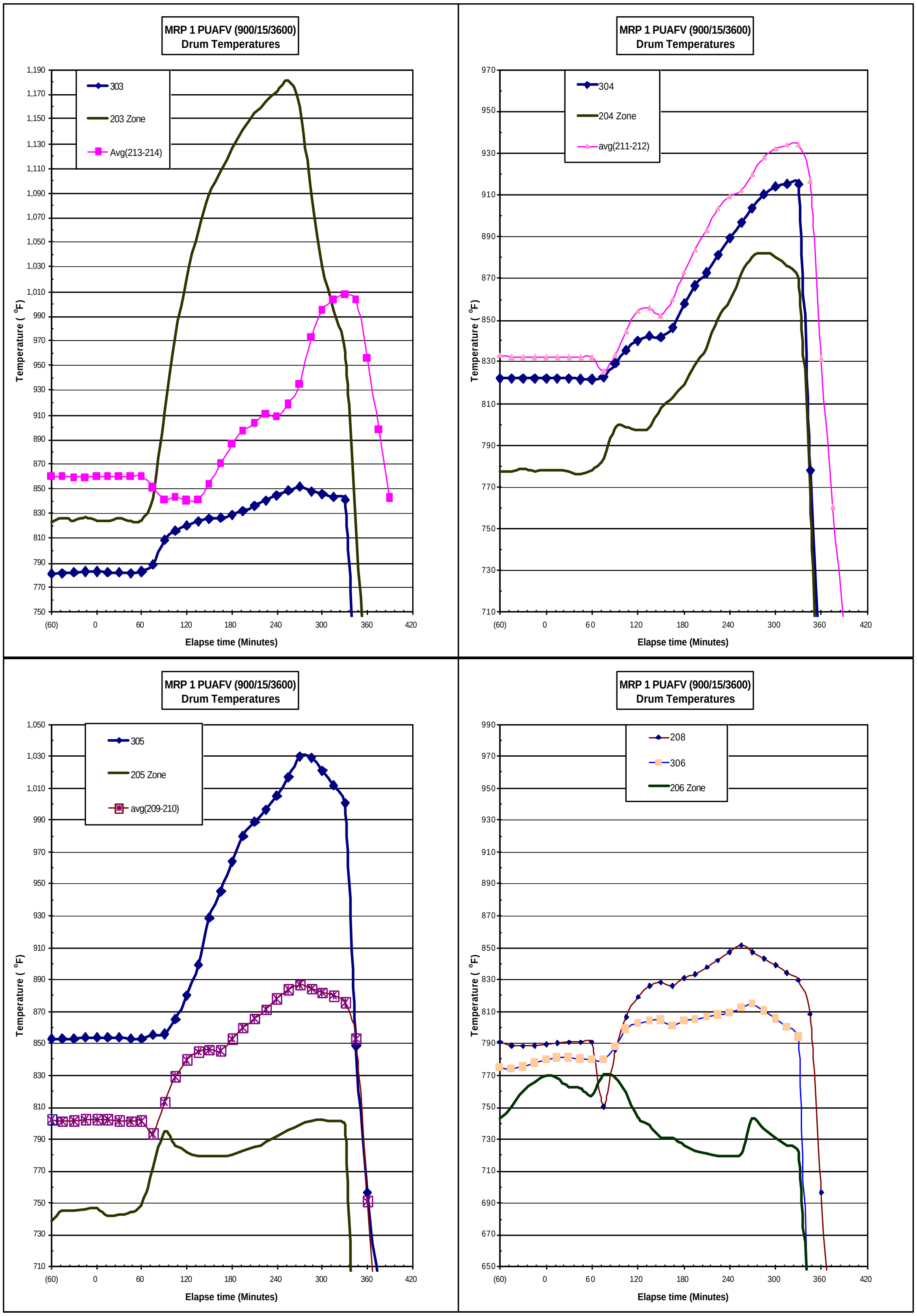


Figure 46: Drum temperature profile for MRP run 1.

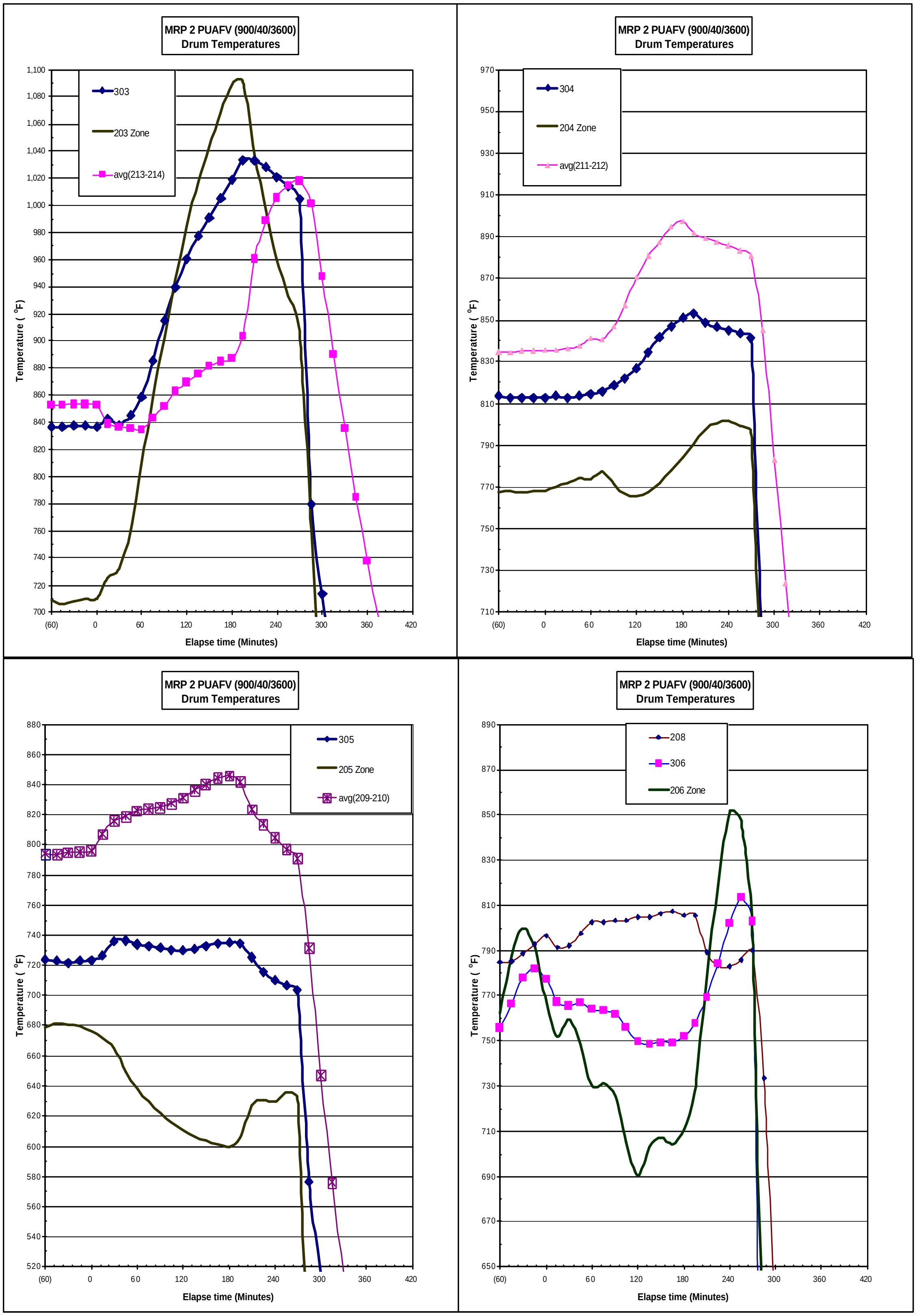


Figure 47: Drum temperature profile for MRP run 2.

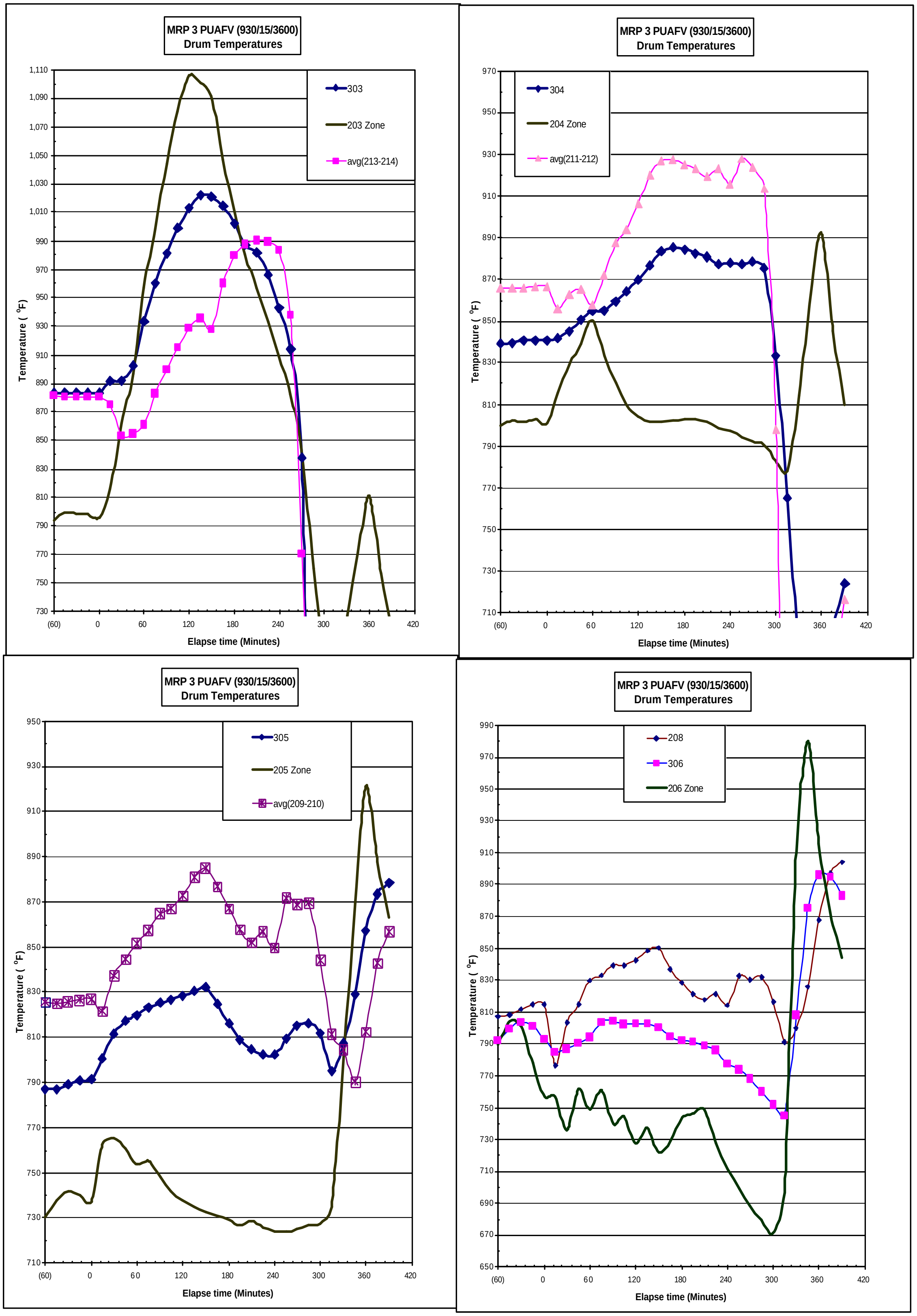


Figure 48: Drum temperature profile for MRP run 3.

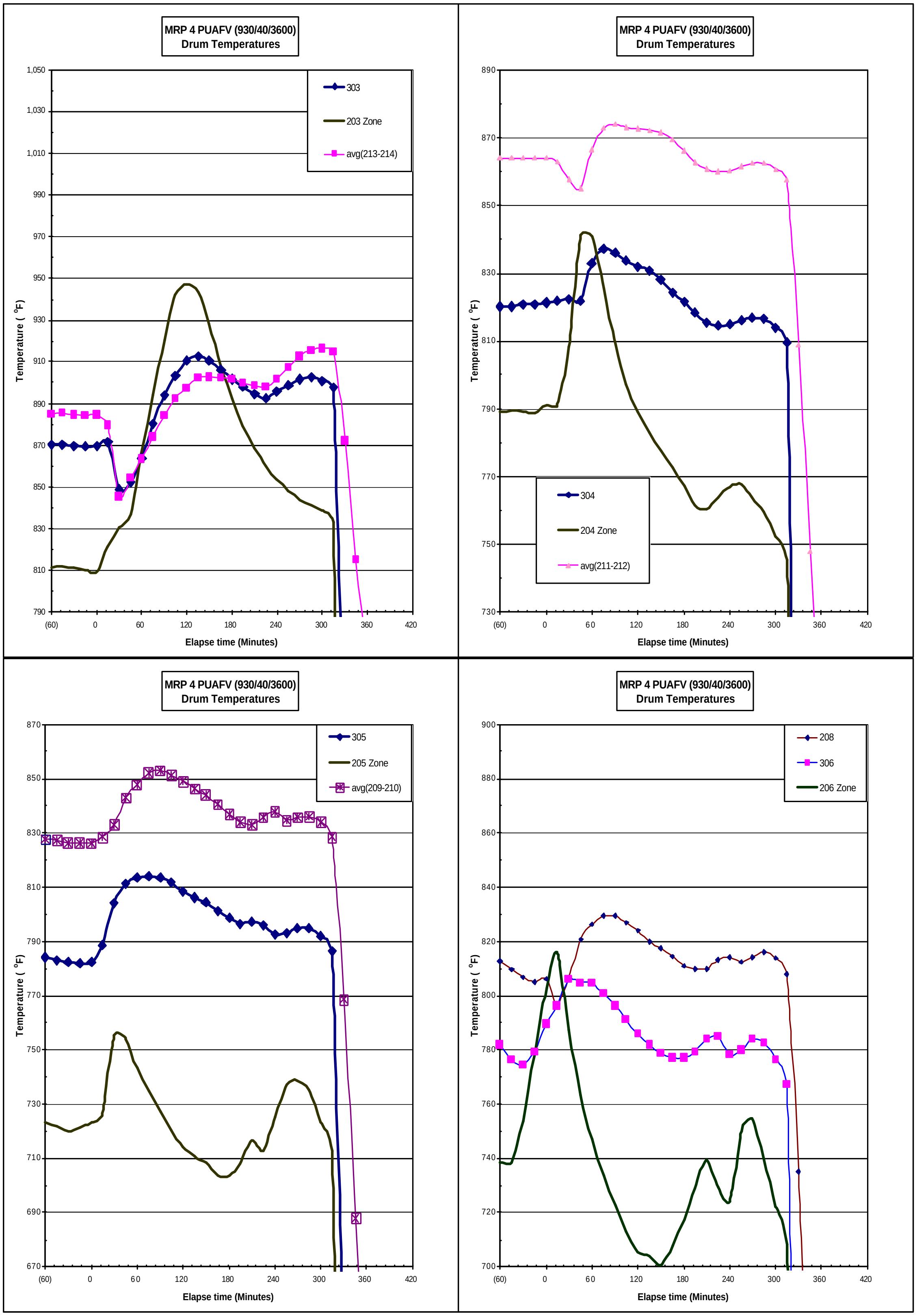


Figure 49: Drum temperature profile for MRP run 4.

B. ***FOAMING MODELS***

1. *Theoretical Discussion*

a) Foams and Foam Model Development

Foams are agglomerations of gas bubbles separated from each other by thin liquid films. They belong to the colloidal system comprising of gas dispersed in liquid. A very large majority of industrial processes require the injection of materials known as antifoams to inhibit the foam growth because the foam formation and continuous growth is sometimes undesirable in chemical processes leading to fouling in equipment. Antifoams such as silica particles dispersed in carrier oil such as mineral oil are important from the standpoint of controlling and inhibiting foam. Consequently foam models that can predict how the foam-antifoam interaction will affect the foam is going to be very important as it will provide insight to rapid foam control whenever required and also optimum antifoam requirements for doing so. Presented here is the theory of two foam models, Pelton's Model and Model 2, that predicts foam volumes for different times during the run. Pelton's Model does so both in the presence and absence of antifoam and correlates foam volumes to the run operating conditions and case specific antifoam effects(if injected) whereas Model 2 interrelates the foam volumes calculated for different times during the run with important resid properties, coke morphology, antifoam effects(if injected), coke pore size distribution and Pelton's Model results.

b) Literature Review of Pelton's Model

Pelton and Goddard in literature[2] have emphasized on the dynamic foam rise test for the development of a foaming model. Literature[2] describes that for the foam test the aqueous surfactant was kept in a graduated cylinder and gas bubbles were produced by passing air or nitrogen through a frit at the bottom of the cylinder. In the experimental setup described in the literature[2], the foaming solution comprised of SDS (sodium dodecyl sulfate) in distilled water. The commercial antifoams that were used, as it states, consisted of hydrophobic silica dispersed in silicone oil and the material was emulsified with a mixture of nonionic surfactants. Then it describes that the antifoam emulsion was weighed into a freshly prepared SDS solution that was added to a graduated cylinder. Pelton and Goddard in literature[2] then go on to describe that humidified nitrogen was introduced through an ace glass pore, ASTM 25-50 μm glass frit attached to the glass tube and suspended down the center of the cylinder and the gas flow rate was controlled by a Matheson 8420 mass flow controller.

c) Description of Pelton's Model

The model foam conceptualized here consisted of the elements shown in Figure 50. The gas entered the liquid phase in the form of "primary bubbles". Also the liquid phase comprised of the antifoam emulsion droplets. The foam phase was present above the liquid phase. The primary bubbles in the liquid phase were assumed to collect the antifoam emulsion droplets by heterocoagulation. On entering the foam phase these primary bubbles were assumed to coalesce with neighboring primary bubbles leading to the formation of "secondary bubbles". The model requires the following input parameters: R_P, R_S, R_E, V, G, Q for predicting the foam volumes.

Primary bubble radius is given by R_P, Secondary bubble radius is given by R_S, the antifoam emulsion droplet radius is given by R_E, V stands for the total volume of liquid phase, G stands for the volume fraction of gas in the liquid phase and Q stands for the volumetric flow of gas into the cylinder. According to the literature[1], the model uses the values of the input parameters described above to calculate certain quantities eventually leading to the calculation of the number of antifoam emulsion droplets(d) and

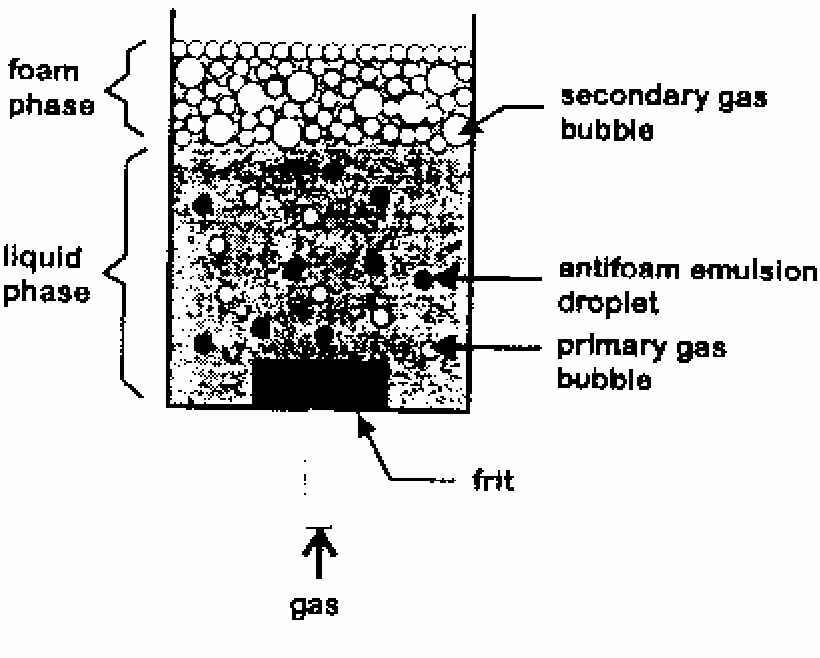


Figure 50 – Schematic Diagram showing the different elements of the Model

the rate of foam rise or fall given by S(t). Once S(t) and d are calculated out, the value for S(t) is substituted in the integral $\int S(t)dt$ and integrated for the time period required to get the foam volumes for different times(t). The time period chosen for doing the integrations will be explained in the later portion of this report. The quantities that are calculated and the different equations involved and the methodology for doing the model calculations are outlined as follows:

The number concentration of primary bubbles in the liquid phase is given by

$$B= 3G/4\pi R_P^3$$

Once B is calculated, utilizing the input parameters R_P, R_S, V, g which is the total number of groups in the liquid phase can be calculated. g is given by

$$g= R_P^3 BV/R_S^3$$

Alternately g can be interpreted as g =[number of primary bubbles/the number of primary bubbles required to produce a secondary bubble]. The concentration of antifoam emulsion droplets at time t is given by

$$E(t)=E_O\exp(-K_S fBt)$$

where E_O= initial antifoam concentration, Factor $K_S= (R_P+ R_E)[(1/ R_P)+(1/ R_E)]2kT/3?$, where T= temperature, k= Boltzmann constant, ?= viscosity of the antifoam, f=coagulation efficiency factor cited in the literature[1](a value of 20,000 has been cited).

