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**Aspen Modeling of the Tri-State  
Indirect Liquefaction Process**

Ray E. Barker  
John M. Begovich *B*  
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Research supported by Morgantown Energy Technology Center,  
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CHEMICAL TECHNOLOGY DIVISION

Fossil Energy Program

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ABSTRACT

The ASPEN process simulator has been used to model an indirect liquefaction flowsheet patterned after that of the Tri-State project. This flowsheet uses Lurgi moving-bed gasification with synthesis gas conversion to methanol followed by further processing to gasoline using the Mobil MTG process. Models developed in this study include the following: Lurgi gasifier, Texaco gasifier, synthesis gas cooling, Rectisol, methanol synthesis, methanol-to-gasoline, CO-shift, methanation, and naphtha hydrotreating. These models have been successfully developed in modular form so that they can be used to simulate a number of different flowsheets or process alternatives.

Simulations of the Tri-State flowsheet have been made using two different coal feed rates and two types of feed coal. The overall simulation model was adjusted to match the Tri-State flowsheet values for methanol, LPG, isobutane, and gasoline. As a result of this adjustment, the MTG reactor yield structure necessary to match the flowsheet product rates was determined. The models were exercised at different flow rates and were unaffected by such changes, demonstrating their range of operability. The use of Illinois No. 6 coal, with its lower ash content, resulted in slightly higher production rates of each of the products as compared to use of the Kentucky coal.

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1. INTRODUCTION

The Tri-State Project was originally conceived as an indirect Fischer-Tropsch liquefaction plant producing approximately 56,000 barrels of fuel oil equivalent per day of transportation fuels and chemicals from Kentucky coal. The preliminary design of this plant was co-funded by the Department of Energy (DOE) and the industrial participants. Within DOE,

the Morgantown Energy Technology Center (METC) has the role of technical lead for gasification systems to DOE-funded projects. In consonance with the role on Tri-State of providing technological review and advice on gasification and related systems, a process model of the overall plant would (1) enhance the capabilities for investigating and evaluating technical uncertainties and alternatives, and (2) provide a permanent record for future reference and use.

Accurate process calculations are necessary for rational design and operation of process equipment. These calculations can range from very simple (requiring only a pocket calculator) to very complex (requiring a large computer). In the latter case, a primary tool in use at ORNL is the ASPEN (Advanced System for Process Engineering) process simulator. ASPEN is a modern, state-of-the-art process simulator recently developed for DOE at a cost of \$6 million. This report details the modeling of an indirect liquefaction flowsheet using the ASPEN simulator. These process models have been developed in modular form so that they can be used to model a number of different process alternatives.

This work has consisted of developing models of the various systems comprising the Tri-State project and integrating the models in a consistent fashion with recycle streams to produce an overall process model using the ASPEN computer code. Adequate property data of liquids have been obtained or estimated and correlated to yield technically consistent models of the critical areas of the plant. Although the Tri-State project has been terminated, the ASPEN models and special purpose subroutines developed for this work should be applicable to many indirect liquefaction flowsheets.

Several modifications to the project and its flowsheet were made during the design phase. The flowsheet of the Tri-State project modeled uses Lurgi moving-bed gasification and synthesis gas conversion to methanol, which is further processed to gasoline using the Mobil MTG (methanol-to-gasoline) process. Synthesis gas not converted to methanol is methanated to produce substitute natural gas. A simplified overall flowsheet of the Lurgi-methanol-MTG process is shown in Fig. 1.

The western Kentucky coal is fed to the conventional dry-ash Lurgi. The Lurgi gasifiers are to be modified for use with caking coals by the addition of a stirrer to maintain good bed porosity. This arrangement has been tested with the proposed coal recently at SASOL.<sup>1</sup> The Lurgi gasification model has been calibrated to reflect those test results. The synthesis gas from the Lurgi is cooled to condense water and the condensable hydrocarbons. The heat released from this cooling is used to generate low- and medium-pressure steam.

