Modeling a Set of Heavy Oil Aqueous Pyrolysis Experiments

Charles B. Thorsness
John G. Reynolds

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MODELING A SET OF HEAVY OIL AQUEOUS PYROLYSIS EXPERIMENTS

Charles B. Thorsness
John G. Reynolds

Abstract

Aqueous pyrolysis experiments, aimed at mild upgrading of heavy oil, were analyzed using various computer models. The primary focus of the analysis was the pressure history of the closed autoclave reactors obtained during the heating of the autoclave to desired reaction temperatures. The models used included a means of estimating nonideal behavior of primary components with regard to vapor liquid equilibrium. The modeling indicated that to match measured autoclave pressures, which often were well below the vapor pressure of water at a given temperature, it was necessary to incorporate water solubility in the oil phase and an activity model for the water in the oil phase which reduced its fugacity below that of pure water. Analysis also indicated that the mild to moderate upgrading of the oil which occurred in experiments that reached 400°C or more using a Fe(III) 2-ethylhexanoate could be reasonably well characterized by a simple first order rate constant of $1.7 \times 10^8 \exp(-20000/T)$ s$^{-1}$. Both gas production and API gravity increase were characterized by this rate constant. Models were able to match the complete pressure history of the autoclave experiments fairly well with relatively simple equilibria models. However, a consistent lower than measured buildup in pressure at peak temperatures was noted in the model calculations. This phenomena was tentatively attributed to an increase in the amount of water entering the vapor phase caused by a change in its activity in the oil phase.
INTRODUCTION

Heavy crude oil with an API gravity below 20 generally has a considerably lower market value than benchmark crudes because of undesirable physical and chemical properties (e.g., high viscosity and high heteroatom content). One strategy to increase the value of these crude oils and allow easier transport by existing pipelines is in-field upgrading. Aqueous pyrolysis is one candidate for in-field upgrading of heavy oils. It involves heating an oil-water mixture under pressure, possibly with a catalyst present, to partially crack and coke the heavy constituents and thus improve the oil quality. This process is attractive since the heavy oils are often associated with some thermally assisted recovery process, such as steam flooding, and as a result are often produced at somewhat elevated temperatures and with considerable water. The produced fluids, therefore, already require some form of dewatering step to allow them to be marketed, and the aqueous pyrolysis process can be viewed as an extension of the dewatering process.

As a first step in exploring the potential of aqueous pyrolysis as an in-field upgrading step, a series of autoclave experiments have been performed to obtain data on the conditions needed to allow significant modification of a typical heavy crude. These experiments yielded information on API gravity change, coke formation, and gas yield over a temperature range of 350-425°C and pressures up to 30 MPa.

Probably the most important parameter in determining the economic viability of an aqueous pyrolysis process is the pressure at which the process must operate. Since in the aqueous pyrolysis process it is necessary to maintain water in a liquid phase, these pressures are potentially quite high—the vapor pressure of water at 350°C is 165 MPa (2390 psia). Results from autoclave experiments are difficult to use directly as a guide for pressure requirements for an actual process. This is because the autoclave is a closed system with a fixed volume. In an actual process, venting of vapor is often desirable to control the process pressure and minimize required reactor volumes. This means that the phase composition of autoclave liquid and process liquids are potentially different.

To be able to estimate the pressure behavior of a proposed aqueous pyrolysis process it is important that some account of the interchange between liquid and vapor states occurring within the autoclave be understood. This is important not only from the standpoint of extrapolating the autoclave data to other more process related systems, but also to allow the maximum amount of data to be obtained from the experiments. Since the autoclave experiments involve heating a mixture from room temperature to reaction conditions and then cooling the system back to room temperature the pressure history of the autoclave can be fairly complicated. This is a result of the production of gas and vapors from the decomposition reactions and the exchange of components between the vapor and liquid phases.
The aim of this report is to analyze available data, primarily the pressure history data, from a series of autoclave experiments. The analysis involves simple material balance considerations and application of mathematical models. Particular attention is paid to the water component since its behavior is a major contributor to overall pressure response of the system.

SUMMARY OF EXPERIMENTAL DATA

The details of the experimental series is given elsewhere. This section is a brief description and summary of the run series. The data of interest was generated using a typical California heavy crude with an API gravity of 13.5°. Selected analytical data for the crude is given in Appendix I.

The autoclave experiments were done in vessels with an approximate volume of one liter. The reactors were typically half filled with oil-water mixtures. The gas space was filled with nitrogen. The experimental setup allowed the reactor and its contents to be heated and gently rocked. During the duration of an experiment, furnace and internal reactor temperatures were recorded along with the reactor pressure. A typical temperature and pressure history for the active period of an experiment is shown in Fig. 1. The active period of the experiment, heatup and isothermal intervals, typically lasted about eight hours while the cool-down period was about 24 hours. Most experiments included a nearly isothermal interval of about 30 minutes at the reaction temperature of choice. For the case of Experiment 126 shown in Fig. 1, the plateau temperature was about 425°C. Immediately following the isothermal interval, the furnace was turned off and temperature began to drop. The rate of initial decrease, based on an average of a number experiments is about 1°C per minute.
At the end of each experiment, after the reactor and its contents had been returned to near room temperature, a small gas sample was removed for gas chromatographic analysis. In addition, coke and oil yield and final API oil gravity were determined.

In many of the experiments, a catalyst was used to improve cracking and a surfactant was employed to enhance the mixing of the oil and water phases. In several experiments only water was added, and in two experiments the system consisted of only water and nitrogen. These water-nitrogen experiments were done to help verify model computations.

Table 1 lists information on oil-water mixture runs. The catalysts are designated by their catalytic action. The actual catalyst were: Fe-III 2-ethylhexanoate, CuCl₂, NaMoO₃, Zn(NO₃)₂, Ni(NO₃)₂ and Co-II 2-ethylhexanoate. The measurements of coke yields were difficult and in many cases required some estimation to be done. Experiment 96 was performed with crude oil which had been totally dewatered using a toluene distillation. It was estimated that approximately 4.5 wt% toluene remained in the final oil after dewatering. In estimating the water content of the mixtures, a value of 1.25 wt% water in the oil obtained from the dewatering test was used in addition to the water actually added to the mixture.
Table 1. Summary information on experimental autoclave runs.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<td>(kg)</td>
<td>(cc)</td>
<td>(%)</td>
<td>Type</td>
<td>Surfactant</td>
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<td>(MPa)</td>
<td>(gm)</td>
<td>Gravity</td>
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<td>1%</td>
<td>Co-II</td>
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<td>403</td>
<td>14.0</td>
<td>10.7</td>
<td>19.3</td>
</tr>
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<td>0.25%</td>
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<td>19.3</td>
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<td>11.8</td>
<td>0.5</td>
<td>16.9</td>
</tr>
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<td>1050</td>
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<td>0.25%</td>
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<td>402</td>
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<td>1%</td>
<td>Zn</td>
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<td>361</td>
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<td>13.7</td>
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<td>1%</td>
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<td>1%</td>
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<td>6.2</td>
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<td>1%</td>
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<td>1%</td>
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<td>1%</td>
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<td>1050</td>
<td>6.0%</td>
<td>0.25%</td>
<td>Fe-III</td>
<td>yes</td>
<td>413</td>
<td>23.8</td>
<td>31.5</td>
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</tr>
</tbody>
</table>

The extent of reaction can be gauged by the change in API gravity from the feed gravity of 13.5, by the amount of coke produced and by the amount of gas produced as measured by the final pressure. Table 1 indicates that experiments in which the peak temperature was below about 400°C show little evidence of reaction. Two of the three experiments, 116 and 126, showing the most reaction reached temperatures above 425°C. Results from the third experiment of this group, 29, indicate nearly as much reaction as runs 116 and 126, but it only reached 413°C. However, this run was held at the plateau temperature for an extended period of time, 150 minutes versus the normal 30 minutes.

PRESSURE DATA ANALYSIS

The first series of experiments (86, 88, 90, and 94) were performed using no catalyst and no surfactant. The maximum temperature was limited to about 350°C. No significant pyrolysis appeared to occur in any of these runs. However, the maximum pressure reached in each run varied over a considerable range. This was a direct result of the varying amount of water included in the mixture. The pressure responses as a function temperature are plotted in Fig. 2. Included in the figure is the vapor pressure of water. The measured pressure for each experiment
tracks the vapor pressure of water up to a given temperature. The point of departure increases in temperature with the amount of water in the feed mixture.

![Figure 2. Pressures for low temperature runs with no surfactant or catalyst.](image)

One explanation for the behavior shown in Fig. 2 is that all the water eventually evaporates. Consequently, the measured autoclave pressure deviates from the water vapor pressure curve because the liquid water phase vanishes. The results shown in Fig. 2 qualitatively are consistent with this hypothesis since the deviation from the water vapor pressure curve occurs and higher pressures in experiments in which more water is present. In Table 2, estimates of the amount of water in the vapor phase have been made for each these runs based on a simple estimate of the void volume and vapor density. The vapor density (assumed to be steam) was obtained from steam tables. The temperatures shown in the table were obtained by estimating a value at which the first significant deviation of the measured pressure from the water vapor pressure was noted for each run. These estimates indicate that deviation from the water vapor pressure curve occurs before all the water is in the vapor phase. This suggests that the liquid water fugacity is reduced by some mechanism. The simplest explanation is that the water is partially soluble in the oil phase and its activity coefficient is such that its fugacity is less than that of a pure water phase.
Table 2. Estimate of the amount of water in the vapor phase.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Water (wt. %)</th>
<th>T (°C)</th>
<th>Sat. Water Density (kg/m³)</th>
<th>Vapor Volume (cc)</th>
<th>Water Vapor, % of Total Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>1.2</td>
<td>190</td>
<td>6.394</td>
<td>491</td>
<td>50%</td>
</tr>
<tr>
<td>86</td>
<td>3.5</td>
<td>260</td>
<td>23.72</td>
<td>477</td>
<td>65%</td>
</tr>
<tr>
<td>88</td>
<td>6.2</td>
<td>300</td>
<td>46.21</td>
<td>478</td>
<td>72%</td>
</tr>
<tr>
<td>90</td>
<td>9.2</td>
<td>310</td>
<td>54.58</td>
<td>482</td>
<td>57%</td>
</tr>
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</table>

Water is known to be somewhat soluble in oils. The results in Table 2 suggest that water in oil solubilities of 0.5 to 5 wt% would be required. Hooper, Michel, and Prausnitz\(^2\) have summarized data for water-organic mixtures including components related to crude oils. They show water solubility in organics increases with temperature, as suggested by Table 2, and solubilities of as high as 80 mol% are reported. The solubility indicated by Table 2 translated into a mole basis are approximately 8-90 mol%. Therefore, it is concluded that water solubility in the oil phase is an important consideration in understanding the pressure behavior of the autoclave experiments.

To further explore the nature of the pressure responses, a computer model, the Autoclave Simulator Model (ACS), has been employed. This model, described more fully in reference 3, was developed to compute the pressure response of a closed autoclave system undergoing a heating and cooling sequence. The model solves mass balance equations and equilibrium constraints for a system which may include decomposition reactions that generate new species. The model can use an ideal gas assumption to compute gas phase component fugacities or a several simple equation-of-state models including the Redlich-Kwong equation. Provisions have been made in the liquid phase to handle the partial solubility of water in an oil phase. Changes in liquid densities are assumed available from simple temperature density tables. Fugacities of liquid components can be computed using an ideal mixing assumption or a simple Hilderbrand-Scatchard model\(^4\).