Thus after the calculation of the factor K_S from model input information and run operating conditions and the choosing of a suitable value for the adjustable factor f, the concentration of antifoam emulsion droplets E(t) can be determined for various times(t). The calculation of the initial antifoam concentration E_O from existing antifoam injection data will be explained later in the report. The average residence time of bubbles in the liquid phase, (z) is given by

$$z = GV/Q$$

The z value determined thus from the model inputs G,V,Q goes into the calculation of the number of antifoam emulsion droplets(d) that heterocoagulate with the primary bubbles.

The number of antifoam emulsion droplets d according to literature, is given by

$$d = [E(t-z)-E(t)]V$$

E(t-z) is basically the antifoam emulsion concentration at time (t-z) and can be determined by replacing t by (t-z) in the expression for E(t) outlined earlier. Hence E(t-z) is given by $E(t-z) = E_O\exp[-K_S fB(t-z)]$ where E_O= initial antifoam concentration as before. After the successful calculation of d, utilizing the value of g determined previously, the rate of foam rise or fall, S(t) can be calculated as

$$S(t) =[1-1/g]^d$$

The foam volume VV(t) is given by VV(t) =?S(t) dt integrated for the particular time period. The choice for the limits of the integral evaluated will be explained in the latter portion of the report. Thus, as can be seen, the model tries to predict what the foam volume is going to be at different times at different run conditions. The following flowchart explains the sequence in which the different quantities are calculated leading to the final determination of foam volumes for various times (t):

LITERATURE CONSULTED:

[1] " *A model of foam growth in the presence of antifoam emulsion*" by Robert Pelton, 1996.

[2] "*A theory for foam growth kinetics in the presence of antifoam emulsion*" by R.H.Pelton, E.D.Goddard, 1986.

[3] "*Foams: theory and industrial applications*" by J.J.Bikerman, Reinhold Publishing Corporation, 1953.

[4] "*Identification of crude oil components responsible for foaming*" by Callaghan et al., Society of Petroleum Engineers of AIME, (Paper) SPE, Jul 18, 1983.

[5] “*Conditions for foam generation in homogeneous porous media*” by Miller et al., SPE paper, April 2002.

[6] “*Foam control methods in delayed cokers*” by Kremer et al., Refining, August 2002.

[7] “*Recent developments in the understanding of foam generation and stability*” by P.R.Garrett, Chemical Engineering Science, v 48 n 2, Jan 1993, 367-392.

[8] Internet resources: www.jechura.com.

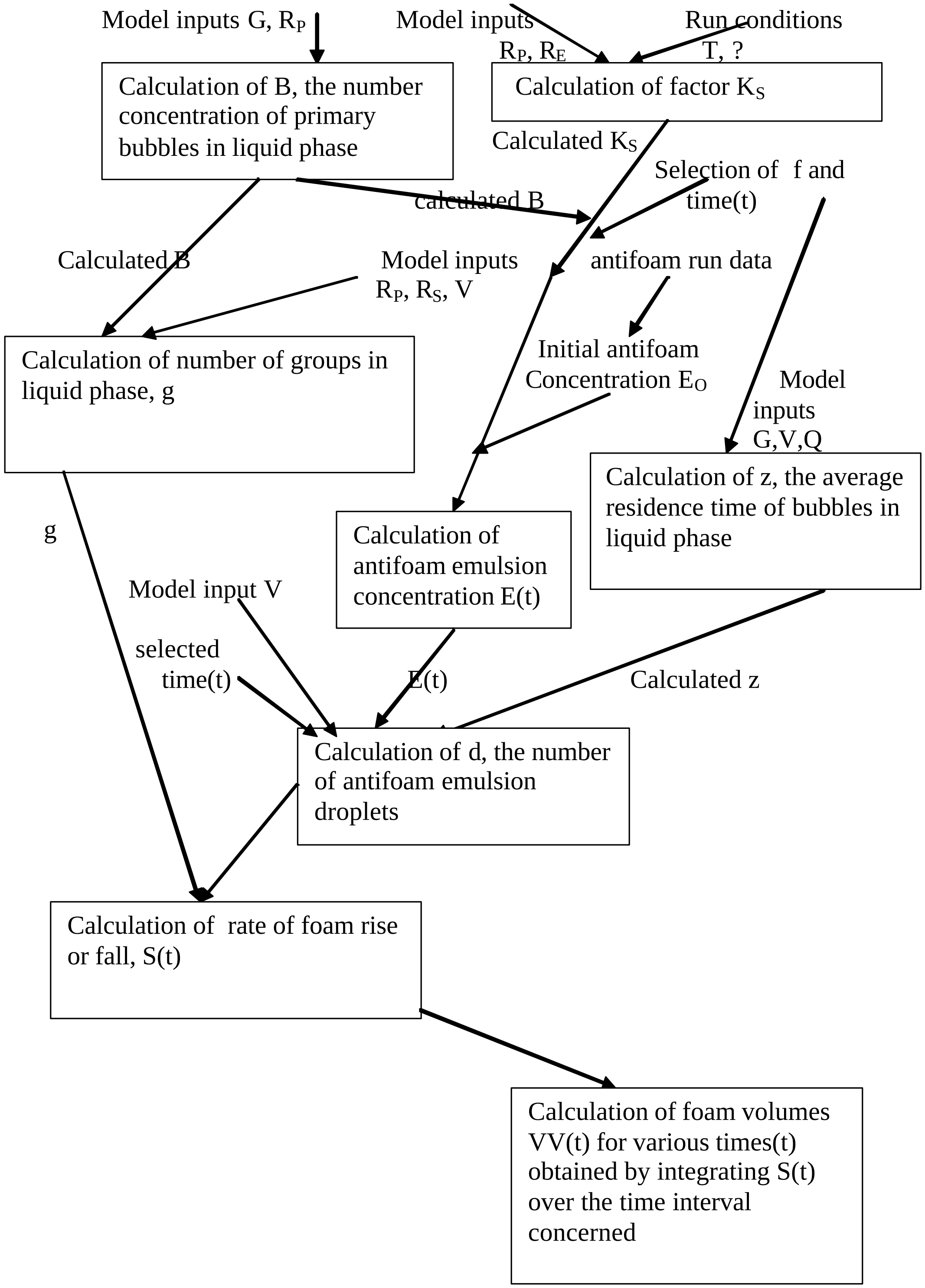


Figure 51 – Flowchart showing the sequence of the model calculations

2. *Application of Pelton's Model to the Delayed Coking Project*

For the runs that produced shot coke, the Bikermans correlation [3] was used to determine primary bubble radius R_P whereas for the sponge coke making runs, R_P was chosen to be equal to the smallest void size that could be seen through the coke particle scans available for the run. The approximation for the primary bubble radius for the sponge and mixed morphology cases was chosen in the absence of any available experimental data on primary bubble radius. For mixed morphology of coke the coke particle scans were chosen to determine the primary bubble radius and the same technique that was applied for the sponge coke cases was applied to them . The secondary bubble radius (R_S) is 10 times the primary bubble radius as literature suggests. A table is appended within the report that lists the values of the different input parameters for Pelton's model for the different runs.

The other input parameters were kept the same, that is, Antifoam emulsion droplet radius was R_E, the total volume of liquid phase was V and the volumetric flow of gas into the cylinder was given by Q. The calculation of the parameter G is explained below. As literature suggests, the coagulation efficiency factor for antifoams f, as explained earlier =20,000 for all the runs. The choice in the determination of the input parameters V and G was dictated by Pelton's Model conceptualization as explained in Figure 50.

Antifoam radius(R_E) was assumed to be 3 µm or $9.84*10^{-6}$ ft, which was a realistic value for the radius as suggested in literature[1].

The total volume of liquid phase (V) was taken as the volume of the bubbly liquid layer that was produced on saturation. It was observed that the volume of the liquid layer does reach a saturation (becomes constant) after some time as shown in Figure 52 for the PET 2 resid.

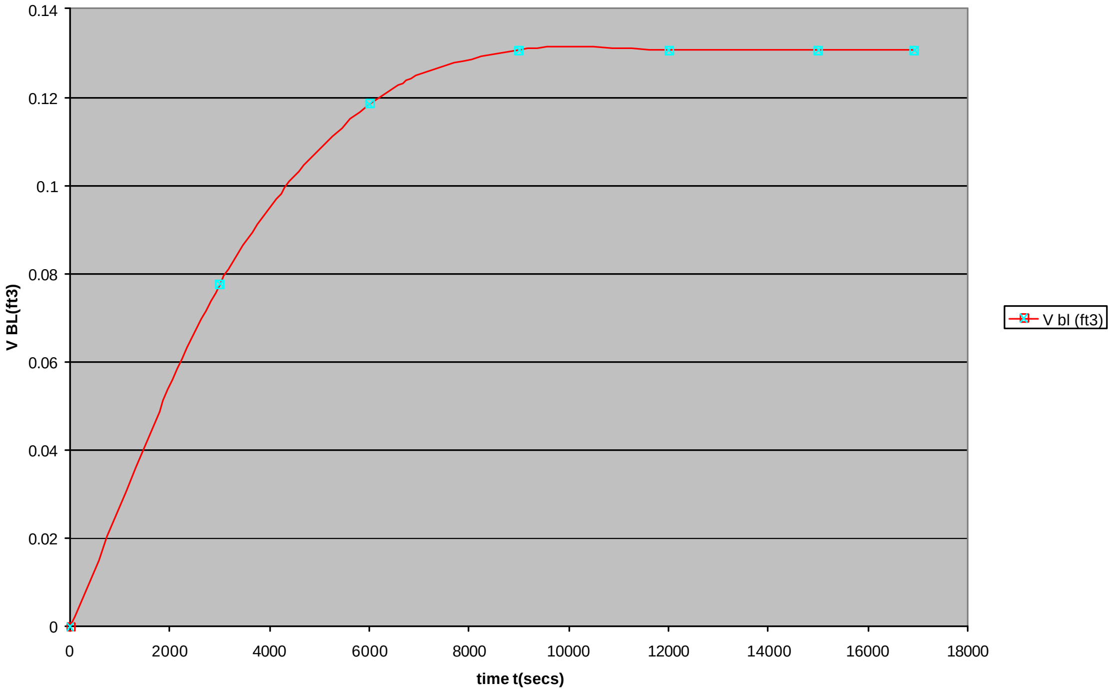


Figure 52 – Constant volume of liquid layer after 150 mins for PET 2

The parameter (G)= [volume of foam produced at saturation stage /total volume of the liquid layer at that stage(V)]. V is determined as explained earlier. The volume of foam at saturation stage was determined from the foam height measured at saturation stage multiplied by the area of the coke drum.

Also Q= the volumetric flow of gas into the cylinder. Now this was directly determined through the Exxonmobil idea of performing HYSYS simulation by taking in the liquid and the gas product streams for the particular run using a mixer and obtaining the vapor flowrate as the outlet stream flow rate out of that simulation. Utilizing the molecular weight of the vapors coming out (obtained through HYSYS)and the run operating conditions and using the ideal gas equation of state, Q was calculated.

From antifoam (AF) data obtained from Baker Petrolite, ?= 84.676 kg/(m)(sec), Specific gravity of antifoam = 0.973,

Here T=temperature for CIT 9 run= 755.22 K (900 F)as obtained from the yield sheets for CIT 9. Also antifoam concentration for CIT 9 as obtained from CIT 9 antifoam data=30cc antifoam/100cc of solution and total antifoam used= 1.56 cc. Hence total AF used amount = 1.56 (Specific gravity of AF) = 1.56(0.973) = 1.517 grams AF. Also density of AF at 60 F from Baker Petrolite data= 60.71 lbs/ ft^3. Hence, utilizing the density of the antifoam and the amount of antifoam injected or used, the initial antifoam concentration can be calculated and is given by E_O= 60.71/(1.517/453.6)= 18144 1/ft3 for CIT 9.

Thus B, g, E(t), d, S(t), VV(t) can all be calculated by the expressions shown earlier. After the calculation of d was completed using the Pelton's Model equations described earlier, the foam volumes VV(t) were determined for the various times t during the run.

The foam heights for different times during the run were obtained from the Gamma Densitometer scans processed for the respective times. The data for obtaining the different time Gamma scans were obtained from spreadsheets from the Delayed Coking Website. Typically the foam development was around the region<0.2 gm/cc in density determined through previous quarterly reports and the bubbly liquid region was around densities>0.2 gm/cc and <0.6 gm/cc.

It was observed during calculation for the various runs with or without antifoam injections that the height of foam and consequently the foam volume increases and decreases during a certain period of time and this period is called the transient state. There is another period during the run preferably towards the ending stage where the foam height and consequently the foam volume is practically constant and this period is called the steady state. The limits of integration used for determination of foam volume integrals in Pelton's model are as follows:

For transient state, upper limit for foam volume integral determination for runs with no antifoam injection= 10z/t_c, where t_c= time for which the foam volumes are calculated and the lower limit=0. For steady state for runs with no antifoam injection, upper limit for the integral= t_{av}* FV(t_{prev})/t_{prev}, where t_{av}=(t_1+t_2)/2, t_1= time for start of steady state, t_2= time when the run ends, t_{prev}= previous time observation just before steady state and FV(t_{prev})= foam volume determined earlier for t= t_{prev}. The lower limit of the integral as usual in this case is 0. For the upper limit of the integral for runs with antifoam injections for the transient state, the upper limit stays the same=10z/t_c and the lower limit=0. For these runs with antifoam effects, for run times during the steady state and at injection time t_{inj}, the upper limit= t_{prev}* FV(t_{prev})/t_{inj} where the terms are as explained previously. The important feature of the Pelton's model is foam volumes slowly rising as time goes on during the run with no antifoam injection and an immediate foam collapse or fall in foam volumes as the antifoam is injected. Antifoam interaction between the foam and the antifoam starts when the antifoam is injected into the system. The antifoam is basically responsible for collapsing the foam after its initial build up. Once the foam volumes are determined, the foam heights(inches) are obtained from the relationship:

Height= FV*12/0.049,
Where FV= Foam volumes(ft^3)determined,
0.049 ft^2= area of the coke drum.

3. *Concept of Model 2*

Model 2 is a continuation in the quest of producing a foam model that relates foaming tendencies to resid properties and is long sought by industries. It is the starting phase in the development of one foaming correlation that will predict foam heights for any run at all times during the run. It is basically extending the foam height results of Pelton's Model and attempts to correlate foam heights for various times during the run with important resid properties, run operating conditions of temperature and pressure, coke morphology, coke pore distribution and antifoam effects(if injected). In order to develop this model it was thus necessary to identify the key components of crude oil that do promote foaming and lead to foam growth. The crude oil components that lead to enhanced foam growth or promote the foam formation suggested in the literature[4] are carboxylic acids and phenols with molecular weight less than 400. Thus it is proposed that the acid number, and nitrogen content (%)of the resid are going to be the key parameters for correlating foam heights with resid properties. Literature also suggests that from the natural surfactant point of view, the asphaltene% and resin% are important for foaming. From the morphology aspect that can affect foaming, literature suggests that the contaminant concentrations of nickel and vanadium are relevant for foaming and also the CCR content of the resid. The coke pore size distribution in the foaming model can be accounted by the interstitial velocity which is in turn the superficial velocity divided by the void fraction of the bed. The two other parameters that are being used for developing the correlation are the run operating conditions, temperature and pressure. All the available data from appropriate spreadsheets for the run characteristics and resid key parameters are tabulated in another sheet and foam heights are calculated for various times during the run utilizing the arrived run specific correlation. Foam heights for various times during the run are the necessary output of this model.

The run specific correlation is as follows:

V2= f*V1

Where f= $[\{A+(N\%/100)+(CCR\%/100)+(ASP\%/100)+(AR\%/100)+(Ni/10^6)+(V/10^6)\}-(E(t)/B)](Y*Q*?*A_C)/(FR*?)$, where the different terms in the equation are as follows:

V2= Foam volumes(ft3)predicted by Model 2 for various times during the run,
V1= Foam volumes(ft3)determined through Pelton's Model correlations for the run,
f= individual dimensionless correlation factor for Model 2(given by the expression) for the particular run,
A= Acid number,
N%= Nitrogen wt % of feed,
CCR%= CCR wt % of feed
ASP%= asphaltene wt % of feed
AR%= asphaltic resin wt % of feed
Ni= Ni ppm content of feed
V= V ppm content of feed
E(t)/B= ratio determined through Pelton's Model correlations and E(t)= number concentration of antifoam(1/ft3) determined for various times t during the run(calculation details explained earlier in the report)
Y= run specific constant factor

=[Gamma densitometer foam volumes(ft3)at steady state/Model 2 predicted Foam volumes(ft3) at steady state determined through the correlation for f without the run specific constant factor Y] which is as follows:

$V2= f*V1$,

$f= [\{A+(N\%/100)+(CCR\%/100)+(ASP\%/100)+(AR\%/100)+(Ni/10^6)+(V/10^6)\}-(E(t)/B)](Q*?*A_C)/(FR*?)$

Q= Pelton's model run operating conditions dependent input parameter explained earlier in the report

?= density of the feed(which is obtained through the API information listed for the different resids)

A_C= area of the coke drum

FR= feed rate(available through the spreadsheets in the Delayed Coking Website for the runs investigated)

?= void fraction of the bed=$1-\{V_T/(V_G+V_L+V_C)\}$,

Where V_T= total volume of the coke drum,

V_G, V_L, V_C are the volumes of gas, liquids and coke produced for the run obtained through correlations suggested in literature. The different feedstock properties are also listed and available through the Delayed Coking Website. The correlation for f has several terms with positive sign attached and the antifoam effect with a negative sign . The signs for the terms were chosen on the basis of their potential impact on the foam volumes and the respective impacts on foaming of the different terms in the equation for f were all checked through available literature. As for example the antifoam effect will gradually diminish the foam volumes and hence the negative sign in the antifoam term in the correlation for f. Once the foam volumes for Model 2 are determined, the foam heights(inches) are obtained from the relationship:

Height= FV*12/0.049,

Where FV= Foam volumes(ft^3)determined,

0.049 ft^2= area of the coke drum.

The final correlation for Model 2 takes the shape:

H2= f* H1,

Where H2= Model 2 predicted foam heights(inches)determined,

H1= Pelton's Model predicted foam heights(inches)determined.

f= same individual correlation factor for Model 2 expressed earlier.

The current correlation for the foaming model is a good starting point taking into account the various factors that different literature describes as having a potential impact on foam development and collapse and is in good agreement with the Gamma densitometer foam heights determined.

4. *Results Attained Using Model 2 and Comparison with Pelton's Model and Gamma Densitometer Findings*

Using the mathematical relationship described earlier, the individual run specific correlations for Model 2 were determined. Once the correlations for the individual runs were determined the foam height results for the various times during the run were compared with the results with Pelton's Model and the foam heights determined earlier through Gamma Densitometer findings and adjusted run specific correlations were attained.

One of the run specific comparison plots comparing adjusted Model 2 foam heights with Pelton's Model and Gamma Densitometer foam heights is shown in Figure 53 and Figure 54.