The cooled synthesis gas is then sent to the Rectisol plant, where it is cooled and the H<sub>2</sub>S is removed by absorption in refrigerated methanol. The Rectisol flowsheet is a standard design for gases containing condensable hydrocarbons (i.e., naphtha). The sulfur-free gas is then compressed and passes to the methanol synthesis reactor. The methanol synthesis process uses the Lurgi reactor, with the heat of reaction being used to generate steam in the reactor jacket. The reactor product is cooled to condense the methanol, and the unreacted gases are recycled to the reactor. In order to prevent buildup of inerts in the reactor recycle, it is necessary to purge a portion of that stream, called the purge gas.

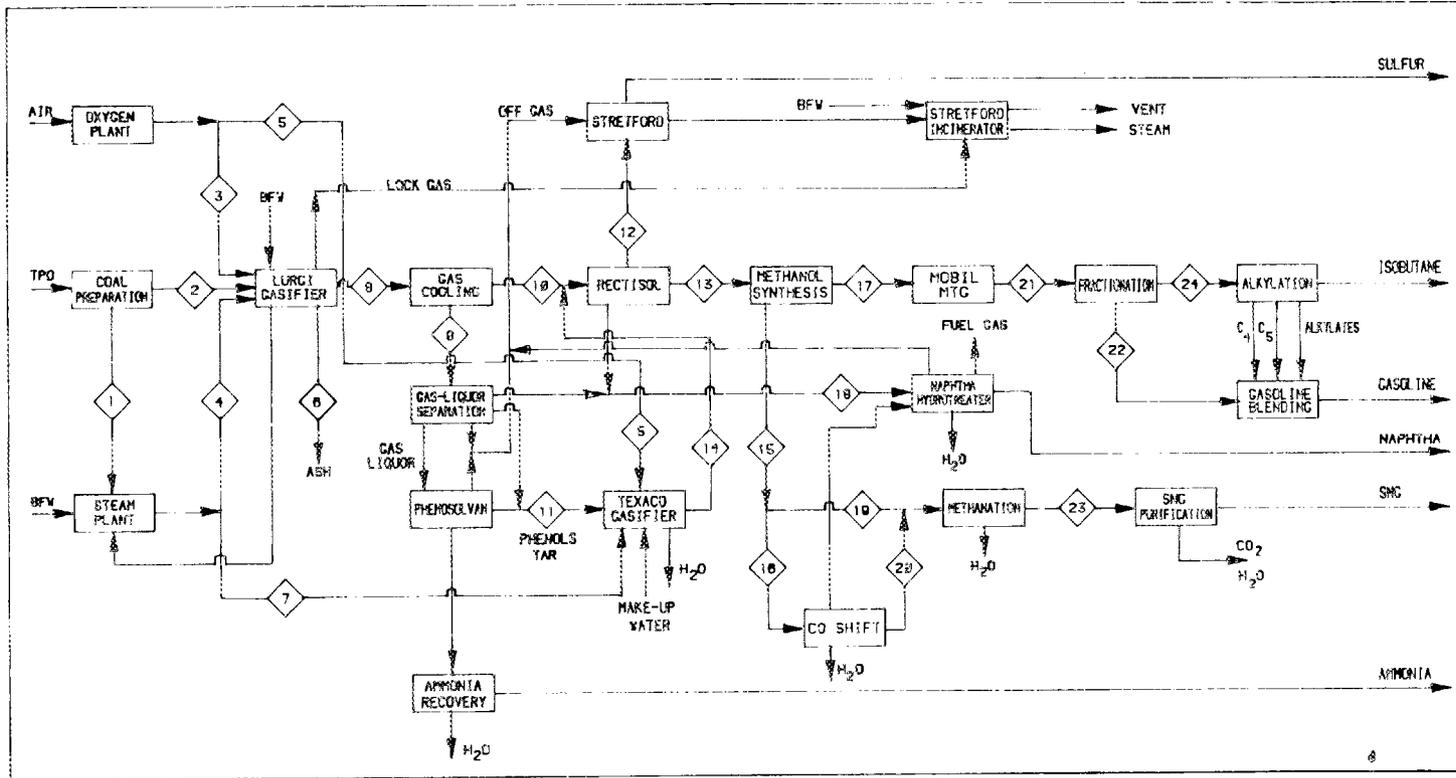


Fig. 1. Simplified overall block diagram of the Tri-State process.