The ACS model was used to look more carefully at the pressure behavior of the first series of experiments. Since the pressures and temperatures reached in these experiments are high relative to the critical point of water (374.2°C and 22.05 MPa) nonideal behavior in the gas phase was included by using the Redlich-Kwong equation of state option. The pure component vapor pressure of the constituents was estimated using simple corresponding state model based on the component's normal boiling point\(^5\). However, the water vapor pressure was obtained from steam tables. Results for simple water-nitrogen only autoclave runs indicate that computed results obtained utilizing the simple Redlich-Kwong equation to compute gas phase fugacities did a fairly good job in matching the measured pressure response. See Appendix II for comparisons between computed and measured pressures.
Pseudocomponents are used to model the complicated crude oil composition. These pseudocomponents and their properties were obtained by using facilities available in a commercial process simulation product, ASPEN PLUS. Using measured boiling point curves, the following set of pseudocomponents were developed to represent the crude oil used in the experiments. They are listed in Table 3 along with their important characterizing properties.

Table 3. Pseudocomponents used to simulate crude oil

<table>
<thead>
<tr>
<th>Name</th>
<th>MW (gm/mole)</th>
<th>wt %</th>
<th>Specific gravity</th>
<th>Boiling Point (°C)</th>
<th>Critical Temp (°C)</th>
<th>Critical Pres (MPa)</th>
<th>Acentric Factor</th>
<th>API Gravity</th>
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<td>HNAPH</td>
<td>142</td>
<td>5.00</td>
<td>0.844</td>
<td>186</td>
<td>387</td>
<td>2.61</td>
<td>0.37</td>
<td>36.1</td>
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<td>178</td>
<td>6.00</td>
<td>0.877</td>
<td>241</td>
<td>443</td>
<td>2.19</td>
<td>0.46</td>
<td>29.9</td>
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<td>12.00</td>
<td>0.911</td>
<td>304</td>
<td>504</td>
<td>1.83</td>
<td>0.57</td>
<td>23.7</td>
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<tr>
<td>LVGO</td>
<td>307</td>
<td>16.10</td>
<td>0.954</td>
<td>388</td>
<td>583</td>
<td>1.48</td>
<td>0.73</td>
<td>16.9</td>
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<td>483</td>
<td>668</td>
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<td>VR</td>
<td>540</td>
<td>34.10</td>
<td>1.04</td>
<td>588</td>
<td>759</td>
<td>0.99</td>
<td>1.29</td>
<td>4.4</td>
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</table>

The first set of computations was done to confirm the importance of the water in oil solubility effect. In the calculations, water was assumed insoluble in oil at all temperatures. Results of the calculations are shown in Fig. 3. The simple model does a fairly good job in matching the no water Experiment 96. However, for those runs containing water, the model predicts, in general, considerably higher pressures than those measured.
Figure 3. Experimental and computed pressure responses for runs with no surfactant or catalyst assuming no solubility of water in the oil phase.

The model calculations were repeated assuming some solubility of water in the oil phase. The amount of solubility was adjusted to give the best fit of the pressure data. The solubility curve developed was constrained to maintain a smooth solubility behavior with temperature. The results of the calculations and the solubility curve used are shown in Figs. 4 and 5. Although not perfect, the computed results agree much better with the measured pressure data than the pressure computed assuming no water solubility.
In the model, the activity coefficient of water dissolved in the oil was estimated using a simple relation suggested by relations used in the ASPEN PLUS simulator package. The simple solution theory relation available in
ACS is inadequate since it does not correctly predict the activity coefficient at the point of full water saturation of the organic phase. This activity coefficient must be given by

\[ \gamma_i = \frac{1}{x_i}, \]

where \( x_i \) is mole fraction of water in the oil phase. For conditions below saturation the following simple relation is incorporated into the model

\[ \gamma_i = \frac{1}{(x_i')^{\alpha_s} x_i^{1-\alpha_s}}, \]

where \( x_i' \) is the water mole fraction at saturation at the temperature of interest and \( \alpha_s \) is a parameter. An \( \alpha_s \) equal to one was used in the calculations which leads to a constant activity coefficient.

After the initial series of runs, most of the experiments were done using a surfactant to increase the contact between oil and water phases. It was found that surfactant influenced the pressure response by reducing it somewhat with respect to the runs with no surfactant and limited water content. This is illustrated in Fig. 6 where the pressure responses from a number of surfactant containing runs are plotted. All these runs had a 6 wt% water content in the initial oil-water mixture. Three pressure curves computed using the ACS model are also shown in the figure. The computed curves were generated using different assumptions about the solubility of water in the oil phase: 1) no water solubility; 2) solubility used to match the no surfactant data; and 3) a solubility curve shifted to match the data for systems with surfactant present. Note that the data for all runs is fairly consistent below about 400°C and is matched fairly well by the pressure computed using the shifted solubility curve. The rapid increase in the pressure above 400°C, seen in Fig. 6, is a result of gas production by the pyrolysis reactions in this region.
Figure 6. Experimental and computed pressure responses for runs have a 6 wt% water content and surfactant present. The computed results are shown for three different assumptions concerning water solubility in the oil phase.

The shifted solubility curve was obtained from the no surfactant curve by multiplying by a simple factor and extending the relation above 350°C. The curves are compared in Fig. 7.

Figure 7. Water solubility in oil for surfactant and nonsurfactant systems
REACTION EXTENT—GAS AND COKE PRODUCTION

The amounts of coke and gas produced are both important measures of the extent of pyrolysis that has occurred. They are also important since they represent potential oil loss to any upgrading process. In addition, vapor evolution can play an important role in determining the system pressure. Unfortunately, experimental complications prohibit directly measuring these parameters. It is difficult to obtain unambiguous coke measurements from the final product because of separation and collection problems. The gas evolution measurements are complicated by condensation and solubility of vapors at low temperatures and the presence of large water partial pressures at elevated temperatures.

Probably the simplest way to deal with the vapor equilibria problem is to assume that the only products of pyrolysis are coke and species which can be detected in the vapor phase at the end of the experiment. Although this assumption neglects, for now, the production of oil components, it allows a useful first look at the pressure temperature behavior of the system, particularly at modest temperatures. The gas species, detected by GC analysis, include hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, methane, ethane, ethylene, propanes, and butanes.

A simple model was constructed using the ASPEN PLUS commercial simulation package to look at the end state of the system. The ASPEN PLUS simulator is primarily tailored for continuous processes. However, through proper choice of modules and other specifications it can be made to simulate the end point, or other selected intermediate points in the batch autoclave experiments. ASPEN PLUS was used for this purpose because it has a rich variety of property models, several of which are tailored for use in hydrocarbon systems. In addition, we plan to use this process simulator package to develop a process model for aqueous pyrolysis.

A listing of the ASPEN PLUS model in ASPEN PLUS input language is given in Appendix III. Several property models available in ASPEN PLUS were explored, but final calculations were done using the GRAYSON property set. This property set was developed for hydrocarbon and light gas containing systems. It is applicable to temperatures between 200-700 K and pressures below 21.3 MPa. It uses the Grayson-Streed correlation for reference state fugacity coefficients and the Scatchard-Hilderbrand model for activity coefficients. The Redlich-Kwong equation is used for vapor fugacities.

The model is setup so that for a given assumption about the pyrolysis stoichiometry, extent of reaction and system temperature, vapor and liquid compositions are computed which satisfy the desired mixture density. This leads to a computed system pressure. The mixture density is established by the amount of feed to the autoclave and the autoclave volume. For each run in which significant system pressure was left after cool down a set of stoichiometric parameters were determined using the ASPEN PLUS model which yielded a fit to the gas composition at the end of the cool-down period.
In doing the fit, carbon monoxide was not included since it appeared in only four of the runs and was at low levels. Also hydrocarbon species above methane were lumped into a single alkane species for each carbon number. Although there is the possibility of the water-gas-shift reaction occurring and involving some of the water, it was not explicitly included as a reactant. The temperatures are fairly low and the amount of hydrogen and carbon monoxide production in the runs was relatively low. The crude oil was modeled with five pseudocomponents as described previously.

Table 4 list the results of the fitting procedure. The reaction extent is measured as a fraction of initial crude oil which has reacted. The coke fraction is a weight fraction of reacted oil which ends up as coke. In the analysis, coke was assumed to be pure carbon. The gas stoichiometry is given as ratios to methane production. The total assumed weight of gas is given by the product of the reaction extent and one minus the coke fraction. The term gas is used here as shorthand for light components produced by the pyrolysis. All these components are not in the gas after the cool-down period. For example, for Run 126, the percentages of each component computed to be in the vapor phase at the end of the cool-down period, when the autoclave conditions were 25°C and 2.38 MPa, were the following: CO₂ - 63%, H₂S - 22%, H₂ - 98%, CH₄ - 78%, C₂'s - 44%, C₃'s - 21%, and C₄'s - 6%.

Table 4. Estimate of extent of reaction, coke fraction and gas stoichiometry for runs with significant gas production grouped according to catalyst present.

<table>
<thead>
<tr>
<th>FE-III Run</th>
<th>Reaction Extent</th>
<th>Coke Fraction</th>
<th>CO₂</th>
<th>H₂S</th>
<th>H₂</th>
<th>CH₄</th>
<th>C₂'s</th>
<th>C₃'s</th>
<th>C₄'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.040</td>
<td>0.500</td>
<td>0.305</td>
<td>0.200</td>
<td>0.130</td>
<td>1.000</td>
<td>0.352</td>
<td>0.320</td>
<td>0.130</td>
</tr>
<tr>
<td>122</td>
<td>0.047</td>
<td>0.470</td>
<td>0.217</td>
<td>0.104</td>
<td>0.107</td>
<td>1.000</td>
<td>0.356</td>
<td>0.320</td>
<td>0.280</td>
</tr>
<tr>
<td>126</td>
<td>0.115</td>
<td>0.480</td>
<td>0.121</td>
<td>0.062</td>
<td>0.025</td>
<td>1.000</td>
<td>0.390</td>
<td>0.269</td>
<td>0.150</td>
</tr>
<tr>
<td>6</td>
<td>0.043</td>
<td>0.470</td>
<td>0.225</td>
<td>0.126</td>
<td>0.107</td>
<td>1.000</td>
<td>0.323</td>
<td>0.255</td>
<td>0.190</td>
</tr>
<tr>
<td>29</td>
<td>0.122</td>
<td>0.540</td>
<td>0.100</td>
<td>0.000</td>
<td>0.058</td>
<td>1.000</td>
<td>0.296</td>
<td>0.152</td>
<td>0.120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mo Run</th>
<th>Reaction Extent</th>
<th>Coke Fraction</th>
<th>CO₂</th>
<th>H₂S</th>
<th>H₂</th>
<th>CH₄</th>
<th>C₂'s</th>
<th>C₃'s</th>
<th>C₄'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>0.039</td>
<td>0.300</td>
<td>0.180</td>
<td>0.000</td>
<td>0.063</td>
<td>1.000</td>
<td>0.400</td>
<td>0.380</td>
<td>0.400</td>
</tr>
<tr>
<td>112</td>
<td>0.052</td>
<td>0.440</td>
<td>0.290</td>
<td>0.120</td>
<td>0.087</td>
<td>1.000</td>
<td>0.380</td>
<td>0.410</td>
<td>0.460</td>
</tr>
<tr>
<td>116</td>
<td>0.147</td>
<td>0.520</td>
<td>0.148</td>
<td>0.030</td>
<td>0.054</td>
<td>1.000</td>
<td>0.386</td>
<td>0.290</td>
<td>0.200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Co Run</th>
<th>Reaction Extent</th>
<th>Coke Fraction</th>
<th>CO₂</th>
<th>H₂S</th>
<th>H₂</th>
<th>CH₄</th>
<th>C₂'s</th>
<th>C₃'s</th>
<th>C₄'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>0.072</td>
<td>0.450</td>
<td>0.225</td>
<td>0.024</td>
<td>0.028</td>
<td>1.000</td>
<td>0.401</td>
<td>0.393</td>
<td>0.330</td>
</tr>
<tr>
<td>10</td>
<td>0.064</td>
<td>0.420</td>
<td>0.214</td>
<td>0.024</td>
<td>0.160</td>
<td>1.000</td>
<td>0.365</td>
<td>0.368</td>
<td>0.330</td>
</tr>
<tr>
<td>14</td>
<td>0.094</td>
<td>0.685</td>
<td>0.172</td>
<td>0.000</td>
<td>0.396</td>
<td>1.000</td>
<td>0.262</td>
<td>0.197</td>
<td>0.130</td>
</tr>
<tr>
<td>18</td>
<td>0.038</td>
<td>0.330</td>
<td>0.225</td>
<td>0.008</td>
<td>0.295</td>
<td>1.000</td>
<td>0.326</td>
<td>0.278</td>
<td>0.140</td>
</tr>
</tbody>
</table>
Although results are shown for all the catalysts, the current focus is on Fe-III. More runs were done with this catalyst and as a result the remaining analysis related to stoichiometry and kinetics will deal only with the Fe-III runs. Analysis of the Fe-III runs show a remarkably consistent coke fraction averaging about 0.5. There is no trend in coke yield, as a fraction of total oil reacted, with extent of reaction. The gas stoichiometry is not as consistent as the coke yield. There appears to be some trend in fraction of hydrogen and carbon dioxide with extent of reaction. The data suggest that at higher conversions these two components tend to make up a lower fraction of total gas production. The C2's remain very consistent from run to run. Less consistency is seen in the other components, with the highest variation in the H2S fraction.