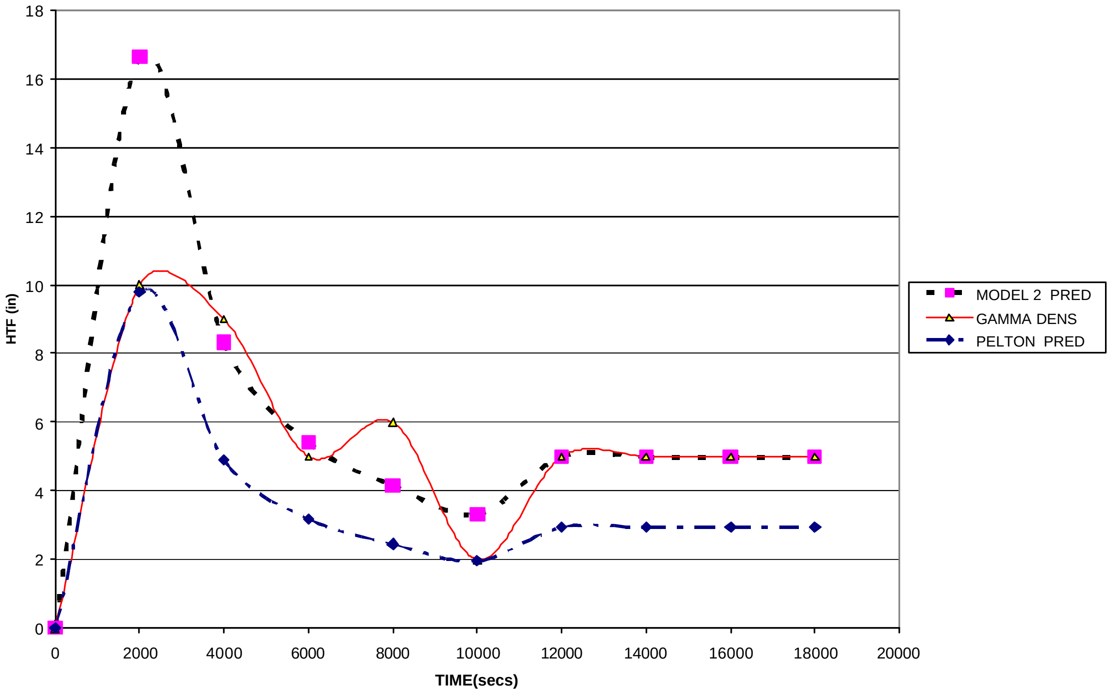


Figure 53 – Foam height comparisons done with the Models and Gamma Densitometer findings for CHEV 3 run(here the y axis represents foam heights and the x-axis, time during the run foam heights are calculated)

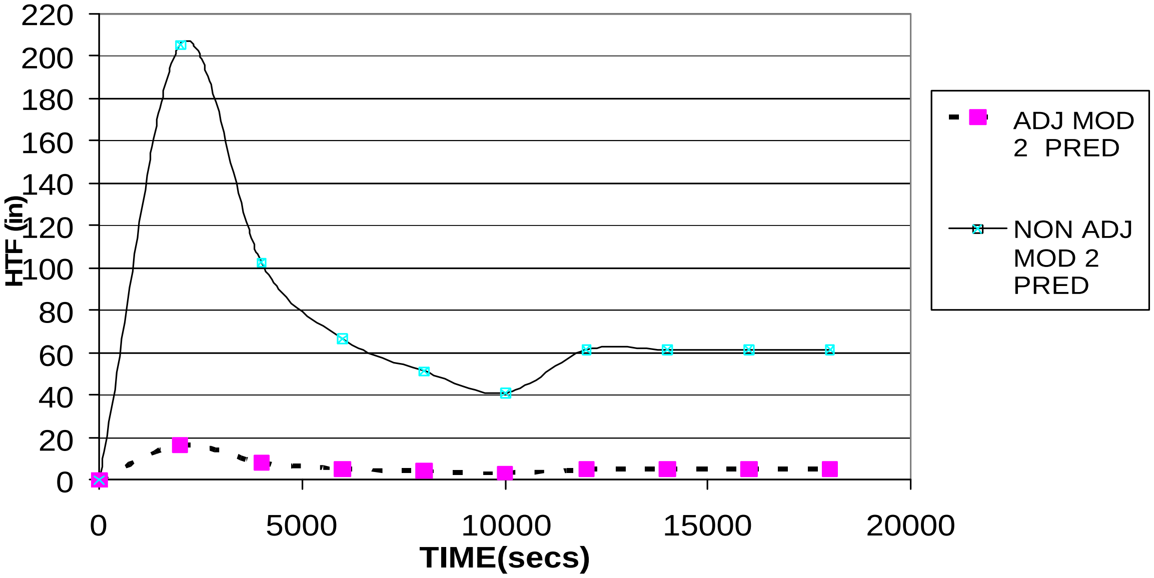


Figure 54 – Foam height comparisons done with the Model 2 Adjusted and Non adjusted for CHEV 3 run (here the y axis represents foam heights and the x-axis, time during the run foam heights are calculated)

5. *General Principle of Working for the Model*

The salient features of the model developed from Pelton's model are:

1. The model predicts foam heights for various times during a pilot unit run and can also be used to calculate the same for the resids at refinery conditions.
2. The model can predict foam heights in the absence of any antifoam and also predict what the foam heights are going to be after an antifoam injection.
3. The model accounts for the important driving forces behind foaming described in literature with a neat correlation involving feedstock properties that are relevant to foaming, feedrate, antifoam effects(if injected) and run specific operating conditions of temperature and pressure.

The basic inputs for the model are given by:

- R_P , the primary bubble radius.
- R_S , the secondary bubble radius.
- R_E , the antifoam radius.
- V , the total volume of liquid phase.
- G , gas volume fraction in the liquid phase.
- Q , volumetric flowrate of vapors leaving.

The auxiliary inputs that the model requires are as follows:

- Temperature of the run
- Pressure
- Feedrate
- The antifoam coagulation efficiency factor, f
- Times(t) for which the foam heights have to be determined.
- Antifoam used amount (if used at all)

- Viscosity of the feedstock.
- Feedstock property data namely,

  AR= Asphaltic resin Wt% of the resid, GO= Gas oil Wt % of the resid, N= Nitrogen Wt% of the resid, ASP= Asphaltene Wt% and Si and Fe are the solid metal content of the resid in ppm.

As can be seen, foam heights for various times during the run(currently the model predicts foam heights at a time interval of 9 mins)are the output of the model. The model calculations were primarily done on Excel spreadsheets with HYSYS used as required .

6. *Important Updates in Calculation of Foam Heights with the Model*

For the pilot unit, the primary bubble radius R_P was chosen to be equal to the smallest void size that could be measured through the coke particle photos or bottom of the coke drum actual coke samples available for the run. This approximation for the primary bubble radius was chosen in the absence of any available experimental data on primary bubble radius. The secondary bubble radius (R_S) is 10 times the primary bubble radius as literature suggests. For the resids at refinery conditions, the Mercury injection pore throat size histograms were utilized to compute the weighted mean from the distributions in the micro and macro levels to obtain the values of R_P and R_S respectively.

The total volume of liquid phase (V) was taken as the volume of the bubbly liquid layer that comes out from a correlation with run operating temperature, pressure and feed rate. The correlation that was obtained through regression techniques in Excel is as follows for the resids at refinery conditions:

$$V= -2.657T+20.633P+0.0019(Tr\times FR)$$

where V is expressed in ft^3, T is temperature expressed in degrees F, P is pressure expressed in psig, Tr is the total run time in secs, FR is the feed rate in lbs/sec.

For the pilot unit, the expression for V obtained earlier for the resids at refinery conditions was scaled down by a factor 173716.19 and finally the magnitude was considered to get the expression for V which is as follows:

$$V= ¦ (-1.53\times10^{-5}T)+(1.19\times10^{-4}P)+(1.094\times10^{-8}Tr\times FR)¦$$

where V is expressed in ft^3, T is temperature expressed in degrees F, P is pressure expressed in psig, Tr is the total run time in secs, FR is the feed rate in lbs/sec.

The scale down factor of 173716.9 comes out by simply taking the ratio of average refinery coke drum volume to pilot unit coke drum volume.

The parameter (G) is given by the expression:

$$G=1-(?_{BBL}/?_{F})$$

where $?_{BBL}$ = density of the bubbly liquid layer based on Gamma Scan densities for each run and $?_F$ = density of the feed (readily available from the API information for the different feedstocks).

The calculation procedure for the input parameter Q remains the same as in previous report.

The foam volume change(ft^3)for each 9 min time span during a run ?FV is given by:

$$?FV= 5V_t\, Q(1-1/g)^d\, A^*(e^{0.488SV})A_C t_R(\, ?t^*)^2/V^2(t-z)(FPF)^2 \;\ldots\ldots\ldots\ldots\ldots\; (10)$$

The relationship was attained through a physical understanding of foam behavior and keeping in mind the dimensional consistency of the equation on both sides. In the equation, V_t is the total coke drum volume(ft^3),

?t*=average time interval in secs, at which the foam height calculations were done
= 270 secs for each run,
A*=8×10^{-6},
A_C= area of the coke drum(ft^2),
t_R=total run time in secs,
SV in the exponential expression = superficial velocity of vapors(ft/sec)at drum inlet,
FPF is the foam promoting factor for each resid that is calculated by the expression given by:

$$FPF= (AR/100)(GO/100)(N/100)/(ASP/100)(Si+Fe)/1000000$$

where AR= Asphaltic Resin Wt% of the resid,
GO= Gas oil Wt % of the resid,
N= Nitrogen Wt% of the resid,
ASP= Asphaltene Wt%
and Si and Fe are the solid metal content of the resid in ppm.

The respective feedstock information are obtained from readily available feedstock data for each resid. The FPF factor is dimensionless as a result of incorporating weight fractions and was built on basis of a famous mathematical Law of Joint Variations which goes as follows:

If x directly varies with y when z is constant and if x also directly varies with 1/z when y is constant then the product x^2 directly varies with y/z.

The implication of this rule is that factors that contribute to foam heights can be grouped together and inserted in the numerator of the factor FPF and factors that will deplete foam heights will go into the denominator of the factor FPF provided obviously that other factors that impact foam heights are constant. By other factors the factors that are referred are run operating temperature, pressure and feedrate and run specific antifoam effects(if injected at all). The different terms in the right hand side of the equation for foam volume change(?FV) were grouped together utilizing the law of Joint Variations. The term

$Q(1-1/g)^d$ comes directly out of Pelton's model correlations and is directly related to foam volume change whereas the other terms are accumulated in the following fashion:

The foam volume change(?FV)on basis of a physical understanding of foam behavior was considered to be mathematically directly related to some fraction of the total coke drum volume and also directly proportional to the probability for foam development=

(1-1/g) described by Pelton. ?FV is also inversely proportional to the total volume of liquid phase(V) and to a particular cofactor of total residence time[(t-z)term in the right hand side of the equation] of a bubble leading to foam development. That particular factor comes out from the feedstock FPF factor. Thus utilizing the law of joint variations,

$$?FV=5V_t\, Q(1-1/g)^d\,(1-1/g)(\, ?t^*)^2/V(t-z)(FPF)^2 \ldots\ldots\ldots\ldots\ldots\; (11)$$

Now the algebraic quantity $V(1-1/g)/A_C t_R$ represents physically the total liquid drum velocity(ft/sec)contributing to foam development. This quantity for forty eight pilot

unit runs was plotted in Excel with superficial velocities SV(ft/sec) at drum inlet computed for the runs and by utilizing the mathematical tools of Excel, the relationship attained for the maximum R^2 value was:

$$V(1-1/g)/A_C t_R= A^* e^{0.488SV} ,$$

where, $A^*= 8\times10^{-6}$.

from this relation, $(1-1/g)= A^* A_C t_R e^{0.488SV}/V$ and replacing this expression for (1-1/g) in Equation(11),

$$?FV= 5V_t\, Q(1-1/g)^d\, A^*(e^{0.488SV})A_C t_R(?t^*)^2/V^2(t-z)(FPF)^2$$

which is Equation (10) discussed earlier. The factor 5 in the right hand side of the relation helps in obtaining foam height results in the vicinity of results attained through Gamma scans.

Once the foam volume changes are determined, the change in foam heights(inches) for each of the 9 min time spans are obtained from the relationship:

$$?\text{foam height}= ?FV\times12/0.049\ldots\ldots\ldots\ldots\ldots (12)$$

where ?FV= foam volume change(ft^3)determined,

0.049 ft^2= area of the coke drum.

A cumulative consequtive summing technique was adopted for determining the foam height values for different times from ?foam height for the pilot unit. For antifoam injections, a negative sign was attached for ?foam height expression(foam height depletion)shown in Equation(12).

For the foam heights calculated for the resids at refinery conditions, the same antifoam settings like the same initial antifoam number concentration(1/ft^3) and continuous injection from start to end were applied to get a prediction of foam heights, bubbly liquid heights and coke heights for various times during the run. The bubbly liquid height comes out from the same correlation for V(ft^3) considering the magnitudes of the individual coefficients in the expression for V and then dividing it by the coke drum area considered for the particular resid run. The drum dimensions for the Citgo resid for refinery conditions was 27 ft diameter, 98 ft height. For the five other resids investigated with refinery conditions, a drum diameter of 30 ft and height of 80 ft was considered. The correlation for determination of bubbly liquid heights for the resids at refinery conditions is :

$$H_B= [2.657T+20.633P+(0.0019\times t\times FR)]/A_{CC}$$

where, H_B= height(ft) of bubbly liquids for a particular time t(secs),
T=temperature expressed in degrees F,
P is pressure expressed in psig,
t is the time in secs for which the bubbly liquid heights are predicted,
FR is the feed rate in lbs/sec,
A_{CC} is the area of the coke drum(ft^2)considered for the resid run at refinery conditions.

The coke height predictions for various times during a resid run at refinery conditions were calculated by developing a correlation that describes the coke heights as the sum of mathematical contributions from the feed plus the contribution due to the linear growth rate of coke height(from pilot unit observations). The mathematical contributions were scaled up by suitable numerical coefficients determined through available refinery coke height data to get predictions for the resids at refinery conditions. For example for Citgo, the correlation developed was:

$$H_C = 1.1543(x)^{0.1821} + 4.142(GR)t,$$

where, H_C= coke height(ft) predicted for time t(secs) for Citgo,
GR= coke height linear growth rate for Citgo(ft/sec),
t= time(secs) for which the coke heights are being predicted,

$$x = (t \times FR)/(?_F \times A_{CC})$$

where t= times(secs),
FR=feed rate(lbs/sec),
$?_F$=density of the feed(lbs/ft^3),
A_{CC} is the area of the coke drum(ft^2)considered for the Citgo run at refinery conditions. As can be seen the dimensions of the algebraic quantity x is ft. A plot showing the distribution of foam heights, bubbly liquid heights and coke heights for the Citgo resid at refinery conditions has been appended in the results section. Incidentally, the total run time considered for all the resids at refinery conditions was 16 hrs whereas in the case of Marathon, a 12 hr total run time was considered as it was specifically known from the refinery data available.

The foam heights for different times during the pilot unit run were also determined from the Gamma densitometer scans processed for the respective times for comparison purposes. The data for obtaining the different time Gamma scans were obtained from spreadsheets from the Delayed Coking website. Antifoam interaction between the foam and the antifoam starts when the antifoam is injected into the system. The antifoam is basically responsible for collapsing the foam after its initial build up.

7. *Foam Height Results and Comparison for the Pilot Unit*

A pilot unit run specific comparison plot comparing the model and Gamma densitometer foam heights for the first Chevron resid test is shown in Figure 55.

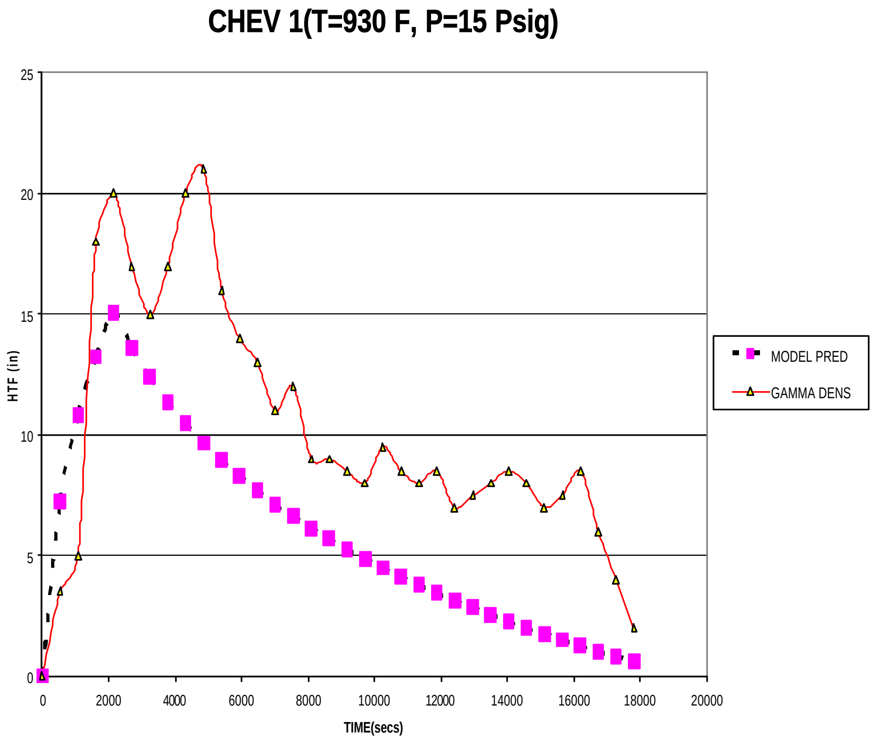
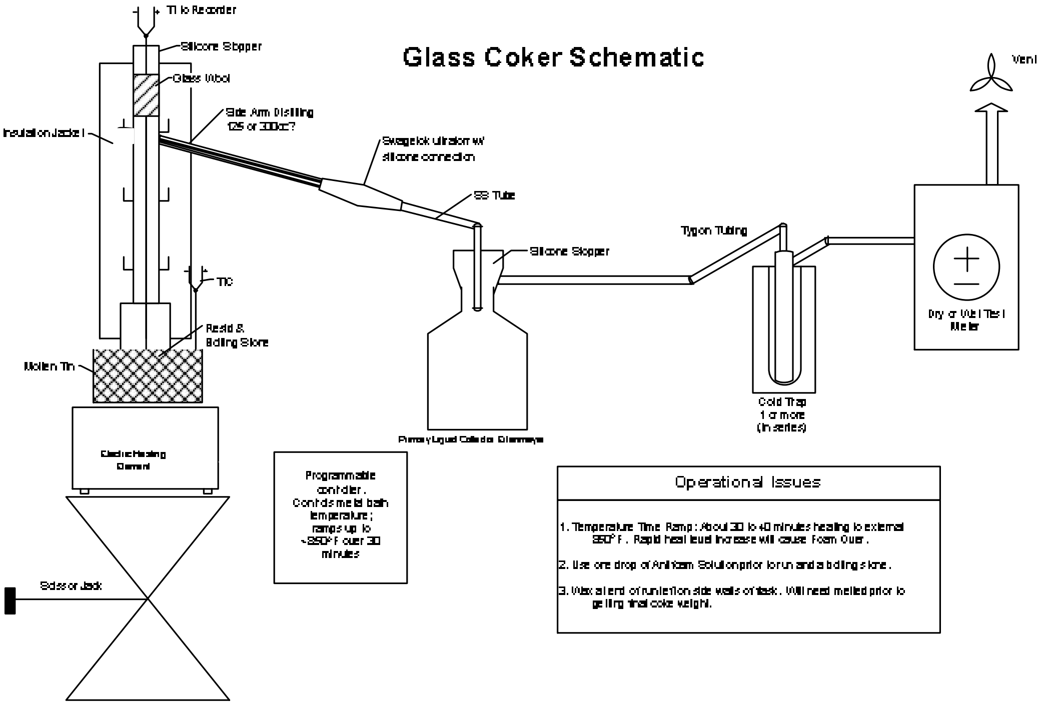


Figure 55 - Foam Height comparisons for different Chevron pilot unit runs
(here the y axis represents foam heights in inches and the x-axis, time in secs, during the run foam heights were calculated)

8. *Testing the Impact of Feedstock Properties on Foam Heights using a Glass Coker*



Glass Coker Schematic

Programmable controller. Controls metal bath temperature; ramps up to ~850°F over 30 minutes

Operational Issues

1. Temperature Time Ramp: About 30 to 40 minutes heating to external 850°F. Rapid heat level increase will cause Foam Over.
2. Use one drop of Antifoam Solution prior to run and a boiling stone.
3. Wax at end of run left on side walls of flask. Will need melted prior to getting final coke weight.

9. *Conclusions*

At this time, the “first pass” model is capable of predicting foaming trends for the individual pilot unit runs as well as for resids investigated at refinery conditions. This model interrelates the major variables that contribute to foam heights through a physical understanding of upward gas bubble movement in the coke drum and factors that can impede the upward movement when using the model to make predictions.

Higher foam heights are observed for Marathon, Petrobras and Chevron resids, at higher feedrates and at a lower temperature(900 F) and pressure(15 psig).

While higher foam heights are observed for the Equilon and Citgo resids at higher feedrates and higher pressure(40 psig).

10. *Future Work*

The following work will be completed in order to improve the predictability of the foam model:

- Refine or innovate the existing model correlations as necessary to increase the efficiency of the model.
- Perform the Glass Coker tests as outlined in this report so that the feedstock property effect is investigated thoroughly and quantified accordingly in the prediction of foam heights.

C. DETAILED HYDROCARBON ANALYSIS

Detailed liquid analyses conducted on the pilot unit liquids include sulfur analysis, silicon analysis, API gravity, and Detailed Hydrocarbon Analysis (DHA) on the lighter liquids, which includes PIONA and RON analysis.

1. *API gravity*

API gravity for the liquid sub-products was correlated with overhead temperature, pressure, and the micro-carbon residue of the feed. A plot of model vs. experimental API gravity is shown in Figure 57. Note that API gravity is predicted within ±10% for nearly all the data.