The purge gas is to be methanated to produce pipeline-quality gas. However, since the ratio of  $H_2$  to CO in the purge gas is too low for feed to a methanator, part of the purge gas is first shifted to produce more  $H_2$ . The shifted gas is remixed with the remainder of the purge gas and sent to the methanator. The methanation flowsheet uses two reactors in series, with recycle to the first reactor and gas cooling by steam generation between the reactors. The methanated gas is treated to remove water and  $CO_2$  and is then ready for pipeline injection.

The synthesized methanol is passed to the Mobil MTG unit for conversion to hydrocarbons. Most of the methanol is converted to liquid fuels, though some light gases are also produced. The MTG product is sent to a two-column fractionation section to separate light gases, alkylation feed, and gasoline. The alkylation feed is sent to the alkylation section for production of additional liquid fuels.

The condensate from the gasifier effluent cooling is phase-separated into hydrocarbon and water phases. The original flowsheet from the Tri-State project called for recycle of the heavy tars to the Lurgi. This practice caused some operating problems at the SASOL tests, so the project was modified to use a Texaco partial oxidation unit to gasify the tars. The original flowsheet also called for an upgrading (hydrotreating) of the naphtha fraction from the gasifier to produce a satisfactory gasoline blend stock. Although the SASOL test report<sup>1</sup> indicated that no naphtha was formed in the gasifier, it is still included in this study to handle the small amount of naphtha likely to be formed in larger-scale processes.

The units modeled in this study include: Lurgi gasifier, Texaco (or other entrained) gasifier, synthesis gas cooling, Rectisol, methanol synthesis, methanol-to-gasoline, CO-shift, methanation, and naphtha hydrotreating. Additionally, two user FORTRAN subroutines have been written for the devolatilization of coal to form char and volatile products and for the decomposition of coal to its elements plus ash and char. These routines are general and very useful in the modeling of many coal conversion processes. One user FORTRAN unit operation model has been written to facilitate modeling of waste heat boilers, which are widely used in coal conversion processes. An enhancement to the ASPEN physical property system has also been made to allow for the direct input of heat of combustion values for coal.

The remainder of this report presents (1) the details of the unit operation models, FORTRAN subroutines, and ASPEN enhancement; (2) how these models were integrated to allow overall material balances to be made; and (3) the results using different types of feed coal and variations in coal throughput. The ASPEN computer input and report files for the models and FORTRAN subroutines developed in this study are being issued as a Supplement to this report. A limited number of copies are available by contacting ORNL. Microfiche copies are available from the National Technical Information Service (NTIS).

## 2. DESCRIPTION OF MODELS

### 2.1 LURGI GASIFIER

The information necessary to formulate the Lurgi gasifier model was taken from the SASOL coal test<sup>1</sup> and a related publication.<sup>2</sup> The model

has essentially four steps: (1) drying/devolatilization; (2) conversion of devolatilized coal to its elements, plus ash and char; (3) conversion of the elements to produce gas-phase components; and (4) equilibration of the gas-phase components. The equilibrated gas-phase components are then remixed with the volatiles to form the raw synthesis gas. The solids from the gasifier are removed in another stream. The ASPEN block flow diagram for this model is shown in Fig. 2.