An average stoichiometry was obtained from the Fe-III data and is listed in Table 5. Run 29 was omitted from the average because H2S was not reported. This stoichiometry was arrived at assuming that the listed components are the only reaction products. Undoubtedly, other components are formed but are too heavy to show up in any significant way in the vapor phase at room temperature. However, some information can be obtained from the changes in API gravity of the oil. This information can be used to speculate about additional changes occurring during the pyrolysis reactions.

Table 5. Average reaction stoichiometry.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
<th>Gas - Ratio with CH4 (mol/mol)</th>
<th>Gas - Ratio with Total Gas (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>0.070</td>
<td>0.19</td>
<td>0.088</td>
</tr>
<tr>
<td>H2S</td>
<td>0.034</td>
<td>0.12</td>
<td>0.055</td>
</tr>
<tr>
<td>H2</td>
<td>0.0015</td>
<td>0.09</td>
<td>0.041</td>
</tr>
<tr>
<td>CH4</td>
<td>0.133</td>
<td>1</td>
<td>0.461</td>
</tr>
<tr>
<td>C2's</td>
<td>0.085</td>
<td>0.34</td>
<td>0.157</td>
</tr>
<tr>
<td>C3's</td>
<td>0.095</td>
<td>0.26</td>
<td>0.120</td>
</tr>
<tr>
<td>C4's</td>
<td>0.082</td>
<td>0.17</td>
<td>0.078</td>
</tr>
</tbody>
</table>

The simplest method of incorporating the change of API gravity into a consideration of overall reaction stoichiometry is to make the simplifying assumption that, in addition to the components already listed, a single relatively light oil is a product of the pyrolysis of the crude oil. To further simplify the system it is assumed that the ratio of this new oil to production of other components is fixed. With these assumptions and the ASPEN PLUS model, computations were done in which the relative amount and nature of the light product oil was adjusted in an effort to obtain the best fit for the measured API gravities for the Fe-III experiments. The results are shown in
Table 6. The light oil component used was a pseudocomponent with a molecular weight of 109 amu and an API gravity of 45°. This component was generated by ASPEN PLUS as one of the potential cuts for describing a crude oil representing the oil fraction with an average boiling point of 121°C. This cut is the next lightest below those present in the feed crude. An even lighter cut was tried, having a molecular weight of about 76 amu. However, this component had enough volatility that upon reduction of pressure to atmospheric levels insufficient material was computed to remain in the liquid to yield the measured API gravity changes.

Table 6. Computed oil gravity assuming a weight fraction light oil production of 0.6. The feed crude had an API gravity of 13.5.

<table>
<thead>
<tr>
<th>Run</th>
<th>Measured API Gravity</th>
<th>Computed API Gravity</th>
<th>Reaction Extent</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>17.5</td>
<td>18.1</td>
<td>0.161</td>
</tr>
<tr>
<td>120</td>
<td>16.8</td>
<td>16.5</td>
<td>0.112</td>
</tr>
<tr>
<td>122</td>
<td>17.9</td>
<td>17.3</td>
<td>0.129</td>
</tr>
<tr>
<td>126</td>
<td>22.0</td>
<td>22.3</td>
<td>0.340</td>
</tr>
<tr>
<td>6</td>
<td>17.0</td>
<td>16.9</td>
<td>0.118</td>
</tr>
<tr>
<td>29</td>
<td>not available</td>
<td>23.4</td>
<td>0.355</td>
</tr>
</tbody>
</table>

It was assumed that the oil used in the gravity measurements was represented by the liquid which would result from flashing the final mixture to one atmosphere and separating out the coke and free-water phase. Note this assumes the vapor above the oil is light gases. This is equivalent to assuming that the sample was kept in a sealed container after depressurization and large amounts of air were not swept over its surface.

The match of measured gravities with this simple model is remarkably good. However, the addition of this somewhat volatile component has the potential for altering the final equilibrium pressure. This is a result of added volatility, but more importantly the change in the liquid properties. This effect was reasonably small and was compensated for by readjusting the reaction extent. The reaction extent used is listed in Table 6. Most of the difference in reaction extent between those reported in Tables 4 and 6 is a result of the introduction of a major new product of the reaction, the light oil, and not the minor change in phase equilibria. The adjustment to reaction extent to compensate for changes in equilibria was only a few percent.

So far the issue of reaction rate has not been addressed. Clearly, the actual changes occurring are very complex and the simplified stoichiometry used above, and any simple kinetic expressions based on them, are rough engineering approximations. However, rough engineering approximations are useful in helping to describe conditions for a proposed process. The simplest rate expression that has a chance of capturing some aspects of the true behavior is one based on the assumption that all
components of the feed oil decompose at the same rate and with the same basic stoichiometry when viewed on a weight basis. If this is true, then the reaction rate for experiments should be roughly constant at a given temperature since the estimated extent of the reactions, as a fraction of original oil, is fairly small.

One way to test this hypothesis is to look at the pressure behavior of the runs during the plateau temperature period. Since light gases are assumed to be products of reaction, one would expect that the pressure of the system would increase with time in some linear fashion. The details of the relation between pressure increase and light-gas production is complicated and will be addressed below. However, here it is useful to determine if the pressure increases are linear during the plateau period. The plots shown in Fig. 8 do indeed indicate a near linear increase in pressure during the plateau period, even for Runs 126 and 29 in which the extent of reaction is as high as 36%.
Figure 8. Plateau period of the Runs 108, 120, 122, 126, 6 and 29 demonstrating the near linear increase in autoclave pressure.

The ACS model was developed to allow rate controlled gas release to be incorporated into the modeling of change within a sealed autoclave. This model was used to integrate the proposed simple first-order reaction over the course of the heating and cooling sequence of those Fe-III experiments in which significant pyrolysis occurred. The assumed reaction stoichiometry was that described above, including the production of light oil. The overall stoichiometry used is listed in Table 7. Other model parameters used relating to densities and phase equilibria are given in Appendix IV.
Table 7. Average reaction stoichiometry including the light oil product P-OIL.

<table>
<thead>
<tr>
<th>Weight Fraction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>0.2</td>
</tr>
<tr>
<td>P-OIL</td>
<td>0.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.028</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.014</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0006</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.053</td>
</tr>
<tr>
<td>C₂’s</td>
<td>0.034</td>
</tr>
<tr>
<td>C₃’s</td>
<td>0.038</td>
</tr>
<tr>
<td>C₄’s</td>
<td>0.033</td>
</tr>
</tbody>
</table>

The pre-exponential kinetic values which best fit the coke yield data for the Fe-III runs are listed in Table 8 along with the computed reaction extent for each run. These were found using the average stoichiometry given in Table 7 and adjusting the pre-exponential rate factor until the best fit of the final autoclave pressure, oil gravity and coke production were obtained. The values of the factors determined in this way are fairly consistent from run to run. An extent-weighted average of these values yields an value of 1.7x10⁸ s⁻¹.

Table 8. ACS determined rates and computed extent of reaction.

<table>
<thead>
<tr>
<th>Run</th>
<th>Pre-Exponential (s⁻¹)</th>
<th>Reaction Extent</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>1.89x10⁸</td>
<td>0.145</td>
</tr>
<tr>
<td>120</td>
<td>1.29x10⁸</td>
<td>0.099</td>
</tr>
<tr>
<td>122</td>
<td>1.36x10⁸</td>
<td>0.110</td>
</tr>
<tr>
<td>126</td>
<td>1.93x10⁸</td>
<td>0.325</td>
</tr>
<tr>
<td>6</td>
<td>1.45x10⁸</td>
<td>0.109</td>
</tr>
<tr>
<td>29</td>
<td>1.84x10⁸</td>
<td>0.368</td>
</tr>
</tbody>
</table>

Since detailed analytical information on the crude oil and products is limited, no attempt in the modeling was explicitly made to guarantee individual atom balances, only overall weight balances are used. However, it is of interest to determine the results of an atom balance based on the stoichiometry shown in Table 7. Analytical data is only available for the sulfur content of the crude oil. Using this number and average values for crude oils from reference 7, in addition to values for the P-OIL product which fall within the range for crude oils (see Table 9), atom balances on carbon, hydrogen, and sulfur were computed. Nitrogen is omitted from the balance since no information on nitrogen bearing products was available. The carbon and hydrogen were balanced by using the atomic composition of oils shown in Table 9.
For oxygen, the balance indicates an excess of oxygen in the product mix. This is attributed to water which enters the reaction as a reactant during secondary reactions such as would occur in the water-gas-shift reaction. The amount of water consumed based on the average stoichiometry would be equal to approximately 4-5 wt% of the feed for runs with the highest extent of reaction.

Table 9. Oil atomic composition in weight percent.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRUDE</td>
<td>85.46%</td>
<td>12.00%</td>
<td>1.00%</td>
<td>1.54%</td>
</tr>
<tr>
<td>P-OIL</td>
<td>85.10%</td>
<td>14.00%</td>
<td>0.05%</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

**COMPUTED PRESSURE MATCHES—RUNS WITH REACTION**

Using the average stoichiometry given in Table 7 and the average rate model which is given by

\[
\text{rate} = W_{\text{crude}} \times 1.7 \times 10^8 \exp \left( \frac{-20000}{T} \right)
\]

where \(W_{\text{crude}}\) is the amount of crude oil in the liquid phase and the rate is given on a weight-per-second basis, computations were performed to look at the time evolution of the pressure within the autoclave during experiments in which significant gas was produced. Results are shown in Fig. 9 for runs with highest gas evolution, runs 126 and 29. Run 126 reached a maximum temperature of 429°C while run 29 was held at 413°C, but the temperature in run 29 was held longer so that the total reaction extent was approximately the same. The calculations were done with the original water solubility curve, for the case in which a surfactant is present, shown in Fig. 7. Notice, that during the active reaction period, the time at highest temperature, the model under predicts the rate of increase in pressure.

Some work was done to determine why the model under predicts this rise. Two candidate reasons are that the equilibrium relations change in a fashion not captured by the model or that a component is formed which appears in the vapor phase at elevated pressures but is absent from the vapor when the system is cooled. The component P-OIL behaves in this way and is present in the model used to develop the curves shown in Fig. 9. Other model products such as pentane, toluene, and n-decane were included in the reaction scheme. None seem to significantly improve the fit at the peak pressures.