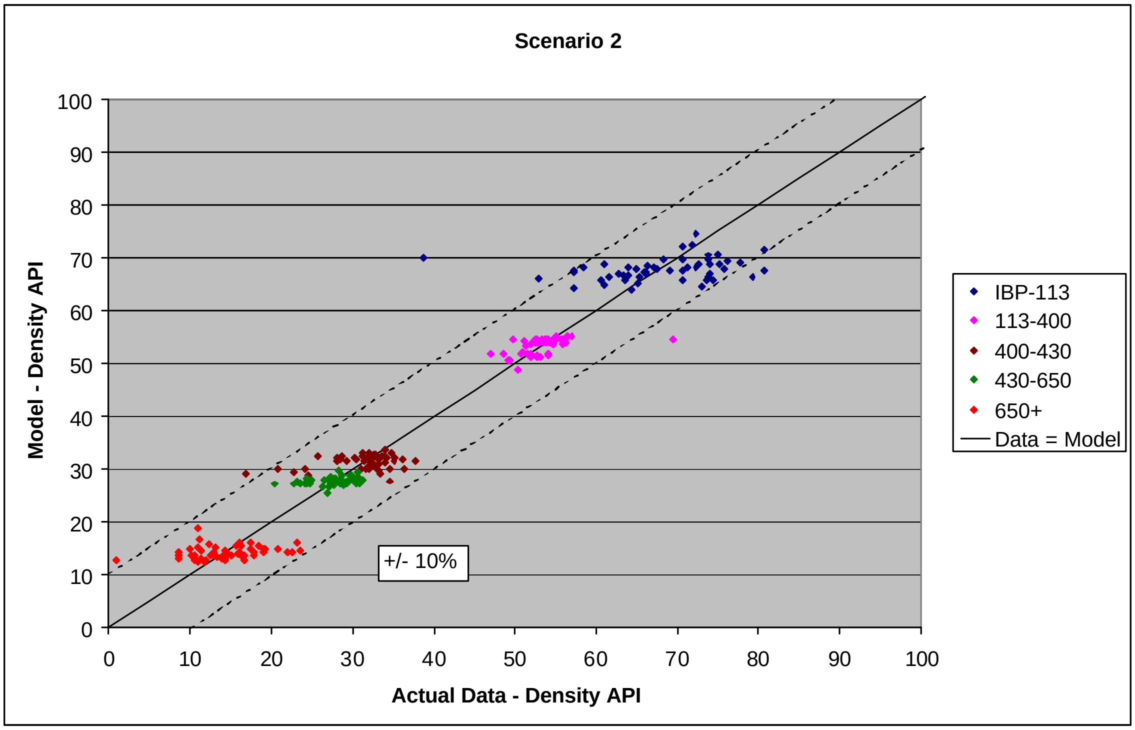


Figure 57 – Actual vs. Predicted API Gravity of Liquid Sub-Products

2. *PIONA correlations*

Paraffin, iso-paraffin, olefin, naphthene, and aromatic content for the IBP-113ºF, 113-400ºF, and 400-430ºF cuts were found from DHA using the HP6890a high temperature gas chromatograph. Correlations were produced both for the raw data and for the normalized data (since there was a fair % of unknowns, especially for the 400-430ºF cut). It was found however, that normalizing the PIONA numbers did not improve the correlation. Comparisons of the model predictions with experimental data are presented in Figure 58 to Figure 63.

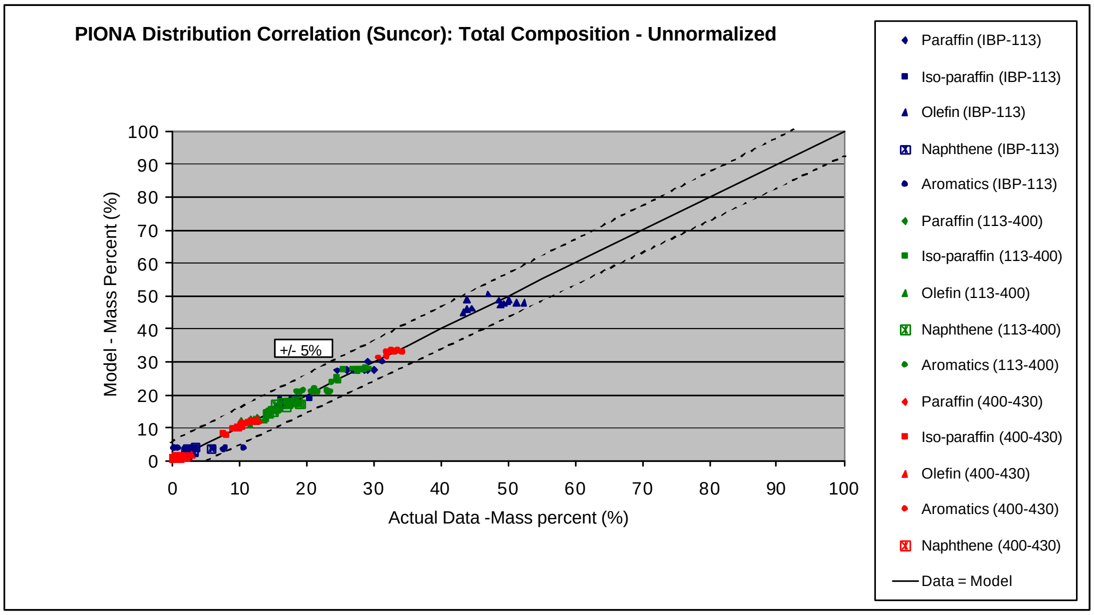


Figure 58 – Suncor PIONA Distribution Correlation (Un-normalized)

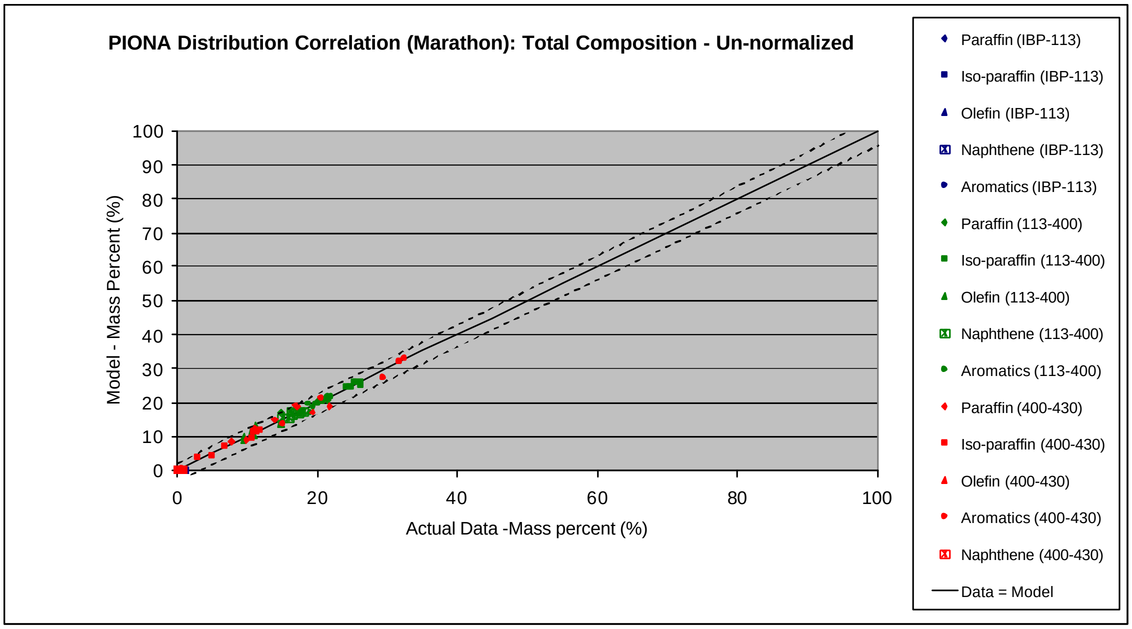


Figure 59 – Marathon PIONA Distribution Correlation (Un-normalized)

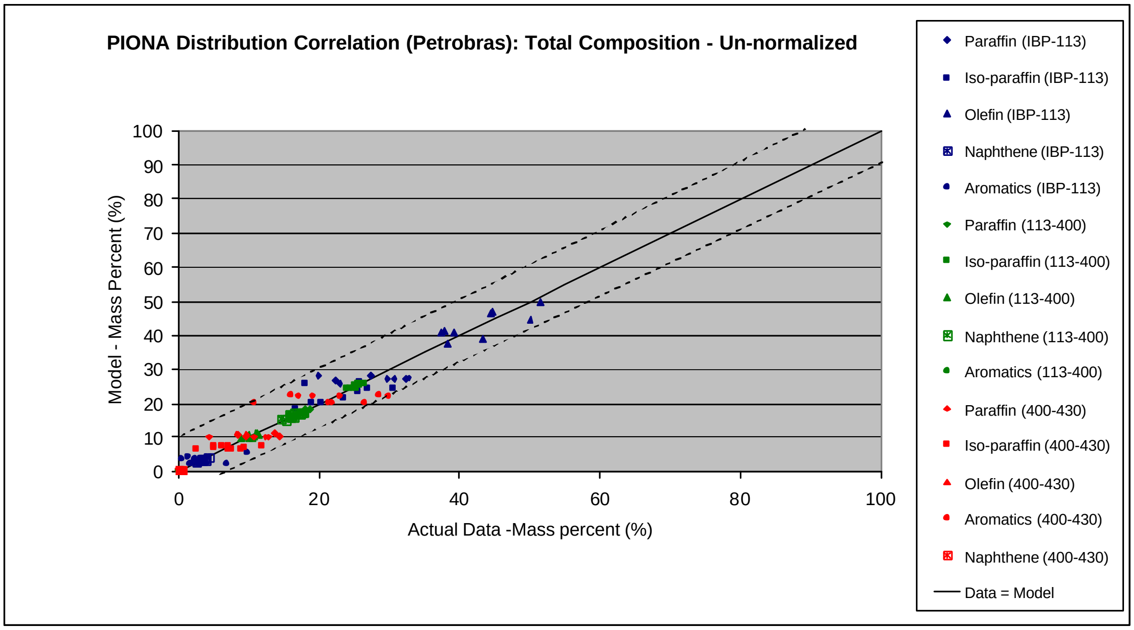


Figure 60 – Petrobras PIONA Distribution Correlation (Un-normalized)

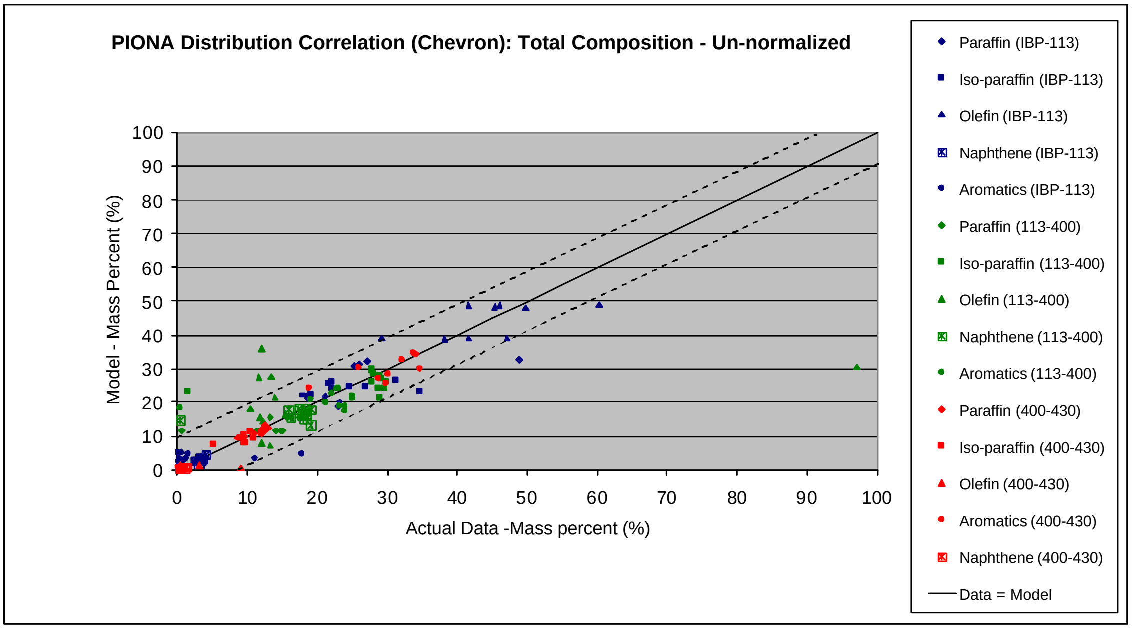


Figure 61 – Chevron PIONA Distribution Correlation (Un-normalized)

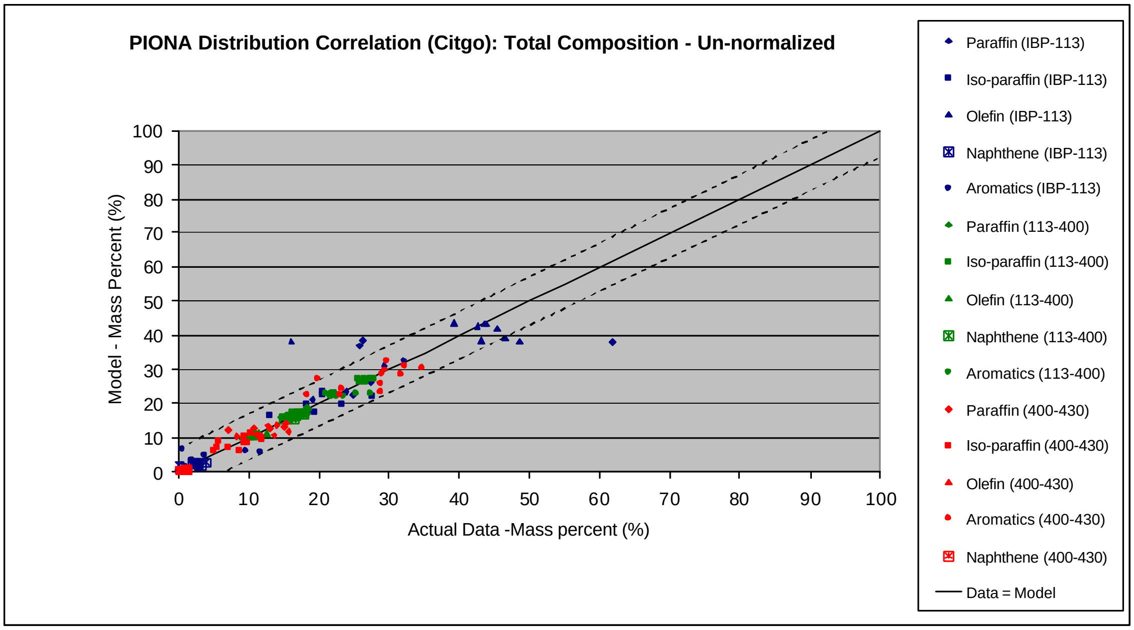


Figure 62 – Citgo PIONA Distribution Correlation (Un-normalized)

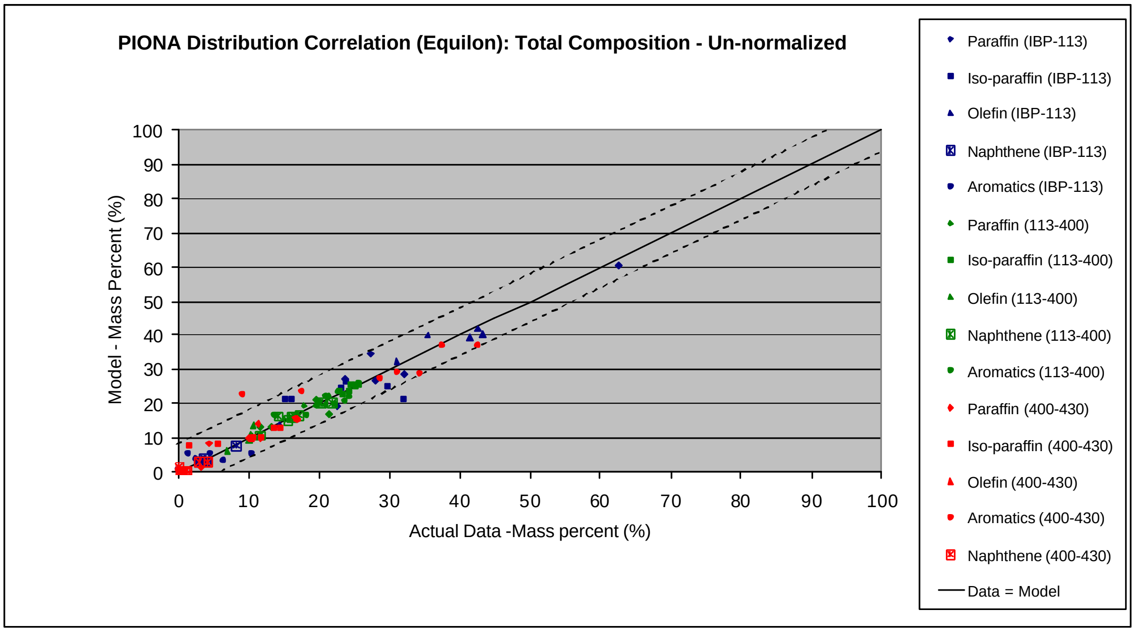


Figure 63 – Equilon PIONA Distribution Correlation (Un-normalized)

Several points are worth noting concerning the feedstock effect on the PIONA. First, the effect of feedstock and of temperature and pressure were clearly discernable. Generally, the paraffins and aromatics increase and the iso-paraffins, olefins, and naphthenes decrease as pressure is raised. On the other hand, the paraffins and aromatics generally decrease with increasing temperature, while the olefins and naphthenes generally increase.

Second, the feedstock characteristic (paraffinic, naphthenic, or aromatic) is sometimes, but not always, an indicator of the characteristics of the liquid products. For example, the Marathon resid is a paraffinic feeedstock, having the highest NMR saturate to aromatic ratio (2.7) of all the feedstocks, and it makes the highest percentage of paraffins of all the feeds. Likewise, the Chevron resid, which is characterized as a naphthenic feed, consistently has the highest percentage of naphthenes in the liquid products. However, the Citgo resid, which is characterized as an aromatic resid and has the lowest NMR saturate to aromatic ratio (1.9) of all the feedstocks, does not make the most aromatic liquid products.

3. *RON analysis*

Research octane number (RON) for the light liquids, were determined by DHA. The results show the highest RON with the least variation with resid for the IBP-113ºF cut, and the lowest RON with the greatest variation for the 400-430ºF cut.

A good correlation between RON numbers and the PIONA results was found.

4. *Sulfur analysis*

Sulfur analyses on the hydrocarbon liquid sub-fractions, carried out on the HP6890a chromatograph, showed variations when different dilution factors were used. This indicated that the dilution factor used was insufficient to prevent the column from being saturated, thus leading to potentially false readings. Samples are being re-run and the proper dilution factor is being determined.

5. *Silicon partitioning*

Partitioning of the silicon from antifoam addition was correlated against total silicon added. It was assumed that any feed silicon present was in the form of sand, which would remain in the coke. In general, most of the Silicon partitioned in the HC.

D. ***COIL FOULING***

The coil fouling data base was updated with the results from the runs using the three new resids. These resids have API's that are lower than the six resids used in the first phase of study. The lower the API the higher the fouling. A trend in pressure was also seen, that is, the higher the pressure, the higher the fouling rate. To put the data in a form that is more useable by the refinery operators, a fouling rate per unit surface area (gms/ft^2-hour) was calculated. Future studies will include examination of the pressure data to establish the pressure change per unit mass deposited as well as a temperature change on a per hour basis. Deposits will also be removed from the coils to try and determine an equivalent thickness per unit weight.

E. ***STEAM STRIPPING STUDIES***

Previous reports have discussed changes occurring in the coke bed during steam stripping as revealed by gamma densitometry measurements. Table 32 shows the run conditions for pilot unit runs completed since the first annual report. All runs used 40 g/hr steam and 0.50 SCFH nitrogen, and steam stripping was done for identical times and steam flow rates for each run. Note that volatile matter testing of the coke is still pending for many of these runs.