The coal devolatilization is done in block PROD using the ASPEN reactor model RYIELD with user yield subroutine DEVOL. Subroutine DEVOL converts half of the volatile matter from the proximate analysis component attribute to volatile products. The products are assumed to be  $H_2$ ,  $CH_4$ ,  $H_2O$ ,  $CO$ ,  $C_2+$ ,  $CO_2$ , phenol, and tar. Their respective yields are passed through the first eight locations of the REAL vector in the ASPEN input language. These yields must be obtained from empirical devolatilization data or from some other source. DEVOL updates the proximate and ultimate analysis of the coal to reflect the changes due to devolatilization; in this manner the element balance is maintained.

After the volatiles are removed in the separation block DEVOL, the devolatilized coal is decomposed to its elements in block CONV. Block CONV also uses the ASPEN RYIELD routine and a user yield routine, DECOMP. Subroutine DECOMP merely decomposes the coal to its elements plus char and ash based on the ultimate analysis. This scheme places the coal (or char) undergoing gasification into conventional components while still maintaining the elemental balance.

The elemental coal constituents are then mixed with the gasifier oxygen and steam feeds. In block GAS1, the ASPEN RSTOIC model is used

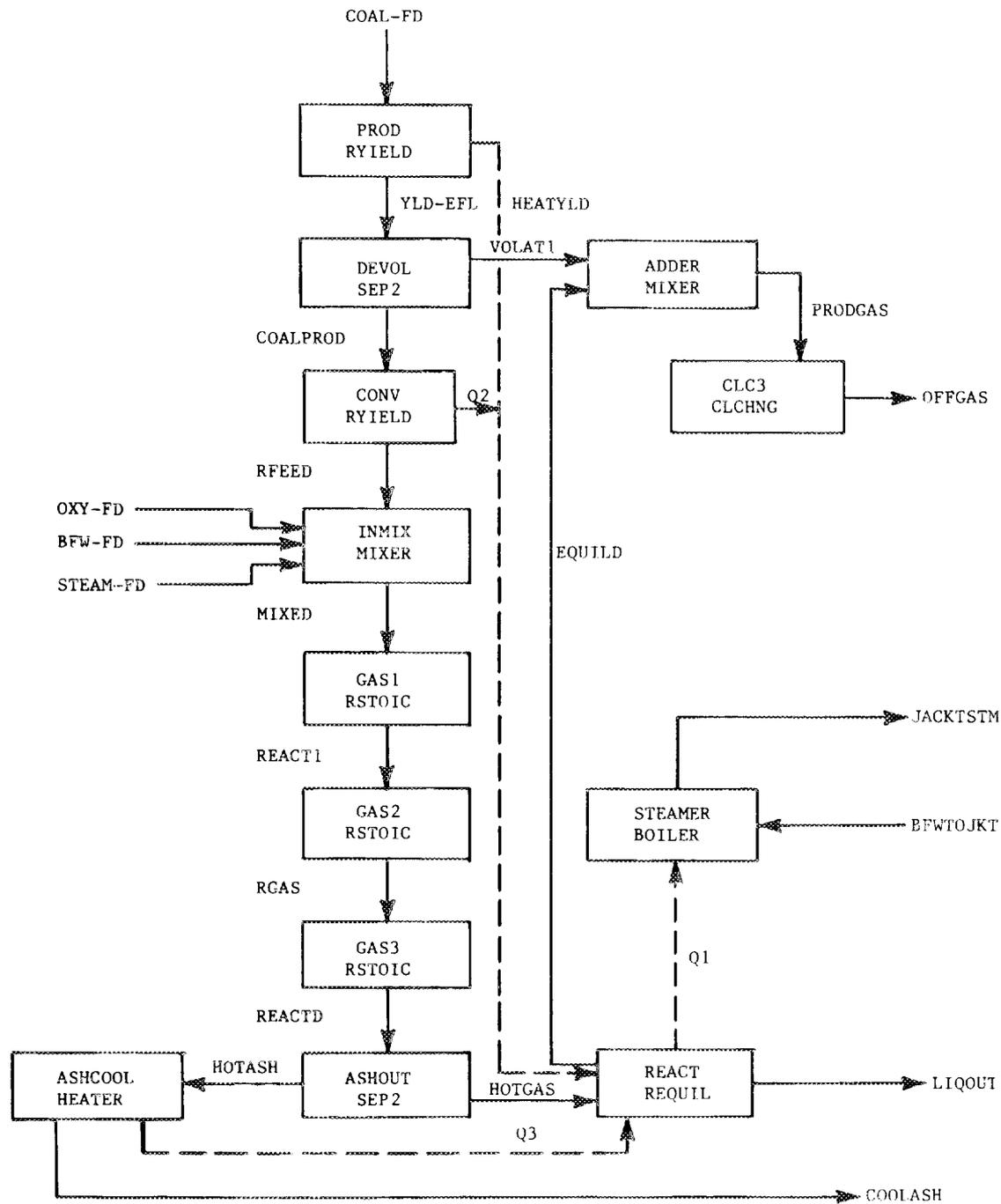
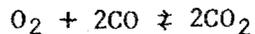
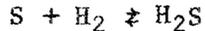
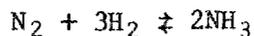
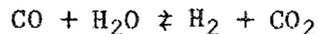