However, some improvement in the pressure fit was found when the water solubility relation was modified to allow more water to enter the vapor phase at the higher temperatures. A modified solubility was developed which incorporated this effect and was used to compute the improved pressure matches for Experiments 126 and 29 shown in Fig. 10. The solubility modification simply involved not extrapolating the solubility curve, shown in Fig. 7, linearly for temperatures beyond
350°C, but instead setting the solubility at 430°C to 9 wt%. This change in solubility should be viewed as a means of changing the activity of the water in the oil phase. The solubility in conjunction with the simple activity coefficient model described previously sets the fugacity of the water dissolved in the oil and, thus, the fugacity of water vapor in the gas phase.

One of the ultimate aims of the current work is to develop an ASPEN PLUS based model for the proposed upgrading process. For this reason, and because of the more sophisticated property models available in the ASPEN PLUS environment, it is of interest to compare ASPEN PLUS computations to the data and the ACS model results. For this purpose, the final overall ACS model which included a flattening of the solubility model was used.

In ASPEN PLUS, the solubility model is forced to have the following form with respect to temperature

\[ s = \exp \left( c_1 + \frac{c_2}{T} + c_3 T \right) \]
where $s$ is the solubility of water in oil on a mole fraction basis, and the $c's$ are coefficients specific to each oil component used. This constraint does not allow exactly the same solubility function to be used in both the ACS model and ASPEN PLUS model. However, the parameters $c_1 = 24.35$, $c_2 = -8000$, and $c_3 = -0.019$ gives computed points similar to those used in the ACS model calculations, these are compared in Table 10. In the table, a molecular weight of 389 amu was used in computing the values. This is the average value for the crude oil based on the pseudocomponent representation used. As describe earlier, the ACS uses a solubility model which is based simply on total weight of oil and water in the oil phase. Using the same coefficients for all crude oil components in the ASPEN PLUS model along with the average stoichiometry given above, pressures where computed at several reaction times for runs 126 and 29. The reaction extent was taken from results computed by the ACS model. Fig. 11 shows that the computed pressure results obtained from the ASPEN PLUS model and the ACS model are very similar. Both do a fair job in computing the autoclave pressures.

### Table 10. A comparison of water solubility used in the ASPEN PLUS model and the ACS model.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ASPEN PLUS Water (wt%)</th>
<th>ACS Water (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>50</td>
<td>0.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>100</td>
<td>0.1%</td>
<td>0.4%</td>
</tr>
<tr>
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<td>2.8%</td>
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Figure 11. Pressures computed using the ASPEN PLUS model compared to experimental data and results from the ACS model for runs 126 and 29.
CONCLUSIONS

Data and modeling work show that autoclave pressures for heavy-crude oil/water systems can exhibit total pressures well below the vapor pressure of water at conditions in which not all the water is in the vapor phase. This is a result of increased solubility of water in the oil phase at elevated temperatures. Further, pressure measurements indicate that the presence of a surfactant increases the apparent solubility. A simple water-in-oil activity coefficient model was used to fit pressure responses for autoclave experiments.

Autoclave aqueous pyrolysis runs in which temperatures of 400°C or above were reached exhibited measurable gas production. This gas production resulted in pressure increases during periods of constant temperature. These pressure increases were remarkably linear with time. A simple first-order decomposition is consistent with such a response if essentially all the original crude oil undergoes similar pyrolysis decomposition. A first-order reaction model was constructed for the runs in which Fe-III was used as a catalyst. The model did a fair job in matching gas and coke production as well as change in oil gravity.

The first-order reaction model was used in a model developed to look at the evolution of pressure within an autoclave with time. Also, an ASPEN PLUS based model gave similar results for selected points. The models tend to underpredict the rate of pressure rise with time at the plateau temperatures. A number of different reaction products were postulated in an attempt to overcome this deficiency. These attempts met with little success. The one parameter which seemed to improve the performance was to assume that at temperatures above 350-400°C, the activity coefficient of water in oil increased, releasing more water vapor into the vapor phase. This was modeled as a decrease in water solubility in the oil phase.

Although the simple reaction model did a fair job in recreating the pressure history of the autoclave experiments, more work is probably warranted. In particular, the problem of matching the isothermal pressure rise needs further exploration, as does the cause of variability in measured gas composition. If the measured gas composition variation persists, a more complicated reaction scheme than the simple one-step pyrolysis reaction used here will be necessary. A more complicated reaction scheme may also help resolve the isothermal pressure rise problem. Also a better model for the activity of water in the oil phase would be required to improve predictive capability. Finally, post-run analysis of the change in the makeup of the oil phase would probably help in formulating a better model for the improvement in oil gravity. This may also help in understanding the vapor-liquid equilibrium behavior.
REFERENCES


APPENDIX I.

CRUDE OIL DATA

Selected data for Midway Sunset crude Oil analyzed by Core Laboratories:

API Gravity
Pour Point
Sediment and water
Sulfur, Total by x-ray

<table>
<thead>
<tr>
<th>Cuts</th>
<th>API Gravity</th>
<th>Wt %</th>
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</thead>
<tbody>
<tr>
<td>1. IBP-375 °F</td>
<td>371.1</td>
<td>0.87</td>
</tr>
<tr>
<td>2. 375-500 °F</td>
<td>29.9</td>
<td>5.36</td>
</tr>
<tr>
<td>3. 500-620 °F</td>
<td>23.7</td>
<td>10.8</td>
</tr>
<tr>
<td>4. 620-800 °F</td>
<td>16.0</td>
<td>14.79</td>
</tr>
<tr>
<td>5. 800-950 °F</td>
<td>13.8</td>
<td>21.94</td>
</tr>
<tr>
<td>6. 950+ °F</td>
<td>4.6</td>
<td>46.08</td>
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</tbody>
</table>

This information along with boiling point curves for each cut were used to determine the pseudocomponent properties and amounts given in the report. The analysis above is actually from oil which has undergone surface dewatering and the loss of some light ends. To arrive at the final weight distribution given in the report, the lighter ends were increased until the mixture had an API gravity of 13.5°—approximately equivalent to that used in the laboratory experiments. The increases used preserved the monotonic nature of component amounts with API gravity.
Two autoclave runs were done with a water nitrogen system to help evaluate the ability of the ACS model to compute autoclave pressures. The first run, #32, was a system with excess water. The amount of water initially in the 1050 cm$^3$ autoclave, 0.3 kg, insured that liquid would be present up to the critical point. In the second run, #34, a much smaller amount of water, 0.033 kg, was used. In this case liquid disappeared before reaching the critical point. For both runs, the system was initially pressurized at room temperature to approximately 1.6 MPa with nitrogen.

In Fig. II-1 computed pressures for Run 32 are compared to measured autoclave pressures. The Redlich-Kwong equation of state was used to compute gas phase fugacities. Results using the ideal gas law yielded similar pressure results. However, the computations using the Redlich-Kwong equation result in twice as much water in the vapor phase as is the case for the assumption of ideal behavior. This is primarily a result of the more accurate gas phase density estimates provided by this equation. The Redlich-Kwong results estimate a gas phase compressibility of 0.57 at 358°C.

![Figure II-1](image-url)

*Figure II-1.* Computed pressure for run 32 using the ACS model and the Redlich-Kwong equation of state for gas phase fugacities.
In Fig. II-2 results for Run 34 are plotted. Here the pressure response based on the Redlich-Kwong equation differs from that obtained assuming ideal gas behavior. This is because liquid disappears and as a result predicting the amount of water in the vapor phase influences the computed pressure directly.

![Pressure vs Temperature](image)

**Figure II-2.** Computed pressure for run 34 using the ACS model and the Redlich-Kwong equation of state and the ideal gas law for gas phase fugacities.

For both runs the ACS model using the Redlich-Kwong equation does a fairly good job in calculating the autoclave pressure as a function of temperature.
APPENDIX III.

ASPEN MODEL

The ASPEN PLUS model described below was used to look at selected states of the autoclave system. It allows three separate states of the system to be computed in one run. The basic philosophy is to use other means to establish the extent of any reactions which occur. This information along with initial conditions are then used to compute the pressure of the autoclave system. The pressure is determined by using an ASPEN PLUS DESIGN-SPEC to set the total density of the autoclave. This density is known from initial loading information.

The basic design of the model relies on two input files. The first is an ASPEN PLUS input file which defines the model. The second file is an ASCII data file to define the parameters specific to a run. The model is structured in this way for two reasons. One reason is to allow repeated runs to execute faster. Although the computation time for the model on an HP-9000/730 is less than a minute, even this time can be annoying when many runs are to be done. By isolating the basic run specific data, the ASPEN PLUS's rerun option can be employed which greatly speeds up execution. The other reason, probably more important, is to allow documentation of runs to be maintained in a more economical fashion and allow model revisions to be made with a minimum of effort. If the basic run data is put directly into the input file then when a revision in the model structure is made, these same modifications must be made in all input files representing other runs. With the basic structure of the model specified by a single input file and the run data separated, only one file needs to be changed to modify the model. Also the run data information is only about 50 lines including generous commenting, while the ASPEN PLUS input file was 1300 lines long.

The description of the model will assume that the reader is familiar with the ASPEN PLUS input language. A complete listing of the model with line numbers is given at the end of this appendix along with a sample input file.

The model is broken into four flowsheets. This is done to allow for the possibility of using different property models in different flowsheet sections. The first three are very similar and use MIXER, FLASH2 and RSTOIC modules to perform the required calculations. Each of these flowsheets works on a separate, but identical, feed stream. The feed streams are meant to represent the material loaded into the autoclave reactor. The simulator is most naturally a continuous flow simulator and the autoclave is a closed system. To simulate the closed system the ratio of flow rates of input material is set so to give the proper ratios and set at levels such that one second of time yields the same quantity of material as is in the autoclave. The fourth flowsheet section is used to simulate what occurs when the autoclave is depressurized. This section uses results from flowsheet three as input. Consequently, to be meaningful the state of the outlet of flowsheet three should be
equivalent to the end state of the system after cool down and just prior to depressurising.

The following discussion refers to the listing of the ".inp" file located near the end of this appendix. At the start of the file are a number of comment lines and a run title. Starting on line 25 is the FORTRAN block SETI. This block is used to read input data from the ASCII input file, do some calculations, and then set parameters in computational modules. These parameters include input flow rates as well as temperatures, pressures and extent of oil pyrolysis for each of three desired system states and for the final depressurized state. Also, pyrolysis stoichiometry is set based on information given in the input file. The setting of stoichiometry is rather lengthy because parameters are set for each oil pseudocomponent in each of three RSTOIC modules. Also embedded in the block are a set of default values for all parameters read from the ASCII input file along with a brief description. Generally all default values are overwritten by data from the ASCII data file. The input from the ASCII file is done using a FORTRAN NAMELIST construct. The data in the ASCII file for a typical run is described later.

The next block in the ".inp" file is also a FORTRAN BLOCK. This block, INIT, is meant to run as soon as the primary input stream has been generated by a MIXF module. This block sets the overall system density, which is invariant until depressurization, and is used by the DESIGN-SPEC's to compute system pressure. The next section of the file, from lines 803 to 824, sets up some control and reporting information. For the ASPEN PLUS model itself, English input units have been used since all the information on the crude oil is in English units. However, the computed results are to be reported primarily in SI units.