Table 32 – Pilot unit run conditions

Sample ID	Date	T	P	Rec.	Feed Flow Rate	Run Length	Overhead Temp. (TI208)			Density of Coke	%VM	%VM	%
		(^{0}F)	(psig)		(g/hr)	(hrs)	Avg (^{0}F)	Min (^{0}F)	Max (^{0}F)	(g/cm3)	top	btm	loss
SUN14PUAF	9/11/2003	900	15	none	2391.43	3.50	792	743	812	0.46	12.3	9.5	5%
SUN15PUAF	9/17/2003	900	15	5%	2404.4	4.50	803	780	880	0.69	11.5	9.7	8%
SUN16PUAF	9/25/2003	900	15	10%	2398.9	4.50	818	801	904	0.60	13.3	8.8	5%
SUN19PUAF	11/11/2003	928	38	5%	3620	3.50	814	758	831	0.74	9.6	8.1	6%
MARA8PUAF	11/18/2003	900	15	none	2413	5.00	790	736	801	0.67			6%
MARA9PUAF	11/21/2003	900	15	15%	2433	5.00	799	739	816	0.69			13%
MARA10PUAF	12/2/2003	900	15	10%	2396	5.00	790	721	800	0.68			11%
MARA11PUAF	12/19/2003	900	15	5%	3618.5	4.05	810	798	831	0.52			17%
MARA12PUAF	1/8/2004	900	15	10%	3601.3	4.00	802	778	812	0.58			13%
MARA13PUAF	1/14/2004	930	15	none	1226	5.00	835	806	884	0.75			-6%
MARA14PUAF	1/21/2004	930	40	none	1220	5.00	814	801	831	0.87			9%
MARA15PUAF	1/27/2004	930	40	none	3588.8	4.00	821	771	833	0.56			14%
MARA16PUAF	1/30/2004	930	40	none	4786.7	3.00	827	745	862	0.77			7%
SUN21PUAF	2/11/2004	930	40	none	1188	5.00	813	793	834	0.75	8.9	7.4	6%
SUN22PUAF	2/17/2004	900	15	none	3610.9	3.50	808	754	830	0.65	8.7	7.7	21%
SUN23PUAF	2/20/2004	900	40	none	3618.9	3.50	819	769	856	0.70	8.0	6.8	8%
SUN24PUAF	3/2/2004	930	40	none	3582.3	3.00	840	789	867	0.83			7%
SUN25PUAF	3/4/2004	930	15	none	4726.4	3.15	840	789	867	0.76			17%
SUN26PUAF	3/16/2004	930	40	none	4775.4	3.13	844	794	877	0.67			2%
SUN27PUAF	3/19/2004	930	40	none	6038.3	2.43	839	775	877	0.70			4%
SUN28PUAF	3/24/2004	930	40	100%	2264.3	3.50	825	812	844	0.77			1%
MARA17PUAF	3/26/2004	930	40	100%	2360.4	5.00	827	792	838	0.81			-1%
EMCN1PUAF	4/1/2004	900	15	none	3613.7	3.50	812	793	827	0.55			8%
EMCN2PUAF	4/6/2004	900	25	none	3595.4	3.66	801	786	805	0.80			4%
EMCN3PUAF	4/8/2004	900	35	none	3582	3.50	794	781	820	0.77			5%
EMCN4PUAF	4/13/2004	900	45	none	3589.7	3.00	810	594	845	0.78			7%

The last column of Table 32 shows the % loss of mass in the coke bed following steam stripping. Runs MARA 13 PUAF and MARA 17 PUAF actually show a gain in mass. The 1% gain in mass for MARA 17 PUAF probably reflects random error, as the gamma scans before and after steam stripping looked nearly identical. For run MARA 13 PUAF, the gamma scans before and after steam stripping also appeared very similar. The increase in mass is due to additional material which appears 3 to 4 inches above the bottom of the drum after steam stripping, and is probably material which was displaced from lower in the bed but was not well detected due to the flange at the bottom of the coke drum, which blocks the density readings.

The loss of material from the bed is plotted in Figure 64 through Figure 69 against feed temperature, pressure, average overhead temperature, coke density, feed flow rate, and run length. These results show that there is a trend toward increased mass loss for runs at low temperature, low pressure, and low coke density. There is no particular trend with feed flow rate or run length.

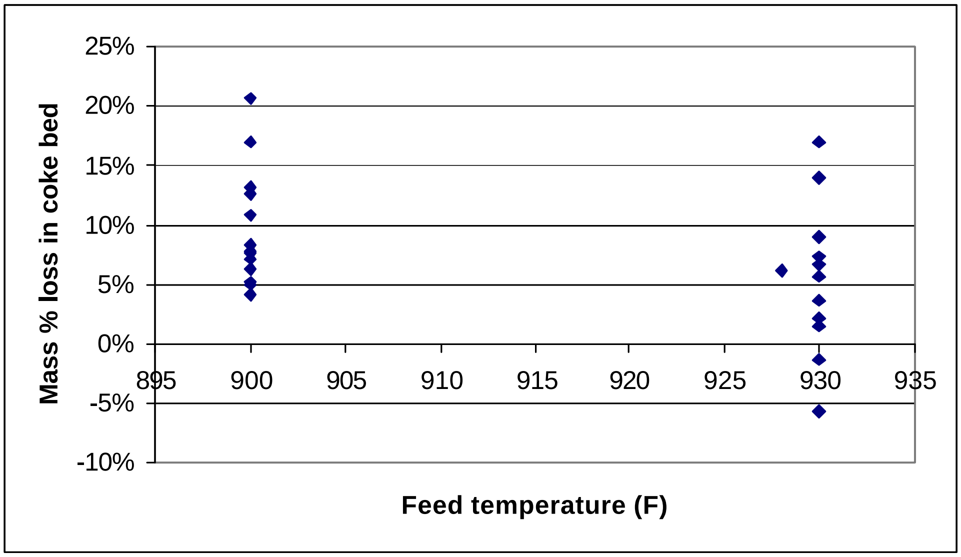


Figure 64 – Mass loss from steam stripping vs. feed temperature

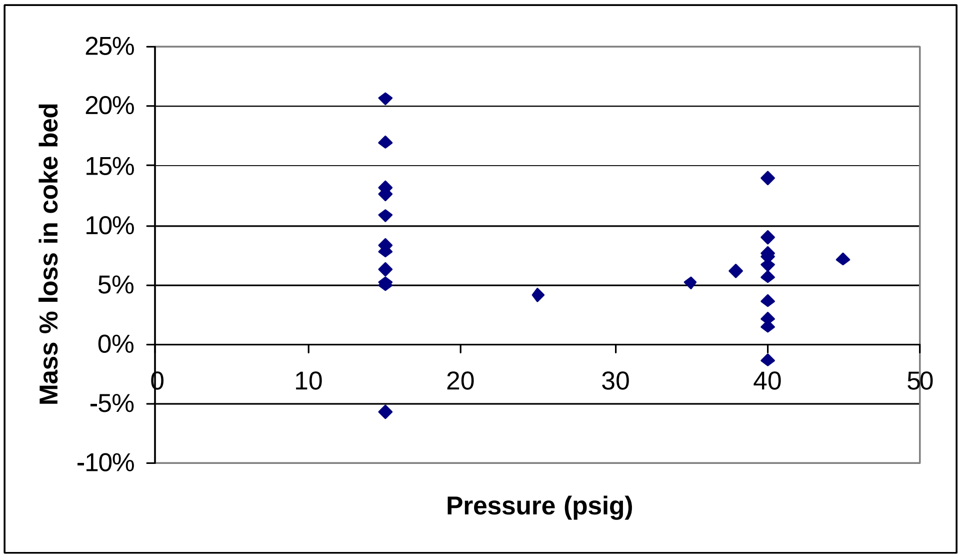


Figure 65 – Mass loss from steam stripping vs. pressure

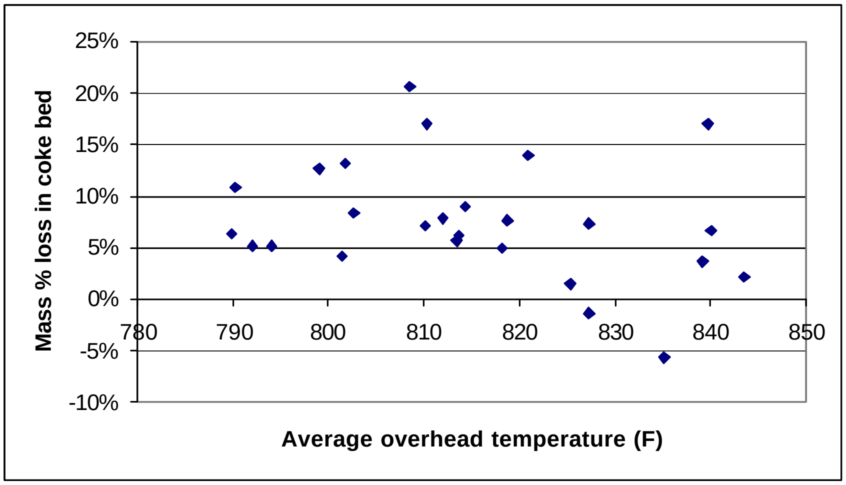


Figure 66 – Mass loss from steam stripping vs. average overhead temperature

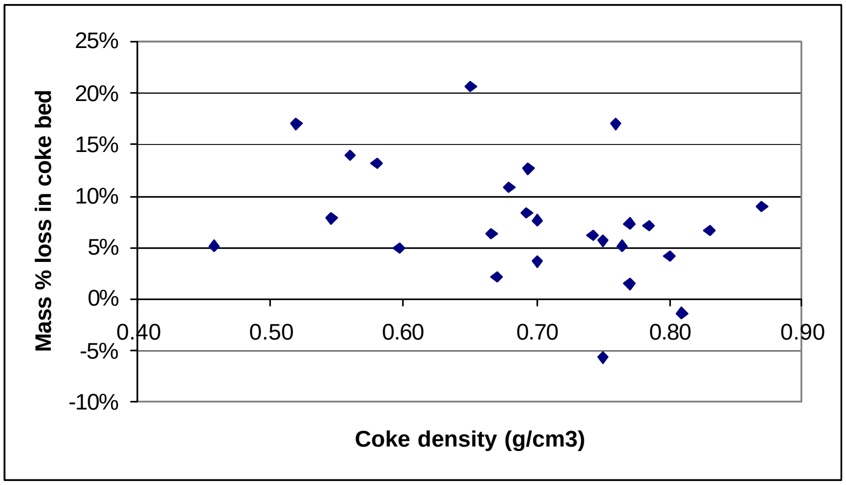


Figure 67 – Mass loss from steam stripping vs. coke density

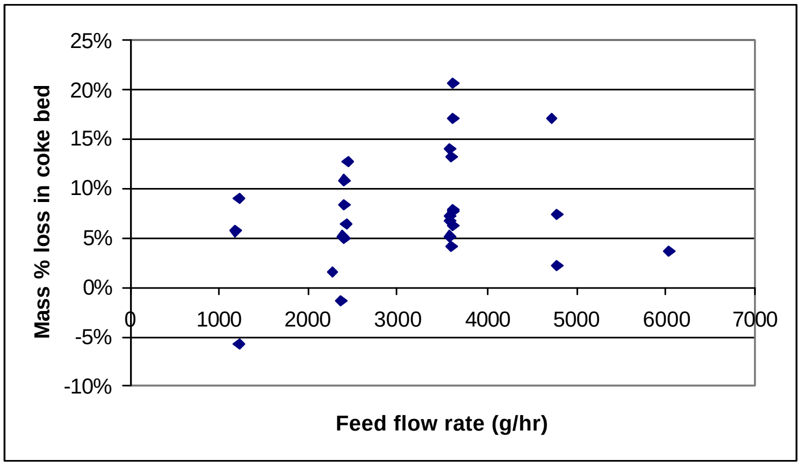


Figure 68 – Mass loss from steam stripping vs. feed flow rate

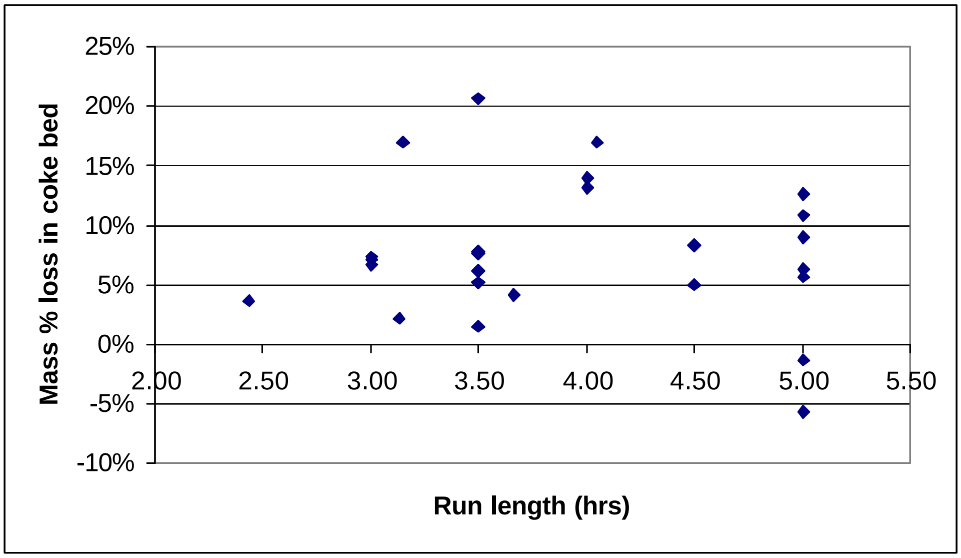


Figure 69 – Mass loss from steam stripping vs. run length

Table 32 shows the net loss of mass of coke, but for many cases steam stripping causes a displacement of material within the coke bed without much net loss of mass. Run MARA 12 PUAF was a case where material is lifted from the upper portion of the bed (35-49 inches from the bottom) and deposited higher up (49-59 inches from the bottom).

Run SUNC 16 PUAF illustrated a case of bed slumping, where steam stripping caused the top of the coke bed to drop by about 5 inches, while increasing the density of the coke throughout the bottom of the bed.

In some cases where material is lost from the bed, the top of the bed is preferentially depleted,. In other cases, material at the top of the bed remains relatively unchanged, while material is depleted elsewhere from the bed. Run SUNC 14 PUAF had material depleted both from the top and the middle of the bed. Other Suncor runs, however, had little or no loss of material (runs SUNC 15 PUAF, SUNC 19 PUAF, SUNC 21 PUAF, SUNC 27 PUAF, and SUNC 28 PUAF.

None of the Heavy Canadian runs showed any significant loss of material from the top of the bed during steam stripping. In some of the runs, with feed temperatures of 900ºF, there was a small amount of bed material lost from near the bottom of the bed.

13. Morphology Studies

A. *COKE MORPHOLOGY*

1. *MICP Results*

Mercury Injection

This technique requires injection of a 1" core plug of coke material with mercury at incremental increases of pressure. The volume of mercury injected at each pressure is recorded. Since fluid flow is controlled by the narrowest connections between void space, capillary pressure tests provide information about the pore throats of the total porosity network. A distribution curve can be derived relating pore volume to mean throat diameter. This test is necessary to characterize the pore-throat network in 3-D. Nineteen coke samples were sent to Core Laboratories and two coke samples to PMI for Mercury Injection Capillary Pressure analysis (MICP).

Samples for MICP measurements were selected using the following criteria:

1. Coke morphology highest frequency.
2. Taking into account the range of resids.
3. Variety of coke morphology.
4. Samples with known porosity and permeability.

Apparent injected mercury volumes were corrected using a conformance value determined for each sample from a plot of the apparent injected volume versus injection pressure. The conformance value is the volume of mercury pressed into surface roughness and around sample edges after the penetrometer chamber is initially filled. This volume is subtracted from all subsequent apparent injection volumes.

Due to the nature of the coke samples, some mercury invaded large surface pores (greater than 200 microns diameter) during the 0.5 psia initial fill of the penetrometer, reducing the apparent bulk volume of the sample. This volume was corrected by adding mercury to the apparent injected volume. The final (in-situ) Micromeritics volume returned to atmospheric pressure was equalized with the actual residual mercury volume calculated by a gravimetric determination after removal from the instrument.

2. *Pore Throat Size Distribution*

Pore throat size distribution was calculated from the mercury injection test results. These data are typically used for pore geometry characterizations and comparisons. Pore throat size distribution can often help to evaluate the results of other analyses performed on the same or similar companion, samples. Textural effects and pore size distribution are major factors affecting irreducible water saturations.

In general, pore throat radius can be divided into several categories which can be used in the classification and grouping of the test samples. Microporosity is often defined as pore throat radii of less than 0.50 microns. The following classification is utilized for this discussion:

Number	Classification	Minimum	Pore Radius, microns
Classification	Pore Radius	Maximum	
1	micro	<0.50	0.50
2	meso	0.50	2.5
3	macro	2.5	>10.

Macro pore size distributions were commonly found in sponge coke. Meso porosity doesn't seem to have a significant influence on porosity. The pore size distribution for EQSO-1-PUAF BOT Sp3 was the only coke sample that distributed across all the pore size classifications. Chev-2-PUAF 20-30 Sp7 and MARA-13-PUAFV 0-5 Sp9 also demonstrate multiple pore size distributions. Citgo, Petrobas, and Marathon Rose Picth samples have little micro porosity, the pores are mainly macro porosity.

Two samples coming from the same location in the coke drum and both having the same appearance were sent to different labs (Core Labs and PMI), to check differences in procedure. Not much difference was observed in the micro and macro structures but the meso structure seems to be the main characteristic for agglomerated shot coke. With thin section microphotography we will investigate the differences in these classes. Meso porosity could be a key factor to differentiate Agglomeratted shot coke from Sponge shot coke. Water at atmospheric pressure can freely flow through meso pores and those greater than these during the quenching process.

There is a remarkable difference in the data for the Suncor, Chevron, Heavy Canadian, Cerro Negro & Equilon tests. BB shot coke differs from Buck Shot Coke in its roundness, sphericity and packing. Packing plays a major role contributing to lower porosity values. By observing BB shot coke samples and Buck shot coke samples, the BB shot coke appears to have a better packing due to its smaller and regular sizes. So packing could be responsible for the differences shown above, between Buck and BB shot coke. More analysis will confirm this difference between BB and Buck shot coke pore size distributions.

3. *Thin Section Microphotography*

Observing generalities of rocks formed as sediments, four main aspects come out by observing under microscope a thin sectional sample, these four observed generalities are: grain, matrix, pore and cement.

Coke samples have numerous morphology shapes. Coke samples are composed of grains, matrix, pitch and pores. The grains are the particles which generally form the framework of the coke. Matrix is the finer layer which occurs within the framework. There is no arbitrary size distinction between grains and matrix. Agglomerated shot coke generally has a matrix of fine loose shot coke. Cement is post-depositional carbon growth which occurs between the voids of the coke, fine loose coke sediments deposited between the voids of the coke after chemical reactions and the cooling process has finished. Pores are the hollow spaces not occupied by grains, matrix or pitch.

The microphotography below is characterized by individual "grains" that are mostly unconsolidated. Open "intergranular" macro pores (IG) are common and well interconnected and individual "grains" have fair amounts of intraparticle pores (IP). These intraparticle pores, however, do little to contribute to the overall interconnectivity of the pore system. Some elongated intraparticle pores are slightly interconnected (Plate 1D, red arrows). The associated pore throats would most likely be recorded in the micro-sized pore throat radii measured in the mercury injection tests.

Notice some pores have not been filled with blue-dyed epoxy (white arrows). This occurred when open pores were not completely relieved of air/gas (forming a bubble) during sample preparation. Because these samples were prepared under vacuum and these bubbles were not evacuated, these pores are likely isolated and not interconnected.

Although pore throats and their associated intergranular areas may have been expanded during sample preparation, some grains are cemented together (Plate B, yellow arrows). This suggests the pore structure, in part, is intact.

A – 12.5X	B – 40X
C – 100X	D – 100X

Figure 70 Thin Section Microphotography of Sample ID = SUNC-25-PUAFV 5-19.5 BB21

4. *Permeability and Porosity*

a) Porosity

Conventionally porosity has been defined as:

$$Porosity = \frac{\text{volume of total pore space}}{\text{volume of coke sample}} x100\ \%$$

Effective porosity is the amount of mutually interconnected pore spaces present in coke. It is the effective porosity which is economically important to us, and it is effective porosity which is determined by many, but not all, methods of porosity measurement.

We have used water to saturate coke samples; working with differences of buoyant forces we determined the bulk volume of the coke sample. A major drawback using this technique is the low surface tension between water and coke at atmospheric temperature and pressure, the biggest pore sizes, which contribute most to fluid flow, are not measured. The porosity measurements from samples sent to outside labs are higher than those measured in house accordingly.

b) Permeability

It is the presence of effective porosity that gives coke the property of permeability. Permeability is the ability of a liquid or gas to flow through a porous solid. Permeability is controlled by many variables. These include the effective porosity of the coke, the geometry of the pores, including their tortuosity, and the pore size distribution, the capillary force between the coke walls and the invading fluid, its viscosity and pressure gradient. Permeability is conventionally determined from Darcy's law using the equation:

$$Q = \frac{KA\ \Delta P}{m L}$$

Where Q is the rate of flow in cm^3/s, ?P is the pressure gradient in atmospheres, A is the cross-sectional area, µ is the viscosity in centipoises, L is the length and K is the permeability. A fluid (water, viscosity 1 cp) of viscosity µ is passed through a sample of known cross-sectional area A, and length L. The rate of flow is measured, together with the pressure differential recorded on gauges at either end of the sample. Permeability (miliDarcies [mD]) is the calculated according to Darcy's law, as described previously.

The permeability of coke samples are highly variable, both depending on the direction of measurement and vertically up or down sections. We have measurements of permeability from samples taken from different stages along the coke drum, we made efforts to measure vertical permeability, but as explained before the cross-sectional area facing to fluid flow can change dramatically regarding the direction of the flow, up or downwards, then permeability measurement values from the same core sample are different, even wider is the permeability variation range when comparing permeability values from cores drilled horizontally, i.e., perpendicular to fluid flow.

BB shot coke had the highest permeability values from all the coke morphologies considered, followed by Sponge coke, Transitional shot coke, Agglomerated shot coke and finally Buck shot coke

Transitional shot coke samples considered here were, Transitional Sponge-Agglomerated coke (TSA), Transitional BB-Agglomerated shot coke (TBBA) and Transitional Sponge-BB shot coke (TSSB), the correspondent tendency line lies right between the main morphologies where they come from, i.e., BB shot coke, Agglomerated shot coke and Sponge coke.

Buck shot coke has a lower permeability than BB shot coke due to a "packing effect", the Buck shot coke pieces are not uniformly shaped, and usually Buck shot coke clusters have a greater ability to get stuck among them than BB shot coke clusters, so that both effects: packing and coherency can influence its permeability (see Figure 72).

Even though Sponge coke does not rank the highest permeability values, as expected by observing its larger macro pore distribution. Thin Section Microphotography will help us better understand this phenomena as we study the effective and ineffective porosity. The low permeability might be occurring because of the influence of ineffective porosity and not interconnected pores (pores not contributing to the pore network).

The morphology of the agglomerated shot coke tested appears to be similar to sponge; therefore the same effects as those observed in sponge shot coke can be expected. Additional testing is planned.

Figure 71 Sphericity and Roundness

$$Sphericity = \frac{\text{surface area of the particle}}{\text{surface area of a sphere of equal volume}}$$

$$Roundness = \frac{\text{average radius of corners and edges}}{\text{radius of maximun inscriabed circle}}$$

Figure 72 Porosity and Permeability independence

Figure 72 shows how porosity and permeability are independent properties of coke samples. Note that permeability is low if porosity is disconnected, whereas permeability is high when porosity is interconnected and effective.

5. *Porous Plate Results*

Fifty three samples were analyzed using the porous plate technique; we were working at pressures near atmospheric pressure. When vapor and liquids bleed off in the coke drum they do so at low pressures (< 40 psig), so we were accounting for the corresponding pore sizes affecting these flows. Using water – air system (contact angle 0º and a surface tension of 72 Nm/m) we were able to measure pore radii up to 1 micron (Meso porosity). This analysis procedure was discontinued because we could not completely saturate the samples. We switched to Mercury Injection Capillary Pressure analyses because the technique quantifies all pore throat sizes.

6. *Morphology Discussion (6 in house vs. 3 new resids)*

Since a fair amount of transitional morphology was seen in the tests with the three new resids, the coke morphology description was expanded to include the Transitional coke sub classification.

Exxon-Mobil Cerro-Negro shows a wide variety of coke morphology, Heavy Canadian is basically sponge coke and Marathon Rose Pitch is widely distributed over the coke morphology classification.

7. *Effects of P and T on coke morphology*

The following pictures show the influence of Pressure and Temperature on coke morphology. Four set of conditions were established: (900 ºF, 15 psig); (900 ºF, 40 psig); (930 ºF, 15 psig); (930 ºF, 40 psig). For tests run at 15, 25, 35, and 45 psig.

Every set of conditions was arranged as shown below:

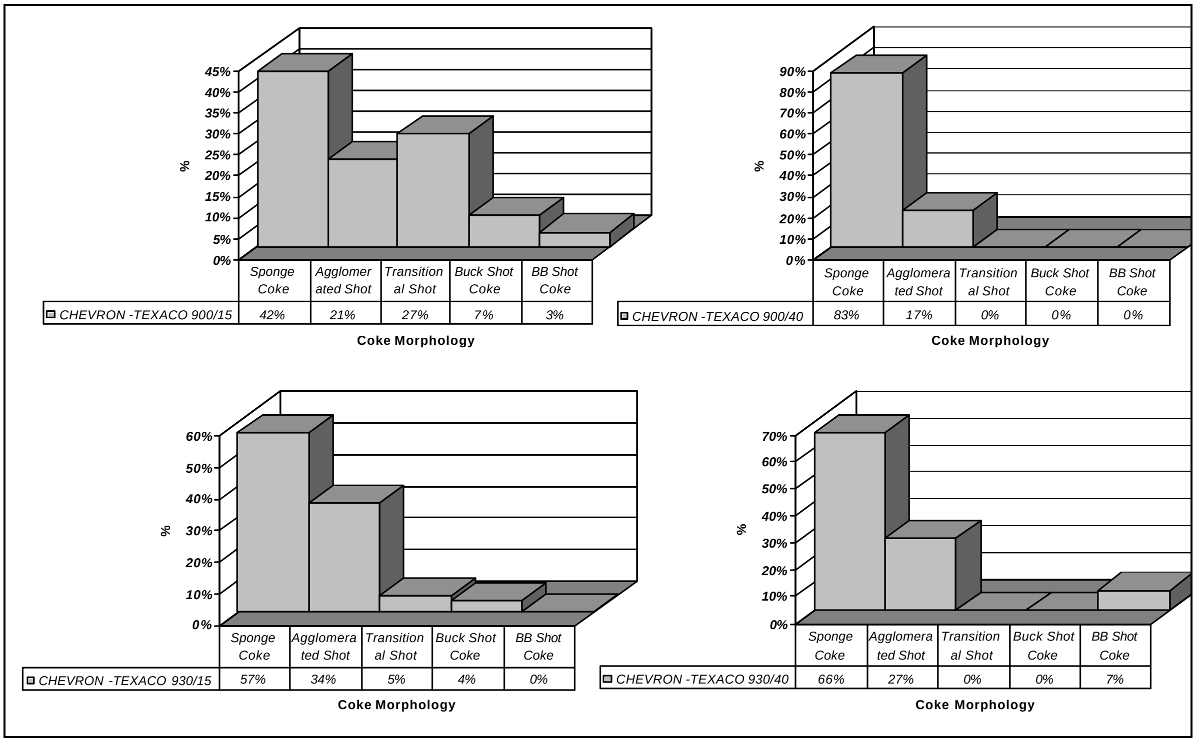


Figure 73 Chevron-Texaco coke morphology distribution

For the Chevron-Texaco resid and increase in pressure at 900 F seems to facilitate sponge formation and reduce shot coke formation as shown in Figure 73. Some classes of agglomerated shot coke are hard to classify, especially those close to sponge, therefore the remaining 17% of Agglomerated shot coke observed at Chevron-Texaco 900 ºF / 40 psig could be some form of agglomerated sponge-like material. At 930 ºF the same effect is observed but with smaller changes, i.e., sponge highs from 57% to 66% and once again Agglomerated shot coke is still occurring. Transitional coke found at the 930 ºF level is correspond to sponge and agglomerated transitional forms; this kind of coke is the proof to the weak segregation of sponges and agglomerated shot coke. BB and Buck shot coke are influenced by a pressure increase; i.e. at higher pressure lesser buck shot coke and BB shot coke are observed.

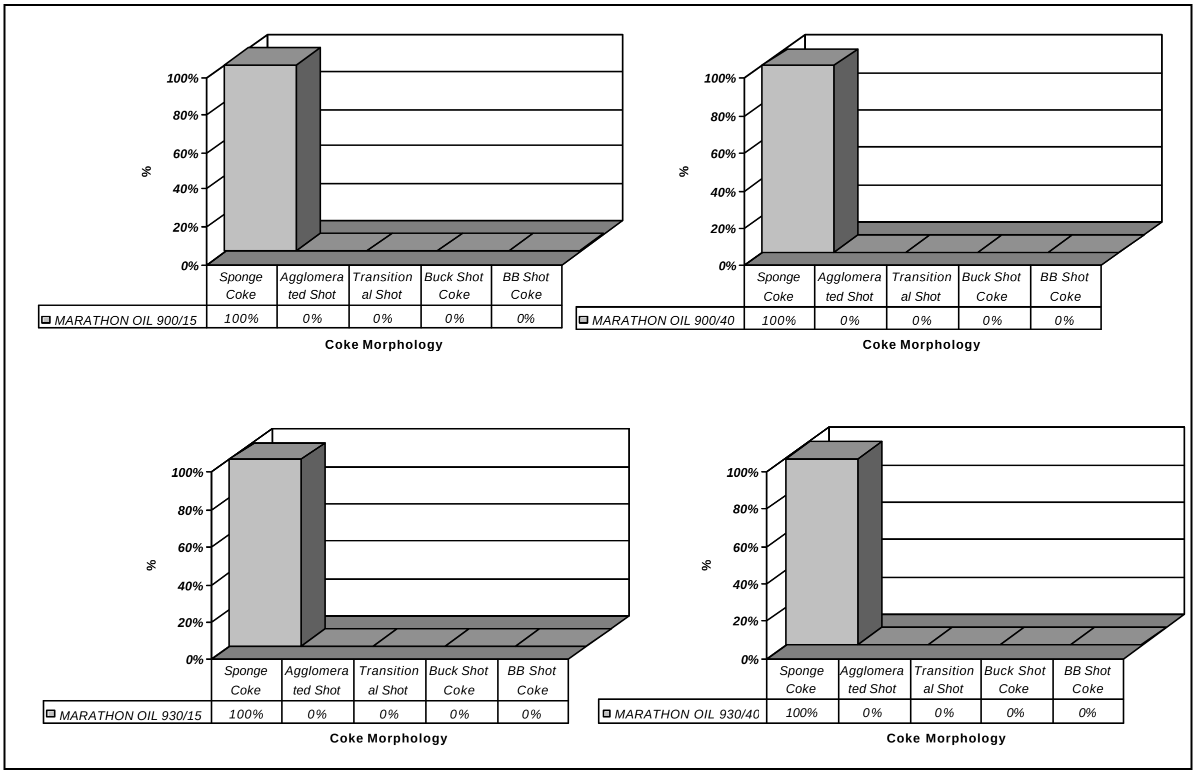


Figure 74 Marathon Oil coke morphology distribution

As shown in Figure 74 no changes in morphology are observed for the Marathon resid for all sets of test. In all runs sponge coke was made.

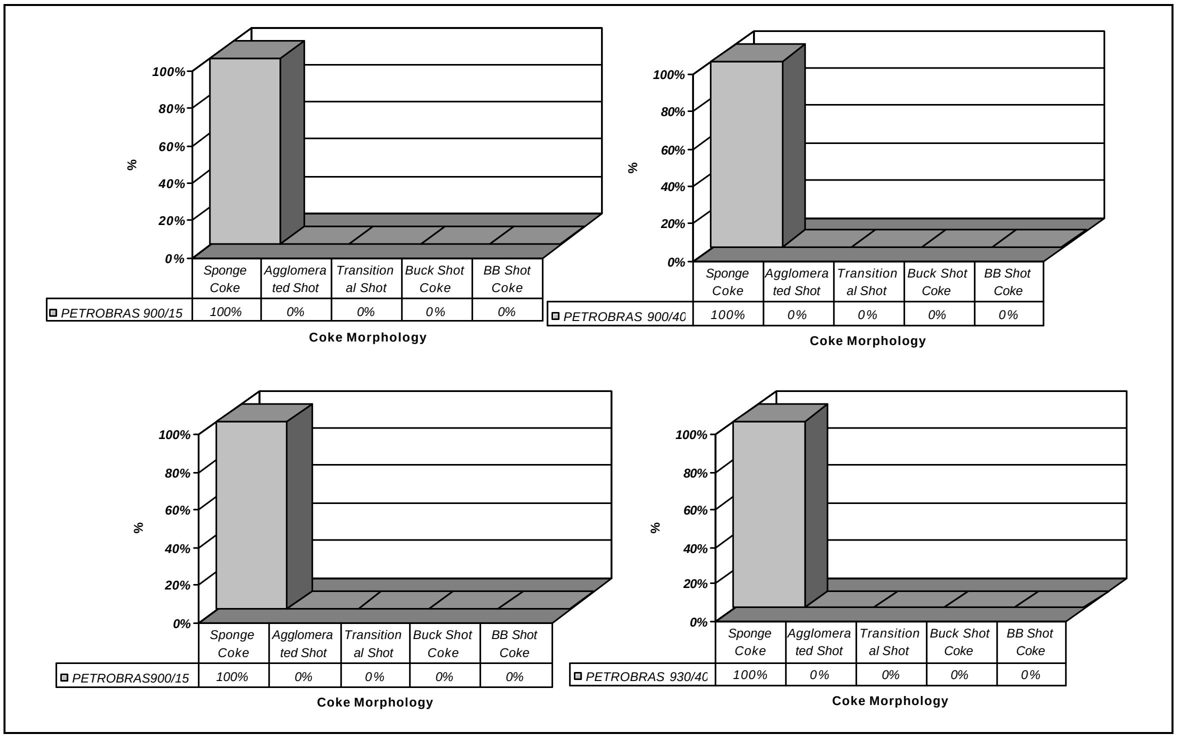


Figure 75 Petrobras coke morphology distribution

As shown in Figure 75 no changes in morphology were observed for the Petrobras resid. For all the conditions tested. In all runs sponge coke is made.

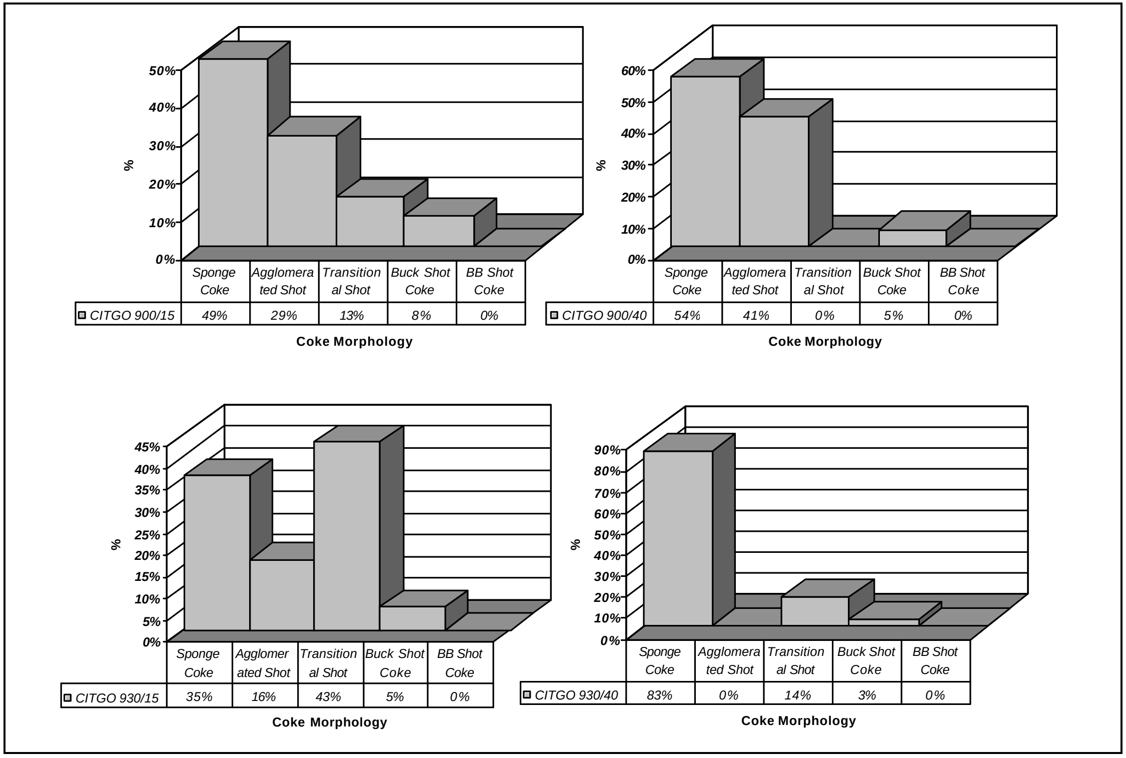


Figure 76 Citgo coke morphology distribution

Morphologies produced for the Citgo resid are shown in Figure 76. In general, higher pressures and temperatures facilitates the production of sponge coke over shot coke.

Sponge-Agglomerated, BB-Agglomerated and Sponge-BB shot coke are the main transitional forms observed for 930 ºF and 15 psig test conditions.

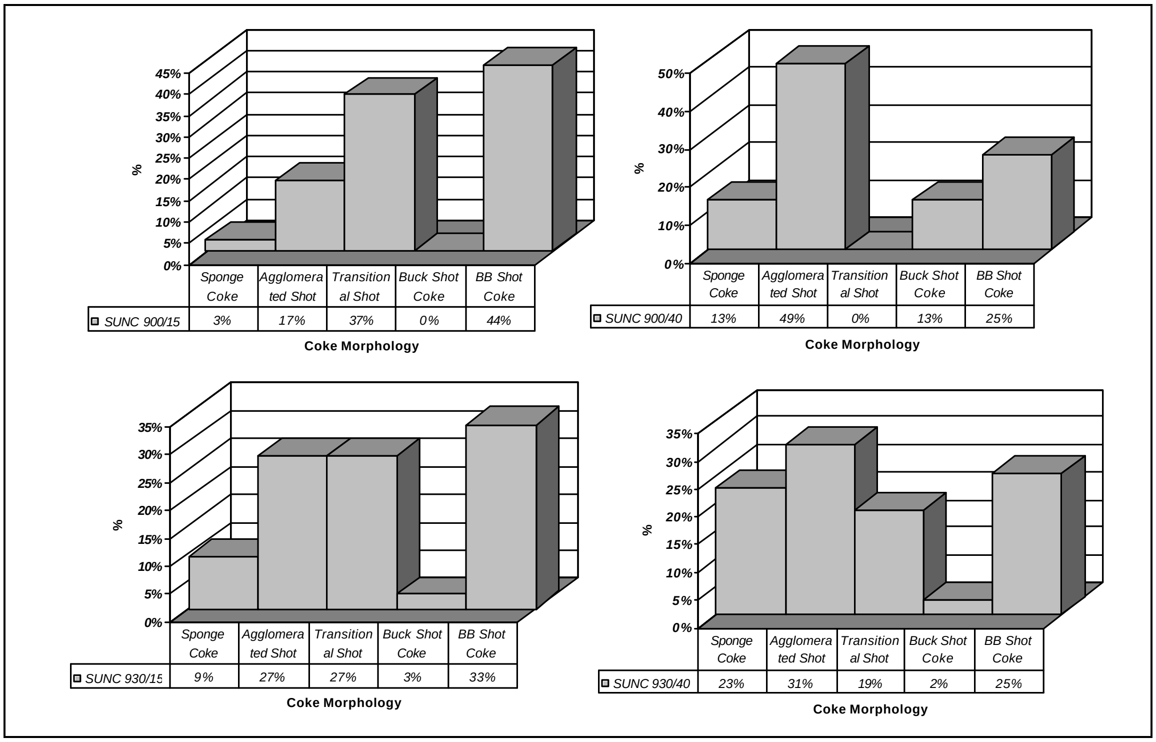


Figure 77 Suncor coke morphology distribution

Morphologies produced for the Suncor resid are shown in Figure 77. Clearly, temperature and pressure increase sponge formation, note that the effect of pressure increase is greater than the effect of temperature increase on sponge formation. Agglomerated shot coke formation is helped out by temperature increasing at both pressure levels. BB shot coke formation is facilitated at low pressure and temperature, whereas at high pressures and temperatures a more uniform distribution of morphology is observed. BB and Buck shot coke seem to have a complementary effect by compensating each other. But at 930 ºF level pressure increase reduces buck and BB shot coke formation.

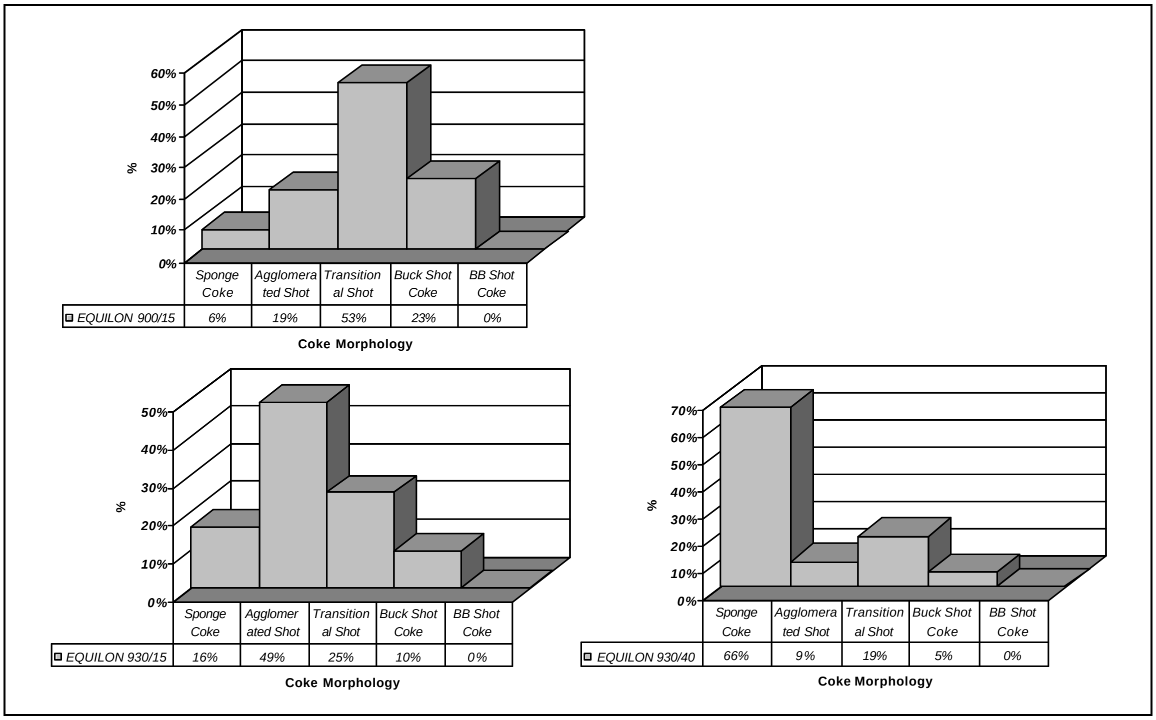


Figure 78 Equilon coke morphology distribution

Morphologies produced for the Equilon resid are shown in Figure 78. It should be kept in mind that not as many runs were made with this resid as with the other resids. Higher pressures and temperatures seem to enhance sponge formation for Equilon Resid at higher temperatures.