The next section, lines 825-973, define the property options and sets up the pseudocomponents used to represent the crude oil. The ASPEN PLUS FREE-WATER option is used along with a so called API method for computing liquid volumes tailored for petroleum liquids. A number of possible property model sets are commented out, the preferred GRAYSON set is active. The SOLU-WATER=1 refers to the type of activity model chosen for water in the oil phase. This is the model described in the body of the text. The list of components includes standard species and several others used to complete the description of the stoichiometry of the oil pyrolysis. The component HHC is a generic name intended to be used for a light hydrocarbon product of pyrolysis not included in the set list. This allows runs in which various species are used without effecting the coding in the model. The current version uses normal butane. If this species is changed, then its molecular weight needs to be set accordingly, see notes in lines 850-851. P-OIL is the assumed oil product of the pyrolysis and its properties are set using its assumed boiling point and gravity. Other oils similar to the pseudocomponents used in the crude representation are included in comment lines for reference. If the properties of P-OIL are changed, then the molecular weight, set in SETI line 544, should be changed as needed. The PROP-DATA paragraph beginning on line 870 is included so that the water solubility parameters for oil components can be modified from their ASPEN
PLUS default values. Solubility of water in all components except the crude oil components are set to very small values. Those component names not included in the COMPONENTS list are for the pseudocomponents used to define the crude oil. For reference a number of types of solubility relations are included in comment lines. The active set is for the modified surfactant solubility set described in the report body. The final portion of this section, lines 917-973, defines the pseudocomponents used to represent the crude oil. This is done using ASPEN PLUS implemented routines to develop amounts and properties from crude oil cut information. This section must be modified if a different crude oil is used in the simulation. The final BLEND paragraph sets the crude oil composition. The comments document how the lighter ends were increased in order to modify the composition of the 11.5 API gravity crude oil to represent the 13.5 API gravity oil used in the experiments.

The next section, lines 974-1006, describes the four flowsheets used in the model. Notice a DUP module is used to feed the same stream to each of the first three flowsheet areas. These three areas perform essentially identical calculations but can have different reaction extents and temperatures. The pressures are set by DESIGN-SPECS based on density as described above. The fourth area allows vapor to flash off setting the desired final pressure.

The next section simply defines default values for input streams. The flow rates are generally overwritten by data from the ASCII input file.

Starting on line 1022 is the block specification section where parameters for all process modules are defined.

The next section, lines 1137-1190, defines the design specifications used to compute the pressure in the autoclave based on a known overall system density. Three DESIGN-SPEC paragraphs are used, one each for flowsheets 1-3.

The final section, starting on line 1191, is a FORTRAN block used to collect selected computed information and print it in a summary table to the ASPEN PLUS report file. This table can be found in the ".rep" file by searching for the "=========" pattern.

As stated above, a given simulation is meant to get its primary input information not from the ".inp" file but rather from a ASCII input file. This file is read with the FORTRAN namelist feature. The namelist format has been slightly augmented by coding in the SETI block to allow comment only lines to be included. The comment lines must begin with "+". A sample input file is included after the ASPEN PLUS input file at the end of this appendix and its contents are briefly describe below. The input variables used can be linked to the ASPEN PLUS file by there names. Some additional comments on variable are present in the ".inp" file.
The first data entry in the sample ASCII input file is on line 5 and sets the amounts of crude oil, water and nitrogen, in kilograms, loaded into the autoclave. Lines 12-21 define the stoichiometry of the pyrolysis reaction. This same stoichiometry is applied to each of the crude oil pseudocomponents. The first two variables "wtfc" and "wto" are the weight fraction of reacted component which forms coke (taken as carbon in the model) and the oil product P-OIL. The remaining variables define all other products on a relative mole basis. In the input shown, they are all ratioed to methane.

Lines 25-31 define a measured dry-gas composition and are only included for convenience in looking at the output. They are not used in any of the model calculations. This same comment is true of the next input, the amount of coke in kilograms, in line 34.

Lines 39-44 define the extent of the pyrolysis reactions which are desired to occur in each flowsheet area. The variable "er" is the extent of reaction as a fraction of the reactant (i.e., each crude oil component) and is used as the reaction extent in flowsheet area 3. The variables "fer1" and "fer2" define the amount of reaction occurring in flowsheet area 1 and 2 respectively relative to "er". That is, the extent of reaction in flowsheet area 1 is the product of "er" and "fer1".

The temperatures desired for flowsheet areas is specified in degrees celsius in lines 49-52. With each temperature specification "tcn" where "n" is 1,2 or 3 a corresponding pressure is entered. These pressures are for output only and are not used in the model calculations. The temperature for the fourth flowsheet area is assumed to be the same as that in the third, "tc3", the pressure is set in the ".inp' file to 0.1 MPa in the fourth flow sheet area.

The following is the listing for the ASPEN PLUS ".inp" file.

```plaintext
1 ;=================================================================================
2 ; Lawrence Livermore National Laboratory
3 ; C. B. Thorsness
4 ; rstoic.inp. Rev 1.0
5 ;=================================================================================
6 ;=================================================================================
7 ; TITLE 'Model of autoclave (rstoic.inp)'
8 ;=================================================================================
9 ; Overall stream description
10 ;=================================================================================
11 ; Input Streams:
12 ; FEEDO - Crude oil stream
13 ; FEEDW - Primarily water but can include other components such as nitrogen
14 ;=================================================================================
15 ; Set input parameters
16 ;=================================================================================
17 ;=================================================================================
18 ;=================================================================================
19 ;=================================================================================
20 ;=================================================================================
21 ;=================================================================================
22 ;=================================================================================
23 ;=================================================================================
24 ;=================================================================================
25 ;=================================================================================
26 ;=================================================================================
27 ;=================================================================================
28 ;=================================================================================
29 ;=================================================================================
30 ;=================================================================================
31 ;=================================================================================
```
FORTRAN SETI

F common/usr1/ dens,p=1,p=2,p=3,x(9),vol,t1c,t2c,t3c,t4c,coke
F character line*80,file*20
F namelist /indata/ fch4,fc2h6,fc3h8,fhhc,fco2,fh2,fh2s,vol,
F & wfo,wtfc,x,er,ferl,fer2,t1c,p=1,t2c,p=2,t3c,p=3,
F & flcr,fln2,flh2,coke,t4c,p=4
;

Can't set crude flow therefore use two streams

DEFINE flcrx STREAM-VAR STREAM=FEEDO MASS-FLCW

DEFINE fln2x MASS-FLOW STREAM=Fmm ccMxmNr=N2

DEFINE flh20x MASS-- STREAM=FEEUV CMwENP H20

DBFINB tl

DEFINE t1 BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=TEMP

DEFINE t1 BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=PRESS

DEFINE p1 BLOCK-VAR BLOCK=HTR2 SENTENCE=PARAM VARIABLE=PRESS

DEFINE t1 BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=TEMP

DEFINE t1 BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=PRESS

DEFINE t1 BLOCK-VAR BLOCK=HTR4 SENTENCE=PARAM VARIABLE=TEMP

DEFINE p1 BLOCK-VAR BLOCK=HTR4 SENTENCE=PARAM VARIABLE=PRESS

DEFINE aext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV VARIABLE=CONV

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DEFINE bext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV VARIABLE=CONV

ID1=2

DEFINE cext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV VARIABLE=CONV

ID1=3

DEFINE dext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV VARIABLE=CONV

ID1=4

DEFINE eext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV VARIABLE=CONV

ID1=5

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DEFINE bo1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF &
ID1=2 ID2=MIXED ID3=P-OIL

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ID1=3 ID2=MIXED ID3=P-OIL

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190 ID1=1 ID2=MIXED ID3=C2H6
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192 ID1=1 ID2=MIXED ID3=C3H8
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200 ID1=1 ID2=MIXED ID3=H2S
201 DEFINE ao2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
202 ID1=1 ID2=MIXED ID3=P-OIL
203
204 DEFINE bc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
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213 ID1=2 ID2=MIXED ID3=CO2
214 DEFINE bh22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
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DEFINE bhhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
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DEFINE bh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=2 ID2=MIXED ID3=H2S
DEFINE bo2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=2 ID2=MIXED ID3=P-OIL
DEFINE cc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=CISOLID ID3=C
DEFINE cch42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=CH4
DEFINE cc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=C2H6
DEFINE cc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=C3H8
DEFINE cc022 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=CO2
DEFINE ch22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=H2
DEFINE chhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=hhc
DEFINE ch2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=H2S
DEFINE ch2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=3 ID2=MIXED ID3=H2
DEFINE dhhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=4 ID2=MIXED ID3=hhc
DEFINE dh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=4 ID2=MIXED ID3=H2S
DEFINE dh2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=4 ID2=MIXED ID3=P-OIL
DEFINE ec2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=CISOLID ID3=C
DEFINE ech42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=CH4
DEFINE ech2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=C2H6
DEFINE ecc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=C3H8
DEFINE eco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=CO2
DEFINE eh22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=H2
DEFINE ehhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=hhc
DEFINE eh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=H2S
DEFINE eo2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
ID1=5 ID2=MIXED ID3=P-OIL
DEFINE fc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=CISOLID ID3=C
DEFINE fc2h42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=CH4
DEFINE fc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=C2H6
DEFINE fc2h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=C3H8
DEFINE fco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=CO2
DEFINE fh22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=H2
DEFINE fhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=HHC
DEFINE fh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=H2S
DEFINE fo2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF &
   ID1=6 ID2=MIXED ID3=P-OIL
DEFINE aext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=1
DEFINE bext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=2
DEFINE cext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=3
DEFINE dext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=4
DEFINE eext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=5
DEFINE fext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV VARIABLE=CONV &
   ID1=6
DEFINE ac3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=CISOLID ID3=C
DEFINE ach43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=CH4
DEFINE ac2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=C2H6
DEFINE ac3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=C3H8
DEFINE aco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=CO2
DEFINE ah23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=H2
DEFINE phc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=HHC
DEFINE ah2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=H2S
DEFINE ao3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=1 ID2=MIXED ID3=P-OIL
DEFINE bc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=CISOLID ID3=C
DEFINE bch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=MIXED ID3=CH4
DEFINE bc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=MIXED ID3=C2H6
DEFINE bc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=MIXED ID3=C3H8
DEFINE bco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=MIXED ID3=CO2
DEFINE bh23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &
   ID1=2 ID2=MIXED ID3=H2
407 DEFINE fc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
408 ID1=6 ID2=MIXED ID3=C  
409 DEFINE fch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
410 ID1=6 ID2=MIXED ID3=CH4  
411 DEFINE fc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
412 ID1=6 ID2=MIXED ID3=C2H6  
413 DEFINE fc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
414 ID1=6 ID2=MIXED ID3=C3H8  
415 DEFINE fco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
416 ID1=6 ID2=MIXED ID3=CO2  
417 DEFINE fh23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
418 ID1=6 ID2=MIXED ID3=H2  
419 DEFINE fhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
420 ID1=6 ID2=MIXED ID3=hhc  
421 DEFINE fh2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
422 ID1=6 ID2=MIXED ID3=H2S  
423 DEFINE fo3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF &  
424 ID1=6 ID2=MIXED ID3=P-OIL  
425 ;  
426 ; Input Data Below  
427 ;  
428 ; Input flows - use kg's for all species  
429 F flcr=0.46  
430 F fin2=0.00061  
431 F fh2o=0.03  
432  
433 ; Input basic reaction stoich. wtfc-weight fraction coke  
434 ; wtfo-weight fraction oil  
435 ; fch4, fc2h6 rel moles of noncoke prods  
436 F wtfc=0.25  
437 F wtfo=0.0  
438 F fch4=1.0  
439 F fc2h6=0.35  
440 F fc3h8=0.21  
441 F fco2=0.113  
442 F fh2=0.025  
443 F fhc=0.0  
444 F fh2s=0.0  
445 ;  
446 ; Dry N2/O2 + trace free gas composition (For printout only)  
447 ; 1-CO2 2-H2 3-CH4 4-C2H6 5-C3H8 6-Toluene 7-H2S  
448 F x(1)=0.069  
449 F x(2)=0.022  
450 F x(3)=0.703  
451 F x(4)=0.154  
452 F x(5)=0.053  
453 F x(6)=0.017  
454 F x(7)=0.013  
455 ;  
456 ; Coke (kg) printout only  
457 F coke=0.0315  
458 ;  
459 ; Input extent. er-fraction of input reacted  
460 ; fer1-fraction of er in reactor 1, etc  
461 F er=0.176  
462 F fer1=0.112  
463 F fer2=0.563  
464 ;  
465 ; Input temperatures(C) and pressures(Bar)  
466 F t1c=426  
467 F p1=151  
468  
469 F t2c=429  
470 F p2=194
471 F t3c=48
472 F p3=29
473 ; final blow down on opening density not set
474 F t4c=25
475 F p4=1
476 ; Input density, vol is reactor volume in Liters
477 ; (assumes input flow is charge in kg/s)
478 F vol=1.05
479 ; Read dat from input file
480 F write(ntrmnl,'(/'"Data file name ? "')
481 F read (ntrmnl,'(a)') file
482 F open(222,file=file,er=900,iostat=ier,status='OLD')
483 C use scratch file to remove comment lines (lines beginning
484 C with '*')
485 F open(222, file='scratch',status='UNKNOWN', iostat=ier, err=900)
486 F 100 read (222, '(a)', er=900, iostat=ier, end=800) line
487 F if (line(1:1) .ne. '*')
488 F & write (221, '(a)', er=900, iostat=ier) line
489 F goto 100
490 F 900 write(ntmnl,'(/"%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%")')
491 F write(ntmnl,'(/"Error occurred in nsmelist input. ier="
492 F & i6")') ier
493 F & write (ntmnl, '"979: Variable name not found."')
494 F write(ntmnl, '"%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%")')
495 F stop
496 F 500 continue
497 ; convert flows (from kg/s) to lb/hr
498 F fln2x=fln2/0.454*3600.0
499 F flh2ox=flh2o/0.454*3600.0
500 F flcrx=flcr/0.454*3600.0
501 ; convert T's to F
502 F t1=1.8*t1c+32
503 F t2=1.8*t2c+32
504 F t3=1.8*t3c+32
505 F t4=1.8*t4c+32
506 ; convert to reaction extents
507 ; ern-fractions of total reaction occurring in mn
508 F er1=fer1*er
509 F er2=fer2*er
510 F er3=er
511 ; stor P's in common
512 F px1=p1
513 F px2=p2
514 F px3=p3
515 F px4=p4
516 ;
; define gas mw's for later use
535  F wch4=16.0428
536  F wc2h6=30.0696
537  F wc3h8=44.0965
538  F wco2  =44.0098
539  F wh2  = 2.01588
540  F wh2s = 34.0819
541  F wc  =12.0110
542
543 ; butane
544  F whhc= 58.1234
545
546 ; P-OIL
547 ; (1. Pentane 2. Octane)
548  F wo= 72.8688
549  F wo= 109.04
550
551 ; normalize gas
552  F sum=fch4+fc2h6+fc3h8+fco2+fh2+fhhc+fh2s
553  F fch4=fch4/sum
554  F fc2h6=fc2h6/sum
555  F fc3h8=fc3h8/sum
556  F fco2=fco2/sum
557  F fh2=fh2/sum
558  F fhhc=fhhc/sum
559  F fh2s=fh2s/sum
560
561 ; Compute density from flow (flow from ASPEN in lbs/hr)
562
563 ; compute gas average mw
564  F wmix=fch4*wch4+fc2h6*wc2h6+fc3h8*wc3h8+fco2*wco2+fh2*wh2
565  F & +fhhc*whhc+fh2s*wh2s
566
567 ; compute extents
568  F aext1=er1
569  F aext2=er2
570  F aext3=er3
571  F bext1=aext1
572  F bext2=aext2
573  F bext3=aext3
574  F cext1=aext1
575  F cext2=aext2
576  F cext3=aext3
577  F dext1=aext1
578  F dext2=aext2
579  F dext3=aext3
580  F eext1=aext1
581  F eext2=aext2
582  F eext3=aext3
583  F fext1=aext1
584  F fext2=aext2
585  F fext3=aext3
586
587 ; For VR reaction
588  F wm=540.2436
589  F wtc=wm*wtfc
590  F wto=wm*wtfo
591  F wtg=wm-wtc-wto
592  F xmolg=wtg/wmix
593  F acl=wtc/wc
594  F aol=wtc/wo
595  F ach41 =xmolg*fch4
596  F ac2h61=xmolg*fc2h6
597  F ac3h81=xmolg*fc3h8
598  F aco21 =xmolg*fco2
For IWGO reaction

\begin{align*}
\text{wtc} &= \text{wm} \cdot \text{wtfc} \\
\text{wto} &= \text{wm} \cdot \text{wtfo} \\
\text{wtg} &= \text{wm} \cdot \text{wtc} - \text{wto} \\
\text{xmolg} &= \text{wtg} \cdot \text{wmix} \\
\text{bcl} &= \text{wtc} / \text{wc} \\
\text{b1} &= \text{wtc} / \text{wo} \\
\text{bc41} &= \text{xmolg} \cdot \text{fch4} \\
\text{bc2h61} &= \text{xmolg} \cdot \text{fc2h6} \\
\text{bc3h81} &= \text{xmolg} \cdot \text{fc3h8} \\
\text{bco21} &= \text{xmolg} \cdot \text{fco2} \\
\text{bh21} &= \text{xmolg} \cdot \text{fh2} \\
\text{bh21} &= \text{xmolg} \cdot \text{fhhc} \\
\text{bh21} &= \text{xmolg} \cdot \text{fh2s} \\
\text{bc1} &= \text{bc1} \\
\text{bo3} &= \text{bo1} \\
\text{bc41} &= \text{bc41} \\
\text{bc2h61} &= \text{bc2h61} \\
\text{bc3h81} &= \text{bc3h81} \\
\text{bco21} &= \text{bco21} \\
\text{bh21} &= \text{bh21} \\
\text{bh21} &= \text{bh21} \\
\text{bhc2} &= \text{bhc1} \\
\text{bh2s2} &= \text{bh2s1} \\
\text{bc3} &= \text{bc1} \\
\text{bo3} &= \text{bo1} \\
\text{bc43} &= \text{bc41} \\
\text{bc2h61} &= \text{bc2h61} \\
\text{bc3h81} &= \text{bc3h81} \\
\text{bco23} &= \text{bco21} \\
\text{bh23} &= \text{bh21} \\
\text{bh23} &= \text{bh21} \\
\text{bhc3} &= \text{bhc1} \\
\text{bh2s3} &= \text{bh2s1} \\
\end{align*}

For LVGO reaction

\begin{align*}
\text{wtc} &= \text{wm} \cdot \text{wtfc} \\
\text{wto} &= \text{wm} \cdot \text{wtfo} \\
\text{wtg} &= \text{wm} \cdot \text{wtc} - \text{wto} \\
\text{xmolg} &= \text{wtg} \cdot \text{wmix} \\
\text{cl} &= \text{wtc} / \text{wc} \\
\text{cl} &= \text{wtc} / \text{wo} \\
\text{wm} &= 410.7407 \\
\text{wm} &= 306.6466 \\
\text{wm} &= 410.7407 \\
\end{align*}
cch41 =xmolg*fch4
cc2h61=xmolg*fc2h6
cc3h81=xmolg*fc3h8
cco21 =xmolg*fc02
ch21 =xmolg*fh2
chhc1=xmolg*fhhc
ch2s1 =xmolg*fh2s
cc2=cc1
c02=c01
ch42 =cch41
cc2h62=cc2h61
cc3h82=cc3h81
cco22 =c02
ch22 =ch21
chhc2=chhc1
ch2s2 =ch2s1
cc3=c01
cch43 =cch41
cc2h63=cc2h61
cc3h83=cc3h81
cco23 =c02
ch23 =ch21
chhc3=chhc1
ch2s3 =ch2s1

For AGO reaction

wm=228.1870
wtc=wm*wtfc
wto=wm*wtfo
wtg=wm-wtc-wto
xmolg=wtg/wmix
dcl=wtc/wc
dol=wto/wo
dch41 =xmolg*fch4
dc2h61=xmolg*fc2h6
dc3h81=xmolg*fc3h8
dco21 =xmolg*fc02
dh21 =xmolg*fh2
dhhc1=xmolg*fhhc
dh2s1 =xmolg*fh2s
dc2=dcl
dc2=dol
dch42 =dch41
dc2h62=dc2h61
dc3h82=dc3h81
dco22 =dco21
dh22 =dh21
dhhc2=dhhc1
dh2s2 =dh2s1
dc3=dcl
dc3=dol
dch43 =dch41
dc2h63=dc2h61
dc3h83=dc3h81
dco23 =dco21
dh23 =dh21
dhhc3=dhhc1
dh2s3 =dh2s1

For KERO reaction

wm=178.2905
wtc=wm*wtfc
wto=wm*wtfo
727 F  \( wtg = wm - wtc - wto \)
728 F  \( xmolg = wtg / wmix \)
729 F  \( ecl = wtc / wc \)
730 F  \( eol = wto / wo \)
731 F  \( ech41 = xmolg * fch4 \)
732 F  \( ec2h61 = xmolg * fc2h6 \)
733 F  \( ecbh81 = xmolg * fc3h8 \)
734 F  \( eco21 = xmolg * fco2 \)
735 F  \( eh21 = xmolg * fh2 \)
736 F  \( ehhcl = xmolg * fhhc \)
737 F  \( eh2s1 = xmolg * fh2s \)
738 F  \( ec2 = ec1 \)
739 F  \( eo2 = eo1 \)
740 F  \( ech42 = ech41 \)
741 F  \( ec2h62 = ec2h61 \)
742 F  \( ec3h82 = ec3h81 \)
743 F  \( eco22 = eco21 \)
744 F  \( eh22 = eh21 \)
745 F  \( ehhc2 = ehhc1 \)
746 F  \( eh2s2 = eh2s1 \)
747 F  \( ec3 = ec1 \)
748 F  \( eo3 = eo1 \)
749 F  \( ech43 = ech41 \)
750 F  \( ec2h63 = ec2h61 \)
751 F  \( ec3h83 = ec3h81 \)
752 F  \( eco23 = eco21 \)
753 F  \( eh23 = eh21 \)
754 F  \( ehhc3 = ehhc1 \)
755 F  \( eh2s3 = eh2s1 \)
756 F
757 F  ; For HNAPH reaction
758 F  \( wm = 141.7508 \)
759 F  \( wtc = wm * wtfc \)
760 F  \( wto = wm * wto_f \)
761 F  \( wtg = wm - wtc - wto \)
762 F  \( xmolg = wtg / wmix \)
763 F  \( fc1 = wtc / wc \)
764 F  \( fo1 = wto / wo \)
765 F  \( fch41 = xmolg * fch4 \)
766 F  \( fc2h61 = xmolg * fc2h6 \)
767 F  \( fc3h81 = xmolg * fc3h8 \)
768 F  \( fco21 = xmolg * fco2 \)
769 F  \( fh21 = xmolg * fh2 \)
770 F  \( fhhc1 = xmolg * fhhc \)
771 F  \( fh2s1 = xmolg * fh2s \)
772 F  \( fc2 = fc1 \)
773 F  \( fo2 = fo1 \)
774 F  \( fch42 = fch41 \)
775 F  \( fc2h62 = fc2h61 \)
776 F  \( fc3h82 = fc3h81 \)
777 F  \( fco22 = fco21 \)
778 F  \( fh22 = fh21 \)
779 F  \( fhhc2 = fhhc1 \)
780 F  \( fh2s2 = fh2s1 \)
781 F  \( fc3 = fc1 \)
782 F  \( fo3 = fo1 \)
783 F  \( fch43 = fch41 \)
784 F  \( fc2h63 = fc2h61 \)
785 F  \( fc3h83 = fc3h81 \)
786 F  \( fco23 = fco21 \)
787 F  \( fh23 = fh21 \)
788 F  \( fhhc3 = fhhc1 \)
789 F  \( fh2s3 = fh2s1 \)
790 F ;
EXECUTE FIRST