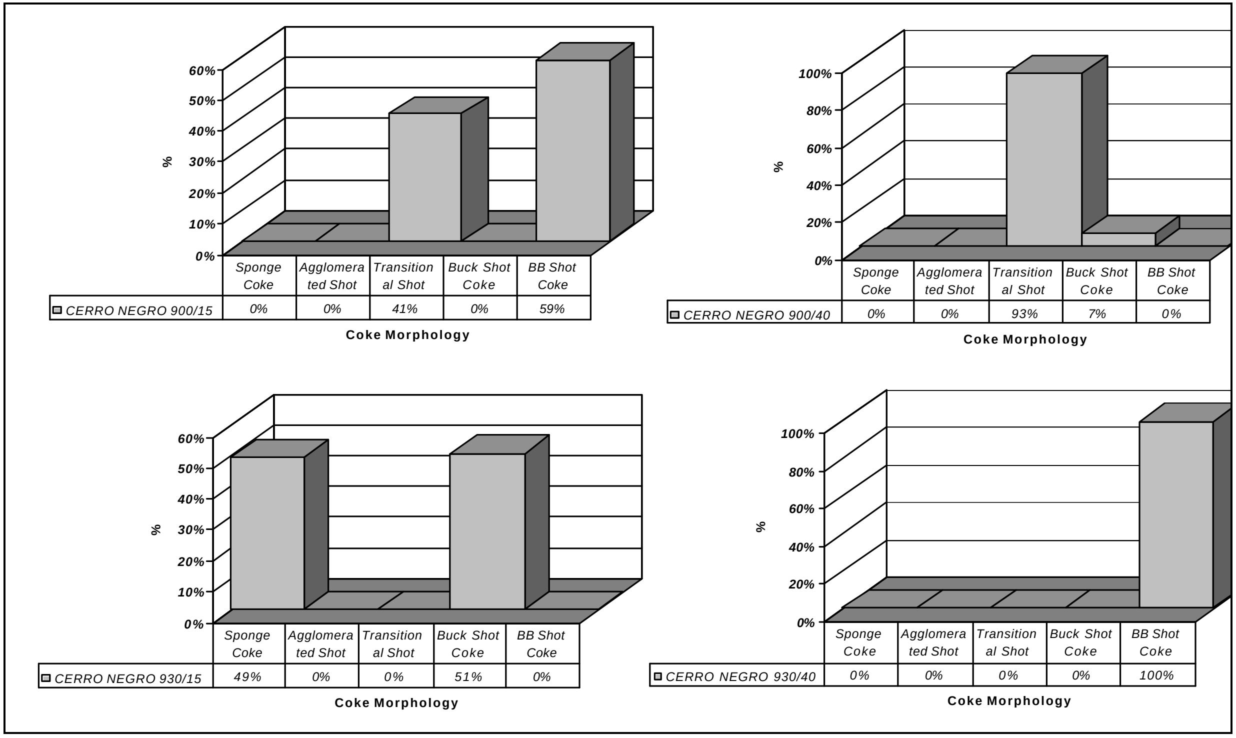


Figure 79 Cerro-Negro coke morphology distribution

Morphologies produced for the Cerro Negro resid are shown in Figure 79. Most of the runs made some from of shot coke and at 930ºF/40 psig only BB shot coke was made. It was also observed that by increasing the temperature at the 15 psig level sponge coke formation was facilitated.

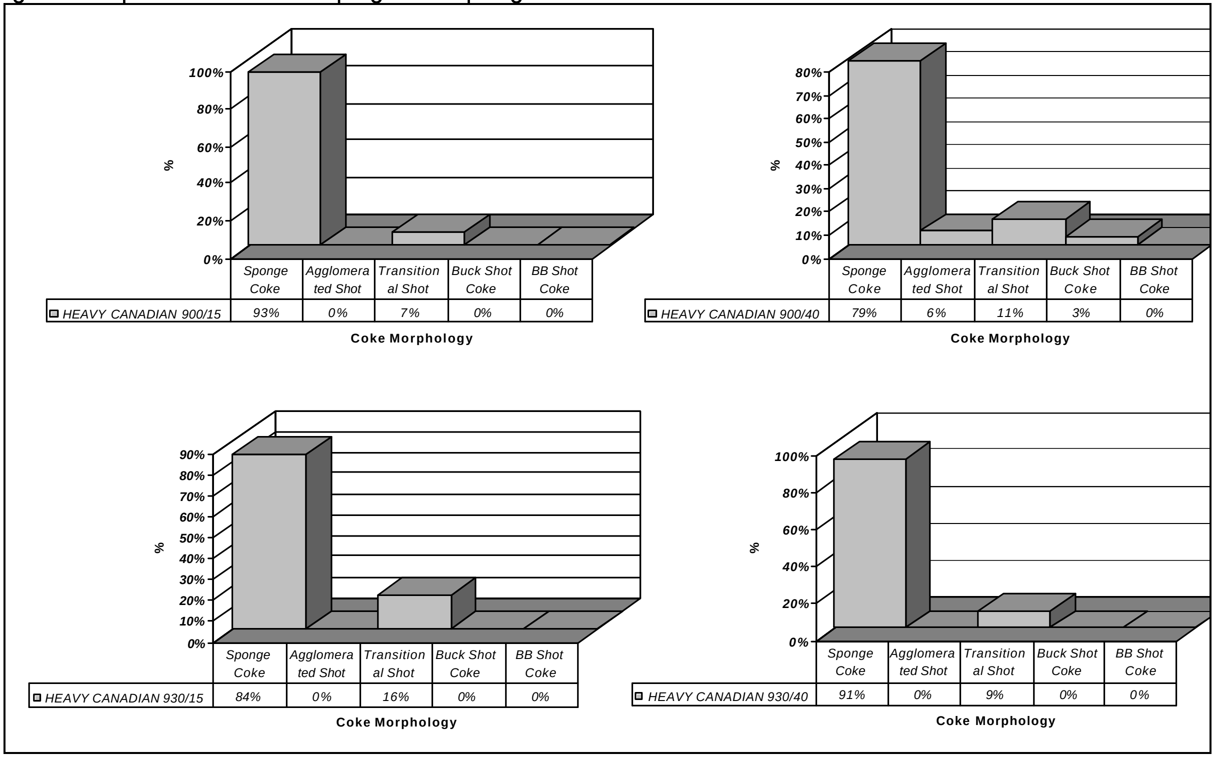


Figure 80 Heavy-Canadian coke morphology distribution

Morphologies produced for the Heavy Canadian resid are shown in Figure 80. No significant coke formation changes are observed by varying pressure and temperature. Sponge coke formation is the predominant morphology at all levels of pressure and temperature.

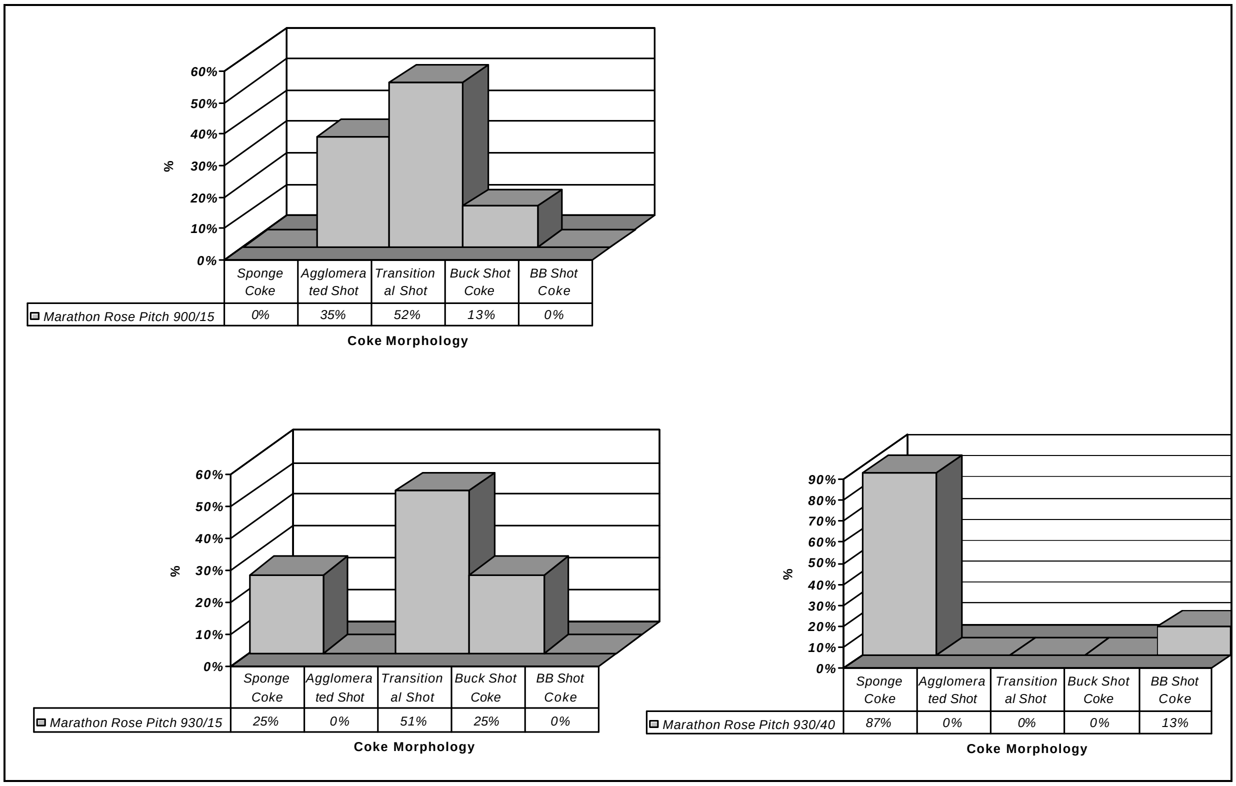


Figure 81 Marathon Pitch Rose coke morphology distribution

Morphologies produced for the Rose Pitch resid are shown in Figure 81. Based on data compiled to date, increases in both pressure and temperature favor sponge coke formation.

The following tables summarize the morphologies for the tests conducted on the 9 resids to date. They show coke formation dependence (positive or negative correlations) of pressure and temperature changes. Blank spaces are intentional in that they point out that no significant change was observed or a run at specified conditions was not performed.

Increasing Temperature ?T at 15 psig

Resid	Sponge coke	Agglomerated shot coke	Transitional shot coke	Buck Shot Coke	BB shot coke
CHEVRON TEXACO	+	+	-	-	-
MARATHON OIL					
PETROBRAS					
CITGO	-	-	+		
SUNCOR	+	+	-	+	-
EQUILON					
CERRO NEGRO	+		-	+	-
HEAVY CANDIAN					
MARATHON ROSE PITCH	+	-	+	+	

Spaces left in blanks are intended to point out that no observable change was observed or a run at specified conditions was not performed.

Increasing Temperature ?T at 40 psig

Resid	**Sponge coke**	**Agglomerated shot coke**	**Transitional shot coke**	**Buck Shot Coke**	**BB shot coke**
CHEVRON TEXACO	**-**	**+**			**+**
MARATHON OIL					
PETROBRAS					
CITGO	**+**	**-**	**+**		
SUNCOR	**+**	**-**	**+**	**-**	
EQUILON					
CERRO NEGRO			**-**	**-**	**+**
HEAVY CANDIAN					
MARATHON ROSE PITCH	**+**	**-**			

Spaces left in blanks are intended to point out that no observable change was observed or a run at specified conditions was not performed.

Increasing Pressure ?P at 900 F

Resid	**Sponge coke**	**Agglomerated shot coke**	**Transitional shot coke**	**Buck Shot Coke**	**BB shot coke**
CHEVRON TEXACO	+	-	-	-	-
MARATHON OIL					
PETROBRAS					
CITGO	+	+	-		
SUNCOR	+	+	-	+	-
EQUILON					
CERRO NEGRO			+	+	-
HEAVY CANDIAN					
MARATHON ROSE PITCH					

Spaces left in blanks are intended to point out that no observable change was observed or a run at specified conditions was not performed.

Increasing Pressure ?P at 930 F

Resid	**Sponge coke**	**Agglomerated shot coke**	**Transitional shot coke**	**Buck Shot Coke**	**BB shot coke**
CHEVRON TEXACO	+	-	-	-	+
MARATHON OIL					
PETROBRAS					
CITGO	+	-	-		
SUNCOR	+	+	-		-
EQUILON					
CERRO NEGRO	-			-	+
HEAVY CANDIAN					
MARATHON ROSE PITCH	+		+	-	+

Spaces left in blanks are intended to point out that no observable change was observed or a run at specified conditions was not performed.

8. *Future work*

20 samples were sent to Mineralogy, Inc. for thin section preparation, we want to optically contrast the MICP information we have with the observable pores in the coke. We are now in the process of taking images by Thin Section Microphotography TSM using a microscope. Microphotography will give us a better understanding of the effect of isolated pores and a better understanding of the four types of porosity that contribute to total porosity.

Scanning Electron Microscopy SEM images can show detailed information related to the surface and coke sample wall roughness. It can reveal fractures and cracks in the observable surfaces of a coke samples. They will also give us a three dimensional view of the pore throats. This analysis might lead to a better understanding of the relationship between porosity and permeability that will lead to better correlations.

So far, MICP results combined with SEM and TSM images will give us a more complete understanding about the pore network structure, its influence on permeability and porosity, and how it is influenced by coke morphology. Permeability and porosity plays a major role in the quenching and foaming models.

B. QUENCHING STUDIES

Table 33 lists the pilot unit foaming study runs to date that have been bottom quenched. There have been 24 bottom-quenched runs through May of 2004.

Table 33 – PUAF runs quenched from bottom

Run	Date
MARA 5	10/29/2002
MARA 6	11/5/2002
CIT 9	11/22/2002
CHEV 11	1/23/2003
EQU 6	2/19/2003
PETR 9	3/13/2003
PETR 10	3/21/2003
PETR 14	4/15/2003
PETR 15	4/18/2003
PETR 16	4/23/2003
EQU 7	6/4/2003
CHEV 12	7/16/2003
SUNC 14	9/11/2003
MARA 14	1/21/2004
MARA 15	1/27/2004
MARA 16	1/30/2004
SUNC 21	2/11/2004
SUNC 22	2/17/2004
SUNC 25	3/4/2004
EM CN 2	4/6/2004
EM CN 6	4/20/2004
EM HC 2	4/28/2004
EM HC 4	5/6/2004
EM CN 7	5/11/2004

Figure 82 shows a typical temperature profile plot for bottom quenching. In this case, it can be seen that the cooling proceeds uniformly from the bottom of the drum to the top. When water is injected in the bottom of the drum, the temperature of the bottom thermocouple decreases drastically upon contact with the water. As the water percolates through the channels and pores of the coke in one zone it fills the entire coke mass of the zone. By that time a large drop in temperature is seen, and after that very little cooling takes place. When the water comes into contact with the very hot coke mass it vaporizes and the vapor rises to the next zone. The vapor initiates the cooling process of the new zone and when water reaches that zone and fills its channels and pores, the temperature again drops abruptly. This phenomenon repeats itself during the time water is being injected until the coke bed is water filled and cold enough that no more steam forms. Note that the zones are evenly spaced: zone 1 corresponds to 6⅛-16⅜ inches from the bottom; zone 2, 16⅜-26⅝ inches; zone 3, 26⅝-36⅞ inches; zone 4, 36⅞-47⅛ inches;

and zone 5, 47? -57 ? inches. The cooling curves between these evenly spaced zones are evenly spaced in time, as one would expect for a coke bed with uniform porosity and permeability.

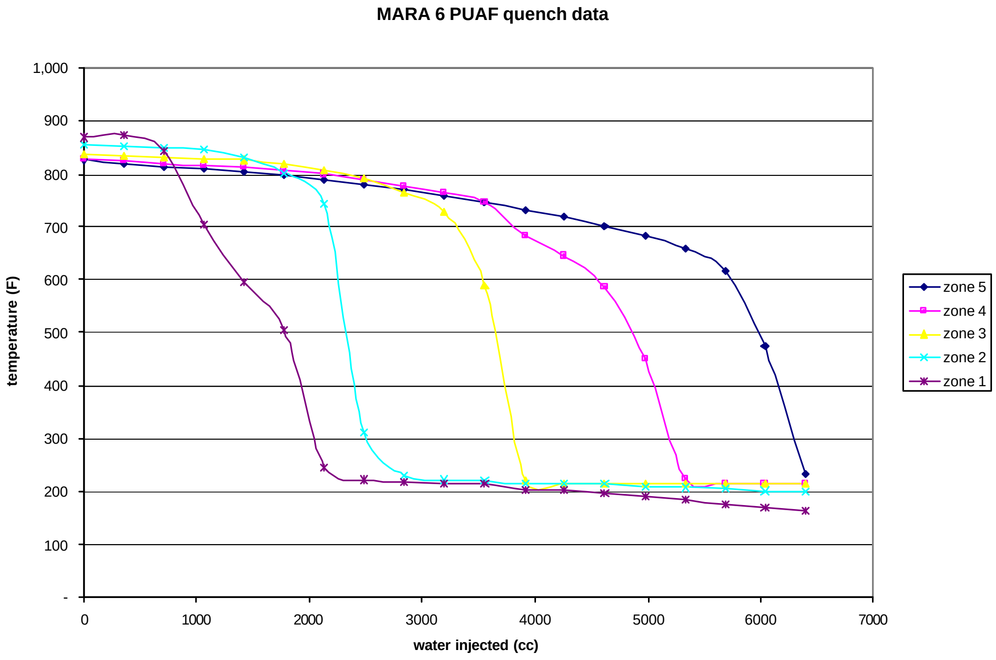


Figure 82 – Typical cooling curve for bottom quenching (run MARA 6)

In examining the cooling data for the 21 bottom-quenched runs, this uniform temperature profile was observed in many cases. However, there are some exceptions. Figure 83 shows the quench data for run CHEV 12 PUAF. The cooling curves for zones 1 through 3 look normal, but the zone 4 curve lies nearly on top of the zone 3 curve. This is due to a void in the coke bed that was noted, 26-36 inches from the bottom of the drum.

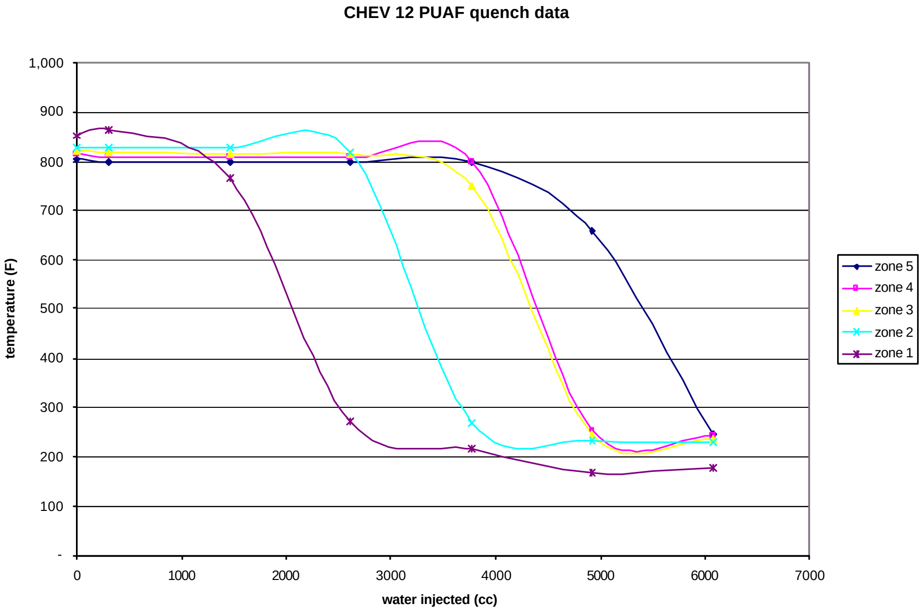


Figure 83 – CHEV 12 PUAF bottom quenching

Figure 84 shows the quench data for run EMCN 6 PUAF. Zone 2 (16? -26? inches) can be seen to cool faster than would normally be expected (as it is relatively close to the zone 1 curve) whereas zone 3 (26? -36? inches) cools slower than expected (as it is relatively far from the zone 2 curve). This is due to the coke morphology: the bottom 20 inches of the drum contained clusters of BB shot, whereas the next 20 inches contained very dense, hard agglomerated shot coke, followed by more clusters of BB shot in the top 7 inches of the drum. The clusters of BB shot cool rather quickly, but the hard agglomerated shot coke cools slowly, apparently due to the permeability or low porosity of the coke.