FORTRAN INIT

F common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke

DEFINE flow STREAM-VAR STREAM=FEED VARIABLE=MASS-FLOW

; Compute density from flow (flow from ASPEN in lbs/hr)
F dens=flow/3600*0.454/vol*1e3
F write(nxpt,'('dens=','f8.1')') dens

EXECUTE AFTER MIXF

;=====================================================================================

; Control input

;=====================================================================================

ACCOUNT-INFO ACCOUNT=HPASPEN PROJECT-ID=P &
PROJECT-NAME="Oil Upgrading" USER-NAME="CHE"

IN-UNITS ENG VOLUME-FLOW='BBL/DAY' ENTHALPY-FLO='MBTU/HR' &
PRESSURE='BAR' VOLUME=BBL HEAD=FT HEAT=MBTU

STREAM-REPORT MOLEFRAC PROPERTIES=TOTAL PETRO

PROPERTY-REPORT PROJECT

OUT-UNITS SI TEMPERATURE=C

PROP-SET TOTAL TBUB PBUB

PROP-SET PETRO VLSTDMDX APISTD SGSTD WAT &
UNITS='BBL/DAY' 'BBL/HR' SUBSTREAM=MIXED &
BASIS=DRY

;=====================================================================================

; Component & Property Setup

;=====================================================================================

SIM-OPTIONS FREE-WATER=YES
;SIM-OPTIONS FREE-WATER=NO

; Insert API method for liquid volumes in all possible option sets

INSERT * API

; GRAYSON preferred

; PROPERTIES PRMHV2 SOLU-WATER=0 ; (see vp_o2.inp)
; PROPERTIES PSRK SOLU-WATER=0 ; (see vp_o2.inp)
; PROPERTIES LK-PLOCK SOLU-WATER=0 ; (see vp_o2.inp)
; PROPERTIES CHAO-SEA SOLU-WATER=1 /
; PROPERTIES CHAO-SEA SOLU-WATER=1

DATABANKS PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
NOASPENPCD

PROP-SOURCES PURECOMP / AQUEOUS / SOLIDS / INORGANIC

; To use different HHC change here & change hardwired mw in FORTRAN BLOCK

SETI at statement which=??.

COMPONENTS

H2O H2O H2O / H2S H2S H2S
/ N2 N2 N2 / CH4 CH4 CH4 / CO2 CO2 CO2 / H2 H2 H2 &
<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>C2H6</th>
<th>C3H8</th>
<th>HHC</th>
<th>C4H10-1</th>
<th>C4H1O-1</th>
<th>P-oII.l</th>
</tr>
</thead>
<tbody>
<tr>
<td>855</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>&amp;</td>
</tr>
<tr>
<td>856</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>857</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>P-oII.l</td>
</tr>
<tr>
<td>858</td>
<td>/</td>
<td>/</td>
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919 PC-IDS OPTION=LIST &
920 LIST=LE IGASO LNAFH HNAFH KER0 AGO IVOG HGOG VR
921 CUTS LIST= 0 60 175 300 400 500 650 800 1000 1600
922
923 ADA-SETUP
924 ADA-SETUP PROCEDURE=REL9
925
926 ASSAY CUT1  ; made up
927 ASSAY-DATA API=37.1
928 DIST-CURVE DB6 0 360 / 20 365 / 80 370 / 100 375
929
930 ASSAY CUT2
931 ASSAY-DATA API=29.9
932 DIST-CURVE DB6 0 430 &
933 / 5 446 / 10 450 / 20 456 / 30 462 &
934 / 40 466 / 50 470 / 60 476 / 70 482 &
935 / 80 490 / 90 504 / 95 508 / 99 514
936
937 ASSAY CUT3
938 ASSAY-DATA API=23.7
939 DIST-CURVE DB6 0 520 &
940 / 5 544 / 10 558 / 20 562 / 30 568 &
941 / 40 570 / 50 574 / 60 580 / 70 584 &
942 / 80 590 / 90 600 / 95 610 / 99 618
943
944 ASSAY CUT4  ; Vac
945 ASSAY-DATA API=16.0
946 DIST-CURVE TBPLV 0 637 &
947 / 5 664 / 10 683 / 20 688 / 30 698 &
948 / 40 708 / 50 718 / 60 737 / 70 755 &
949 / 80 778 / 90 806 / 95 827 / 99 844
950
951 ASSAY CUT5  ; Vac
952 ASSAY-DATA API=13.8
953 DIST-CURVE TBPLV 0 686 &
954 / 5 734 / 10 760 / 20 797 / 30 816 &
955 / 40 834 / 50 851 / 60 868 / 70 887 &
956 / 80 908 / 90 938 / 95 952 / 99 973
957
958 ASSAY CUT6  ; Vac
959 ASSAY-DATA API=4.6
960 DIST-CURVE TBPLV 0 917 &
961 / 5 938 / 10 979 / 20 998 &
962 / 40 1045 / 60 1085 / 80 1130 / 90 1165 &
963 ; Above 20% from log probability curve
964
965 BLEND CRUDE
966 ; core labs crude API 11.5
967 ; MASS-FRAC CUT1 0.0087 / CUT2 0.0536 / CUT3 0.108 / &
968 ; CUT4 0.1479 / CUT5 0.2194 / CUT6 0.4608
969 ; add lights to get API of 13.5
970 MASS-FRAC CUT1 0.0496 / CUT2 0.0764 / CUT3 0.1007 / &
971 CUT4 0.1370 / CUT5 0.2045 / CUT6 0.4295
972
973 ;=====================================================================================
974 ; Flowsheet
975 ;=====================================================================================
976
977 FLOWSHEET ONE
978 ; Mix feeds and create 3 separate & equal streams
979 BLOCK MIXD IN=FEEDO FEEDN OUT=FEED
980 BLOCK DUP IN=FEED OUT=1FEED 2FEED 3FEED
To start constant T period

; FLOWSHEET TWO

; At end constant T period

; FLOWSHEET THREE

; At end

; FLOWSHEET FOUR

; After opening

; Streams

; Block specifications

; BLOCK MIXF MIXER

; BLOCK DUP DUPL

; BLOCK R1 RSTOIC

; STOIC 1 MIXED VR -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &

; STOIC 2 MIXED HOGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &

; STOIC 3 MIXED LGVO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &

; STOIC 4 MIXED AGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &

; STOIC 5 MIXED KERO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 5 MIXED KERO 1
STOIC 6 MIXED HNAP H -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 6 MIXED HNAP H 1
BLOCK SPLT1 FLASH2
PARAM DUTY=0

BLOCK R2 RSTOIC
STOIC 1 MIXED VR -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 1 MIXED VR 1
STOIC 2 MIXED HVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 2 MIXED HVGO 1
STOIC 3 MIXED LVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 3 MIXED LVGO 1
STOIC 4 MIXED AGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 4 MIXED AGO 1
STOIC 5 MIXED KERO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 5 MIXED KERO 1
STOIC 6 MIXED HNAP H -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 6 MIXED HNAP H 1
BLOCK SPLT2 FLASH2

BLOCK R3 RSTOIC
STOIC 1 MIXED VR -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 1 MIXED VR 1
STOIC 2 MIXED HVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 2 MIXED HVGO 1
STOIC 3 MIXED LVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 3 MIXED LVGO 1
STOIC 4 MIXED AGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 4 MIXED AGO 1
STOIC 5 MIXED KERO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 5 MIXED KERO 1
STOIC 6 MIXED HNAP H -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
C3H8 * / CO2 * / H2 * / hhc * / H2S * / &
CISOLID C *

CONV 6 MIXED HNAP H 1
BLOCK SPLT3 FLASH2

48
BLOCK HTR1 HEATER
DESCRIPTION 'Sets desired flash temperature & pressure'
PARAM TEMP=25 <C> PRES=100<bar>

BLOCK HTR2 HEATER
DESCRIPTION 'Sets desired flash temperature & pressure'
PARAM TEMP=25 <C> PRES=100<bar>

BLOCK HTR3 HEATER
DESCRIPTION 'Sets desired flash temperature & pressure'
PARAM TEMP=25 <C> PRES=100<bar>

BLOCK HTR2A HEATER
DESCRIPTION 'Sets desired flash temperature & pressure'
PARAM TEMP=25 <C> PRES=100<bar>

BLOCK HTR3A HEATER
DESCRIPTION 'Sets desired flash temperature & pressure'
PARAM TEMP=25 <C> PRES=100<bar>

; blow down
BLOCK HTR4 HEATER
DESCRIPTION 'Sets desired flash temperature & pressure no density it'
PARAM TEMP=25 <C> PRES=100<bar>

/*
PROP-SET D= RM14X UNITS='KG/CUM'
PROP-SET D= RM14X UNITS='IU40L/CUM'
PROP-SET API APISTD BASIS=DRY
DESIGN-SPX D=
DEFIEN D STREAM=PROP STREAM=I.CHTR PROPERTY=
DEFIEN charl MASS-FLCW STREAM=I.CHTR PROPERTY=
SPEC DENl TO 'dcl'
TOL-SPEC 1
VARY BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=PRES
LIMITS 10 250

DESIGN-SPEC DEN2
DEFIEN D STREAM=PROP STREAM=I.CHTR PROPERTY=
DEFIEN char2 MASS-FLCW STREAM=2HTR SUBSTREAM=CISOLID COMPONENT=C
SPEC DEN2 TO 'dc2'
TOL-SPEC 1
VARY BLOCK-VAR BLOCK=HTR2 SENTENCE=PARAM VARIABLE=PRES
LIMITS 50 300

DESIGN-SPEC DEN3
DEFIEN D STREAM=PROP STREAM=3HTR PROPERTY=
DEFIEN char3 MASS-FLCW STREAM=3HTR SUBSTREAM=CISOLID COMPONENT=C