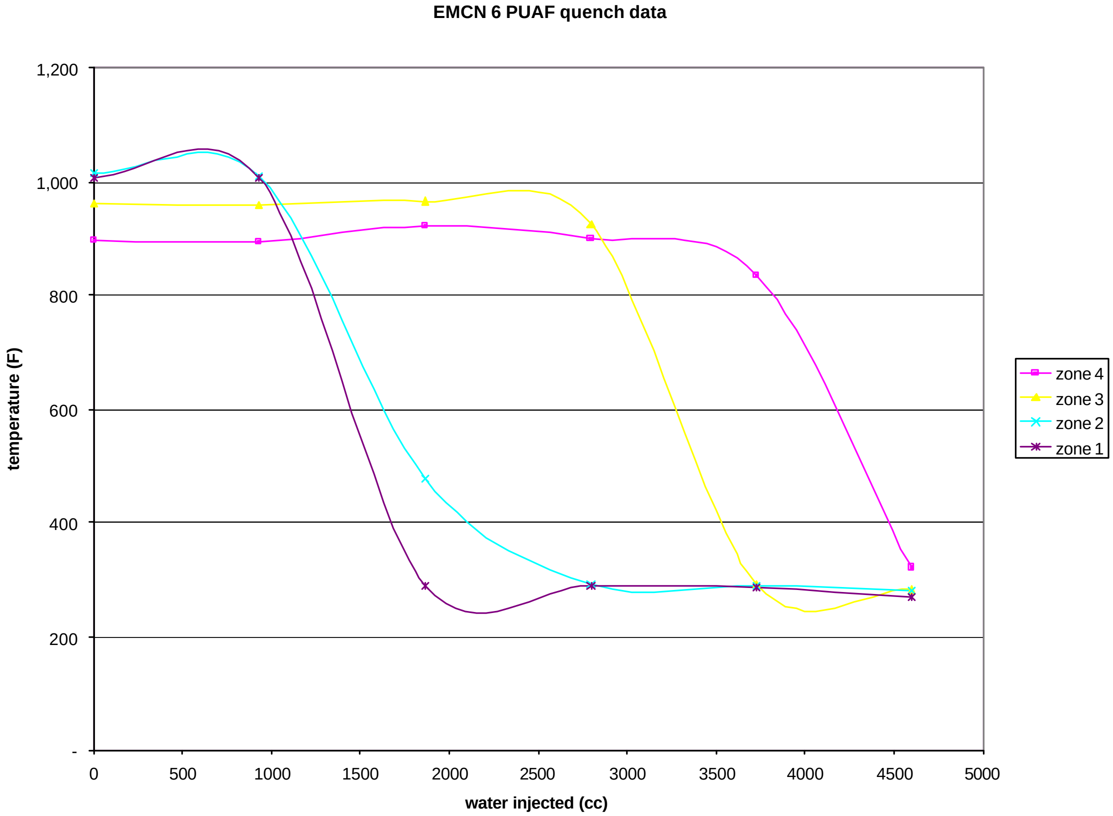


Figure 84 – EMCN 6 PUAF bottom quenching

Figure 85 shows the quench data for run EQU 7 PUAF. Note that zone 1 takes an abnormally long time to quench. For the runs shown in Figure 82 through Figure 84, zone 1 is completely quenched using about 2000 cc of water. For run EQU 7, however, approximately 5000 cc of water is needed to quench zone 1. Zone 2 cools normally, but zones 3 and 4 cool much faster than normal. These observations again correspond to the coke morphology: the bottom 11 inches of coke consisted of a 1-1½ inch layer of hard, solid coke surrounding a core of BB shot, whereas the upper portion of the bed consisted of small clusters of BB shot with large, light clusters of coke at the very top. The solid coke layer at the bottom took longer than usual to cool, whereas the looser BB shot took less time to cool.

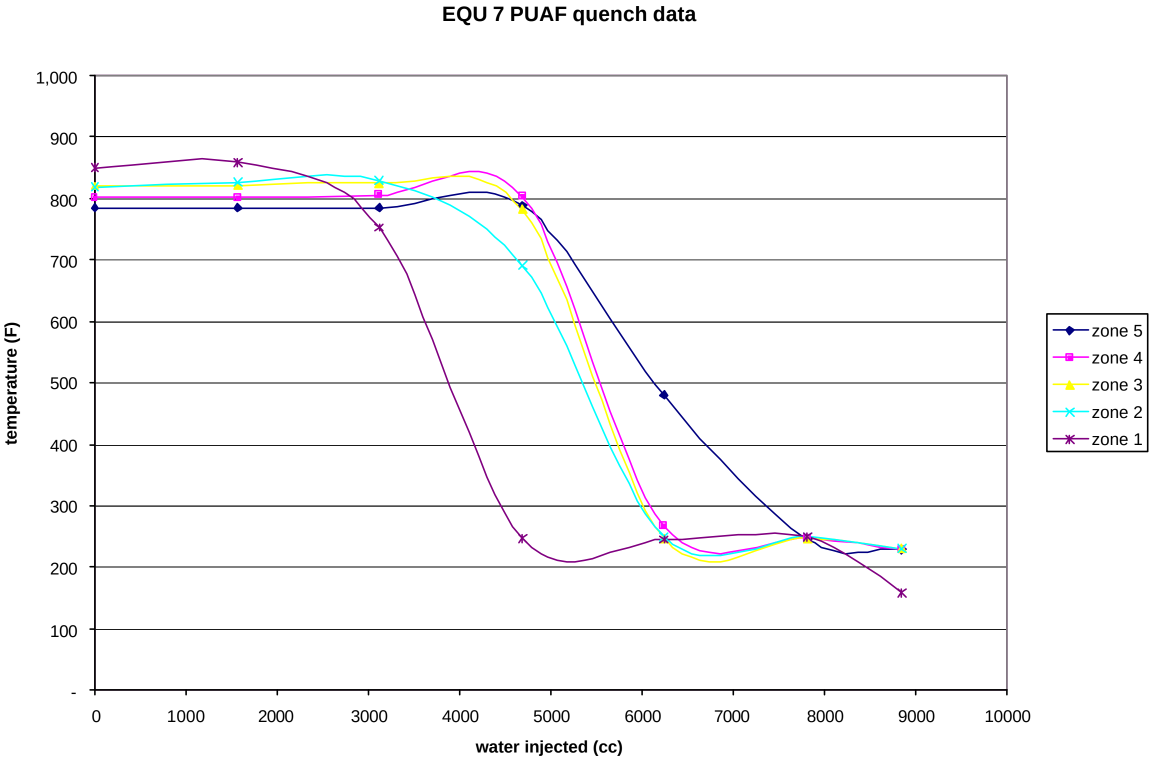


Figure 85 – EQU 7 PUAF bottom quenching

Figure 86 shows the quench data for run MARA 16 PUAF. In this case, zone 1 cools slowly (approximately 2000 cc of water required), but zones 2 and 3 cool at nearly the same time as zone 1. For this run, the bottom 32 inches of coke was very dense, hard and brittle sponge coke; the top (32-36") was sponge with some pitch mixed in the coke. This very dense coke was very slow to cool, and did not completely cool until liquid water filled a large portion of the coke drum, at which time all three of the bottom zones cooled nearly simultaneously. Note that zone 4 (36? -47?) lies above the coke layer. This zone is shown in Figure 86 to illustrate the time at which liquid water reaches this level of the empty drum. Note the very sharp drop in temperature when no coke is present.

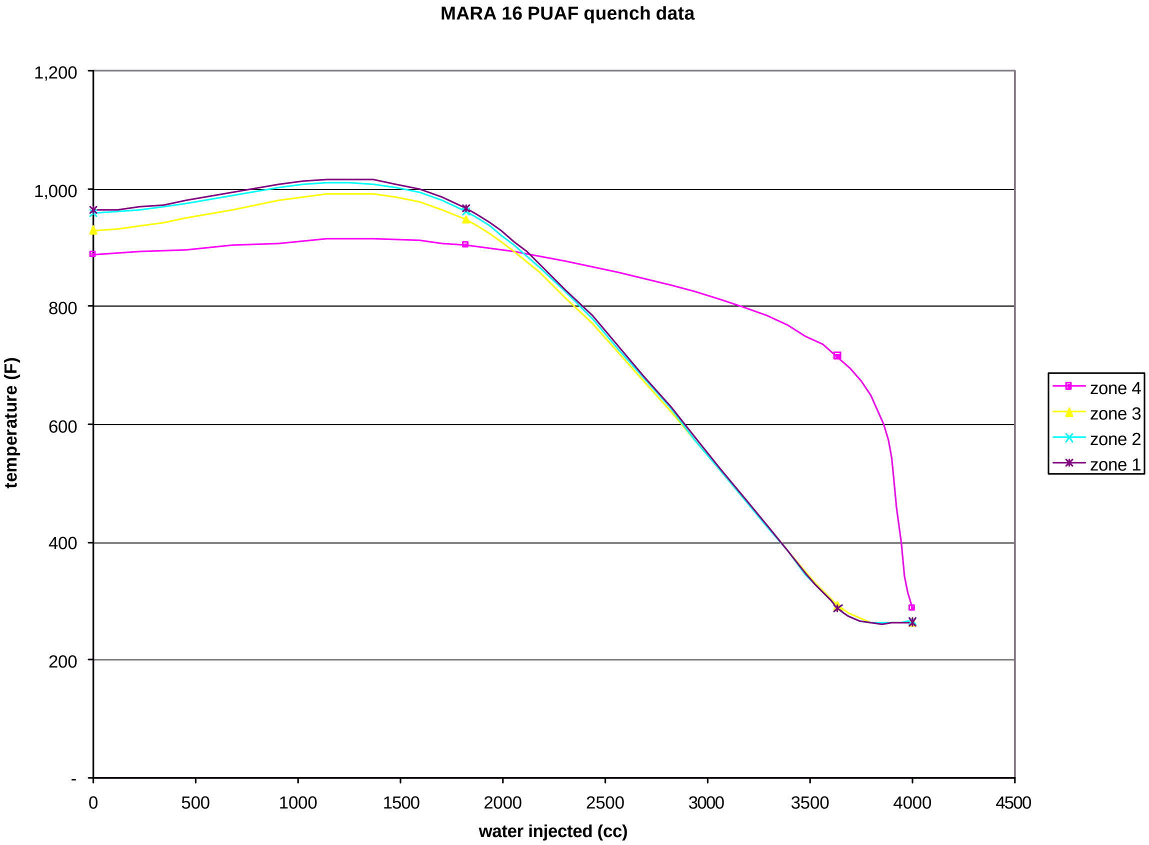


Figure 86 – MARA 16 PUAF bottom quenching

In conclusion, coke morphology can be seen to have an important effect on quenching. Hard, dense sponge or agglomerated shot coke cools very slowly, whereas the presence of loose shot or void spaces within the coke drum correspond to very fast cooling. Efforts are now underway to modify the existing quench model to account for varying porosity/permeability within the coke bed.

An improved quench model has been developed that includes as input parameters the porosity of the coke as a function of position. This model is currently being tested on the quench data, and will be used in conjunction with the coke morphology study. Results will be presented in the next quarterly report.

C. DENSITY CORRELATION FOR COKE

Density of coke made is quite important in the coking process. If the density of coke can be improved, a larger amount of resid can be processed in a given coking cycle. It was noted earlier that the density of the coke varied with temperature, pressure and feedrate. In this section an attempt has been made to correlate both bulk density and gamma densities using these operating variables. Values for temperature and pressure have been directly taken from the test run data. But feedrate is converted into mass accumulation by multiplying feedrate with the % of coke formed for a given test run.

1. *Sponge coke correlation*

For resids that made pure sponge coke (Petrobras and Marathon), the three variables, temperature, pressure and mass accumulation provided a good correlation. Table 34 gives the correlation coefficients of predicted Bulk and gamma densities for Petrobras and Marathon resids which made pure sponge coke irrespective of the operating conditions.

Table 34 – Correlation coefficients of Predicted Bulk and Gamma densities for Petrobras and Marathon resids

	Adjusted R^2	Temperature	Pressure	Mass Accumulation	Intercept
	Coefficient	A	B	C	D
Petrobras Bulk	0.95	3.59E-03	3.01E-03	-1.82E-04	-2.52
Petrobras Gamma	0.72	4.73E-03	2.41E-03	-1.65E-04	-3.69
Marathon Bulk	0.76		4.84E-03	-6.23E-05	0.63
Marathon Gamma	0.80	2.19E-03	3.38E-03	-1.47E-04	-1.45

Equation 1 Density correlation equation for sponge coke.

Density = A* Temperature + B*Pressure + C*Mass Accumulation + D.

Positive coefficients for temperature and pressure indicate that an increase in these operating variables increases the density of coke formed while the negative coefficient for mass accumulation (factor of feedrate) indicates a decrease in coke density with an increase in feedrate. For Marathon resid bulk density prediction using temperature has a coefficient less than standard error so for this case bulk density is predicted only with pressure and mass accumulation.

Considering the overall effects of operating conditions on sponge coke densities, it is observed that an increase of temperature and pressure results in an increase in coke density. Feedrate increase decreased coke density.

2. *Shot coke correlation*

Similar analysis was done for the resids that made shot coke (Equilon and Suncor).

Table **35** gives the correlation coefficients of predicted Bulk and Gamma densities.

Table 35 – Correlation coefficients of Predicted Bulk and Gamma densities

	Adjusted R^2	Intercept	Temperature	Pressure	Mass Accumulation
	Coefficient	D	A	B	C
Equilon Bulk	0.31	1.65	-9.81E-04	4.71E-03	-3.40E-05
Equilon Gamma	0.62	-6.90	7.97E-03	4.10E-03	1.04E-04
Suncor Bulk	0.10	-0.35	8.48E-04	5.39E-03	3.11E-04
Suncor Gamma	0.14	-0.54	1.07E-03	4.99E-03	1.32E-04

Since these resids made agglomerated shot coke which has variable densities, the adjusted R^2 values are poor. The correlations could be improved by including a factor for agglomeration of shot coke.

BB shot:

The Suncor resid made BB's at some locations in the drum depending on the test run. The locations where it made BB's were identified and the densities picked from the gamma traces. A correlation for the resids that made shot coke was predicted using temperature, pressure and mass accumulation as variables.

Table 36 gives the correlation coefficients of predicted BB's density.

Table 36 – Correlation coefficients of Predicted BB density for Suncor resid

	Adjusted R^2	Temperature	Pressure	Mass Accumulation	Intercept
	Coefficient	A	B	C	D
Suncor BB density	0.97	3.00E-03	-1.74E-03	-9.70E-04	-1.33

From the above table it can be observed that positive coefficient for temperature indicates that an increase in temperature increases shot coke density where as negative coefficients in pressure and feedrate (mass accumulation) decreases shot coke density. This is due to the fact that an increase in temperature makes more BB's which are dense spheres, where as an increase in pressure and feedrate reduces shot coke formation which in turn decreases density of shot coke formed.

3. *Sponge v/s shot*

Chevron and Citgo resids made both sponge and shot coke at different locations in the drum at different operating conditions. A similar analysis was done for the resids that made variable morphology in the drum (Chevron and Citgo). Table 37 gives the correlation coefficients of predicted Bulk and Gamma densities.

Table 37 – Correlation coefficients of Predicted Bulk and Gamma densities

	Adjusted R^2	Intercept	Temperature	Pressure	Mass Accumulation
	Coefficient	D	A	B	C
Chevron Bulk	-0.14	-1.41	2.34E-03	1.39E-03	-5.41E-05
Chevron Gamma	0.44	-2.53	3.52E-03	1.26E-03	-1.52E-04
Citgo Bulk	0.17	-2.47	3.04E-03	1.07E-03	3.79E-04
Citgo Gamma	0.11	-2.23	2.98E-03	2.38E-03	-2.61E-05

Since these resids made variable morphology in the drum with variable densities, the adjusted R^2 values are poor. The correlations could be improved by including a factor for this variable morphology.

4. *Comparison of sponge and shot correlations*

Table 38 gives the coefficients for shot coke made by the Suncor resid and overall sponge coke gamma density (Petrobras and Marathon resids). The values are fairly comparable.

Table 38 – Correlation coefficients of Predicted Gamma densities for overall sponge and shot coke

	Adjusted R^2	Temperature	Pressure	Mass Accumulation	Intercept
	Coefficient	A	B	C	D
Suncor BB density	0.97	3.00E-03	-1.74E-03	-9.70E-04	-1.33
Sponge coke Gamma density	0.63	3.45E-03	3.31E-03	-1.38E-04	-2.59

14. Technology Transfer / Administrative Issues

A. COMMITTEE AND COMMITTEE MEETINGS

At the first Advisory Board Meeting three committees were formed and the committee members elected a Chair. For the continuation JIP, discussions will be held at the Advisory Board Meeting regarding election of new chairs or reappointment of the old chairs as well as members of the committees. An updated chart, including only current members that attend the meetings, is shown in Table 39. In addition to the committee chair, a TU representative is on each committee. The first committee deals with the coker facilities and its operation, the second deals with process dynamics and modeling, while the third deals with technology transfer and commercialization issues. Please contact Mrs. Dorinda Alexander at The University of Tulsa if your company wishes to add other members to the committees.

	Coker Facility & Operation	**Process Dynamics & Modeling**	**Technology Transfer & Commercialization**
Industry Chair	Chris Paul GLC	Shri Goyal Shell	Robert Bell ChevronTexaco
TU Representative	Michael Volk	Keith Wisecarver	Michael Volk
DOE Representative	Robert Bell ChevronTexaco	Betty Felber	Betty Felber
Members	Leo Brown Exxon Mobil	Marcos Sugaya Petrobras	Michael Zetlmeisl Baker Petrolite
	Paul Ellis PetroCarbon	Richard Lee KBC Advanced Tech	Richard Lee KBC Advanced Tech
	Chris Eppig ExxonMobil	Fred Hill Marathon-Ashland	Michael McGrath Foster Wheeler
	Larry Kremer Baker Petrolite	Joseph Stark Baker Petrolite	Shri Goyal Shell
	Mitch Moloney ExxonMobil	Mike McGrath Foster Wheeler	
	Michael Zetlmeisl Baker Petrolite		

Table 39 - Committee Organization

B. WEB SITE

The address for the Delayed Coking Web Site is http://www.tudcp.utulsa.edu. The web site has become a useful tool to welcome visitors and tell them about the JIP. It is segmented such that visitors can gain general information while the "Members Only" site contains confidential information generated in the JIP. There is a reading room, applications, a tour of the facility, a place to meet the personnel, JIP news, experimental data from the three cokers, models and correlations, and a discussion board.

During the last six months, significant postings and updates were made to the entire web site. The site is updated as runs are completed and processed. Recent updates include the test data (Micro and Pilot) for the three new resids and technical reports with slide copies.

C. FUTURE MEETINGS

A tentative date for the twelth Advisory Board meeting is Wednesday and Thursday, May 18th & 19th, 2004. The meeting will be held at the University of Tulsa in ACAC. The meeting on the 18h will begin at 1 pm and adjourn at 5 p.m. A social is planned that evening in the Presidents Lounge from 5 to 9 p.m. The meeting on the 19th will begin at 8 a.m. and adjourn at 2:30 p.m.

D. BUDGET/CASH FLOW ANALYSIS

A combined budget and cash flow analysis for a three and one third-year period beginning June 1, 2002 and ending September 30, 2005 is given in Table 40. Included are the actual income and expenses for the period beginning June 1, 2002 and ending September 30, 2004 and a forecast for October 2004 through September 2005.

Table 40 -Three Year Cash Flow Analysis

	Pre-Award June02-Sep. 02 Actual	**FY 2003 Oct. 02-Sep. 03 Actual**	**FY 2004 Oct. 03-Sep. 04 Actual**	**FY 2005 Oct. 04-Sep. 05 Budget**	**Total**
Income					
Industry	$375,914	$494,605	$ 399,246	$ 117,290	$1,387,055
DOE	$0	$340,000	$340,418	$340,000	$1,020,418
TU	$0	$42,756	$19,096	$9,996	$71,848
Total Income	**$375,914**	**$877,361**	**$758,760**	**$467,286**	**$2,479,321**
Expenses					
Salary, IDC, Fringe	$92,832	$569,565	$600,422	$577,399	$1,840,219
Supplies	$17,766	$72,327	$77,504	$70,000	$237,598
Equipment	$0	$5,075	$18,755	$5,000	$28,829
ABM Meetings	$1,396	$2,223	$3,525	$4,130	$11,273
Travel	$483	$3,864	$11,415	$14,000	$29,762
Consulting	$0	$1,340	$0	$0	$1,340
Analytical	$12,470	$62,428	$52,711	$7,500	$135,109
Outside Services	$5,944	$9,263	$7,534	$0	$22,741
Contingency	$0	$0	$0	$7,000	$7,000
Tuition	$11,450	$72,212	$19,096	$9,996	$112,754
Total Expenses	**$142,342**	**$798,296**	**$790,962**	**$695,025**	**$2,426,626**
Cash Flow	**$233,571**	**$79,065**	**($32,202)**	**($227,739)**	**$52,695**
Cumulative Cash Flow	**$233,571**	**$312,636**	**$280,434**	**$52,695**	