*/
convert char from lb/hr to kg/s
ckg3=char3*0.454/3600
compute corrected density
dc3=dens-ckg3/vol*1.0e3
SPEC DEN3 TO 'dc3'
TOL SPEC 1
VARY BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=PRES
LIMS 1 50
SENSITIVITY S1
DEFINE DEN1 STREAM-PROP STREAM=1HTR PROPERTY=DEN
DEFINE DEN2 STREAM-PROP STREAM=2GAS PROPERTY=DENM
DEFINE DEN3 STREAM-PROP STREAM=3GAS PROPERTY=DENM
DEFINE pp1 STREAM-VAR STREAM=1GAS VARIABLE=PRES
DEFINE pp2 STREAM-VAR STREAM=2GAS VARIABLE=PRES
DEFINE pp3 STREAM-VAR STREAM=3GAS VARIABLE=PRES
DEFINE chr1 MASS-FLOW STREAM=1HTR SUBSTREAM=CISOLID COMPONENT=C
DEFINE chr2 MASS-FLOW STREAM=2HTR SUBSTREAM=CISOLID COMPONENT=C
DEFINE chr3 MASS-FLOW STREAM=3HTR SUBSTREAM=CISOLID COMPONENT=C
DEFINE w1 MASS-FLOW STREAM=1LIQ SUBSTREAM=MIXED COMPONENT=H2O
DEFINE w2 MASS-FLOW STREAM=2LIQ SUBSTREAM=MIXED COMPONENT=H2O
DEFINE w3 MASS-FLOW STREAM=3LIQ SUBSTREAM=MIXED COMPONENT=H2O
DEFINE wf1 MASS-FLOW STREAM=1WAT SUBSTREAM=MIXED COMPONENT=H2O
DEFINE wf2 MASS-FLOW STREAM=2WAT SUBSTREAM=MIXED COMPONENT=H2O
DEFINE wf3 MASS-FLOW STREAM=3WAT SUBSTREAM=MIXED COMPONENT=H2O
DEFINE wtt MASS-FLOW STREAM=1HTR SUBSTREAM=MIXED COMPONENT=H2O
DEFINE ft1 STREAM-VAR STREAM=1LIQ VARIABLE=MASS-FLOW
DEFINE ft2 STREAM-VAR STREAM=2LIQ VARIABLE=MASS-FLOW
DEFINE ft3 STREAM-VAR STREAM=3LIQ VARIABLE=MASS-FLOW
DEFINE pc1 STREAM-VAR STREAM=1GAS VARIABLE=PRES
DEFINE pc2 STREAM-VAR STREAM=2GAS VARIABLE=PRES
DEFINE pc3 STREAM-VAR STREAM=3GAS VARIABLE=PRES
DEFINE d1 STREAM-PROP STREAM=1HTR PROPERTY=DEN
DEFINE d2 STREAM-PROP STREAM=2HTR PROPERTY=DEN
DEFINE d3 STREAM-PROP STREAM=3HTR PROPERTY=DEN
DEFINE fch4 MOLE-FLOW STREAM=3GAS COMPONENT=CH4
DEFINE fc2h6 MOLE-FLOW STREAM=3GAS COMPONENT=C2H6
DEFINE fc3h8 MOLE-FLOW STREAM=3GAS COMPONENT=C3H8
DEFINE fco2 MOLE-FLOW STREAM=3GAS COMPONENT=CO2
DEFINE fnh2 MOLE-FLOW STREAM=3GAS COMPONENT=H2
DEFINE fnhc MOLE-FLOW STREAM=3GAS COMPONENT=nhc
DEFINE fnhc MOLE-FLOW STREAM=3GAS COMPONENT=H2S
DEFINE fpoil MOLE-FLOW STREAM=3GAS COMPONENT=P-OIL
DEFINE tch4 MOLE-FLOW STREAM=3HTR COMPONENT=CH4
DEFINE tc2h6 MOLE-FLOW STREAM=3HTR COMPONENT=C2H6
DEFINE tc3h8 MOLE-FLOW STREAM=3HTR COMPONENT=C3H8
DEFINE tco2 MOLE-FLOW STREAM=3HTR COMPONENT=CO2
DEFINE th2 MOLE-FLOW STREAM=3HTR COMPONENT=H2
DEFINE thhc MOLE-FLOW STREAM=3HTR COMPONENT=thhc
DEFINE th2s MOLE-FLOW STREAM=3HTR COMPONENT=H2S
DEFINE tpoil MOLE-FLOW STREAM=3HTR COMPONENT=P-OIL
DEFINE th2o MOLE-FLOW STREAM=3HTR COMPONENT=H2O
DEFINE api3 STREAM-PROP STREAM=3LIQ PROPERTY=API
DEFINE api4 STREAM-PROP STREAM=4LIQ PROPERTY=API

\[ s = f_{ch4} + f_{c2h6} + f_{c3h8} + f_{h2} + f_{co2} + f_{hhc} + f_{h2s} + f_{oil} \]

\[ xl = \frac{f_{co2}}{sum} \]

\[ x2 = \frac{f_{h2}}{sum} \]

\[ x3 = \frac{f_{ch4}}{sum} \]

\[ x4 = \frac{f_{c2h6}}{sum} \]

\[ x5 = \frac{f_{c3h8}}{sum} \]

\[ x6 = \frac{f_{hhc}}{sum} \]

\[ x7 = \frac{f_{h2s}}{sum} \]

\[ x8 = \frac{f_{oil}}{sum} \]

\[ xchrl = chrl \cdot 0.454 / 3600 \]

\[ xchr2 = chr2 \cdot 0.454 / 3600 \]

\[ xchr3 = chr3 \cdot 0.454 / 3600 \]

\[ dlt = dl + xchrl / vol \cdot 1000 \]

\[ d2t = d2 + xchr2 / vol \cdot 1000 \]

\[ d3t = d3 + xchr3 / vol \cdot 1000 \]

\[ xwl = w1 / (ft1 - char1) \]

\[ xw2 = w2 / (ft2 - char2) \]

\[ xw3 = w3 / (ft3 - char3) \]

\[ z1 = (pp1 - 1.0) / (deng1 \cdot 1000 \cdot 8.314 \cdot (t1c + 273.15)) \]

\[ z2 = (pp2 - 1.0) / (deng2 \cdot 1000 \cdot 8.314 \cdot (t2c + 273.15)) \]

\[ z3 = (pp3 - 1.0) / (deng3 \cdot 1000 \cdot 8.314 \cdot (t3c + 273.15)) \]

\[ \text{write(nrpt, '}' \{ 'Gravity before/after blow down (API):', 2f5.1 \}) \]

\[ \text{write(nrpt, '}' \{ 'Dry N2 free gas composition.' \}) \]

\[ \text{write(nrpt, '}' \{ 'Calc Amounts (mol)', 8f6.3', 'H2O' \}) \]

\[ \text{convert from internal l/mol/hr to mol/s} \]

\[ fac = 454.0 / 3600.0 \]

\[ \text{write(nrpt, '}' \{ 'Gas', 8f6.4 \}) (fco2*fac), (fh2*fac), \]

\[ \text{write(nrpt, '}' \{ 'Total', 8f6.4, 8f4 \}) (tc2h6*fac), (tc3h8*fac), (th2*fac), \]

\[ \text{write(nrpt, '}' \{ 'Total coke (kg) =', f6.3, 5x, '[ data =', f6.3,' ]' \}) \]

\[ \text{write(nrpt, '}' \{ 'Total water (kg) =', f6.3,' ]' \}) (w1*fac), (w2*fac), (w3*fac) \]

\[ \text{write(nrpt, '}' \{ 'X02 Xw (kg)', 2f7.3 \}) xwl, (w1*0.454/3600) \]

\[ \text{write(nrpt, '}' \{ 'X02 Xw (kg)', 2f7.3 \}) xw2, (w2*0.454/3600) \]

\[ \text{write(nrpt, '}' \{ 'X02 Xw (kg)', 2f7.3 \}) xw3, (w3*0.454/3600) \]
The following is the listing for the ASCII data file.

```
1 $indata
2  * For Run 126.
3  *
4  * Charges all in kg's (flcr is CRUDE)
5  flcr=0.46    flh2o=0.03    fln2=0.00061
6  *
7  * Reaction Stoichiometry
8  * Input basic reaction stoich. wtfc=weight fraction coke
9  *                   fch4, fc2h6 rel moles of noncoke prods
10  * tuned for ASPEN (low water sol at low T)
11  *         wtfc=0.48 for wtfo=0
12  wtfc=0.192
13  wtfo=0.6
14  fch4=1.0
15  fc2h6=0.390
16  fc3h8=0.269
17  fco2=0.121
18  fh2=0.025
19  fh2s=0.062
20  * butane
21  fhnc =0.150
22  *
23  * Dry N2/O2 + trace free gas composition (For printout only)
24  * 1-CO2 2-H2 3-CH4 4-C2H6 5-C3H8 6-C4s 7-H2S
25  x(1)=0.067
26  x(2)=0.021
27  x(3)=0.084
28  x(4)=0.154
29  x(5)=0.0526
30  x(6)=0.0087
31  x(7)=0.0131
32  *
33  * Coke (kg) for output only
34  coke=0.025
35  *
36  * Input extent. er-fraction of input reacted
37  *         fer1-fraction of er in reactor 1, etc
38  *         er=0.115 for wtfo=0
39  er=0.32
40  *
41  *         fer1=0.42
42  fer1=0.0
43  fer1=0.011
44  fer2=0.75
45  *
46  * Input temperatures(C) and pressures(Bar)
47  *  For reactors 1,2 & 3
48  *         t1c=426  p1=151
49  t1c=233  p1=25.8
50  *         t1c=363  p1=80.5
51  t2c=429  p2=194
52  t3c=25   p3=23.8
53  *
54  * Reactor volume (L)
55  vol=1.05
56  $end
```
APPENDIX IV.

ACS MODEL PARAMETERS

The important parameter used in the ACS modeling of the crude oil systems are described in this appendix. Only those properties not given in the body of the text are included.

Vapor pressures for the five pseudocomponents used for the crude oil and the P-OIL product are calculated using the following simple boiling point relation

$$\ln(P_v) = \left(\frac{T_{br} \ln(P_c)}{1 - T_{br}}\right) \left(1 - \frac{1}{T_r}\right),$$

where $P_v$ is the vapor pressure in atmospheres, $T_{br}$ is the reduced normal boiling point, $T_r$ is the reduced temperature, and $P_c$ is the critical pressure expressed in atmospheres. The values for the all parameters are given in the report body with the exception of the critical temperature and pressure of the P-OIL which was taken as 587 K and 3.1 MPa respectively.

In the simulation, six of the components were treated as Henry's Law components. The values of Henry's Law constants as a function of temperature were derived from results obtained from ASPEN PLUS for the crude oil mixture using the GRAYSON property set. The values used are given in Table IV-1. The hydrocarbons were assumed to be normal alkanes.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>CO₂ (MPa)</th>
<th>H₂S (MPa)</th>
<th>CH₄ (MPa)</th>
<th>C₂H₆ (MPa)</th>
<th>C₃H₈ (MPa)</th>
<th>C₄H₁₀ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.6</td>
<td>1.3</td>
<td>19.1</td>
<td>3.6</td>
<td>0.98</td>
<td>0.19</td>
</tr>
<tr>
<td>50</td>
<td>16.5</td>
<td>2.9</td>
<td>24.0</td>
<td>5.9</td>
<td>2.2</td>
<td>0.55</td>
</tr>
<tr>
<td>100</td>
<td>25.1</td>
<td>5.5</td>
<td>29.6</td>
<td>9.0</td>
<td>4.2</td>
<td>1.46</td>
</tr>
<tr>
<td>200</td>
<td>36.4</td>
<td>10.8</td>
<td>38.2</td>
<td>14.1</td>
<td>8.6</td>
<td>4.2</td>
</tr>
<tr>
<td>300</td>
<td>41.0</td>
<td>16.4</td>
<td>41.3</td>
<td>16.2</td>
<td>12.1</td>
<td>7.1</td>
</tr>
<tr>
<td>400</td>
<td>35.3</td>
<td>19.5</td>
<td>37.8</td>
<td>15.5</td>
<td>13.8</td>
<td>9.3</td>
</tr>
<tr>
<td>450</td>
<td>31.3</td>
<td>19.8</td>
<td>34.0</td>
<td>14.1</td>
<td>13.7</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The model also requires pure component densities to be defined. The most important of these are for the oil pseudocomponents and water. The water densities used were taken from saturated steam tables and are listed in Table IV-2.
Table IV-2. Liquid water density.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>1001</td>
</tr>
<tr>
<td>311</td>
<td>995</td>
</tr>
<tr>
<td>366</td>
<td>965</td>
</tr>
<tr>
<td>422</td>
<td>919</td>
</tr>
<tr>
<td>477</td>
<td>861</td>
</tr>
<tr>
<td>533</td>
<td>786</td>
</tr>
<tr>
<td>589</td>
<td>680</td>
</tr>
<tr>
<td>616</td>
<td>599</td>
</tr>
<tr>
<td>630</td>
<td>540</td>
</tr>
<tr>
<td>644</td>
<td>435</td>
</tr>
</tbody>
</table>

Oil pseudocomponent densities were assumed to be linearly dependent on temperature. Their values were specified by the two points given for each component in Table IV-3.

Table IV-3. Oil component densities at two temperatures.

<table>
<thead>
<tr>
<th></th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 294 K</td>
</tr>
<tr>
<td>HNAPH</td>
<td>847</td>
</tr>
<tr>
<td>KERO</td>
<td>879</td>
</tr>
<tr>
<td>AGO</td>
<td>913</td>
</tr>
<tr>
<td>LVGO</td>
<td>956</td>
</tr>
<tr>
<td>HVGO</td>
<td>972</td>
</tr>
<tr>
<td>VR</td>
<td>1044</td>
</tr>
</tbody>
</table>