Fig. 2. ASPEN block diagram of Lurgi gasifier model.

to react carbon and oxygen to form carbon dioxide, while in block GAS2 carbon and steam are reacted to form carbon monoxide and hydrogen. A third RSTOIC model is then used (block GAS3) to convert the solid sulfur and remaining oxygen according to the following reactions:



Block ASHOUT removes 96% of the remaining ash and 25% of the char in stream HOTASH. The gas-phase components are then equilibrated in block REACT using the ASPEN REQUIL model. The pertinent reactions are assumed to be the following:



The equilibrated gases are then remixed with the volatiles to produce the raw synthesis gas. Care is taken to conserve heat in the model by collecting all heat released in reactions into block REACT. In the SASOL coal test<sup>1</sup> (see Appendix), the Lurgi synthesis gas exited at a temperature of 1030°F. Thus, the experimental temperature of 1030°F has been used to determine the amount of steam generated in the BOILER block STEAMER. The physical properties for tar and naphtha were obtained using the Wilson<sup>3</sup> correlation. Fitted binary interaction parameters were used for all interacting species<sup>4</sup> with the Redlich-Kwong-Soave equation of state. These data were entered into the ASPEN input file using the insert RSKIJ.

## 2.2 ENTRAINED GASIFIER

The Texaco entrained gasifier model is similar to the Lurgi model, except that the entrained gasifier assumes that devolatilization is unimportant. This model has given excellent results for modeling entrained gasifiers; Table 1 shows a comparison between our model predictions and data from Koppers<sup>5</sup> for three widely different coals: western, Illinois, and eastern coals. For each coal, the agreement between the ASPEN predictions and the Koppers data is quite good.

An ASPEN block flow diagram of the entrained gasifier model for a solid coal feed is shown in Fig. 3. The model begins by first decomposing all components having an ultimate analysis attribute to their elements, plus ash and char. This decomposition is done in block CONV using the user yield subroutine, DECOMP, as described in the previous discussion of the Lurgi model. If not otherwise specified, the carbon burnup is assumed to be 100%. It should be noted that DECOMP will also decompose attribute conventional components, such as tar. When a solid coal feed is not used, as in the Tri-State case, the ASPEN flow diagram shown in Fig. 4 is used. The converted elements are then mixed with the oxygen and the solid phases reacted to gas-phase components and adiabatically equilibrated as in the Lurgi model. The hot, equilibrated gases are then quenched with water to a temperature of 1800°F; a design specification is included to vary the quench water flow rate to obtain the specified outlet temperature.

Table 1. Comparison of ASPEN entrained gasifier model and published reports of Koppers-Totzek gasifier performance (basis: 1 ton/h)

	<u>INPUT</u>					
	Coal					
	<u>Western</u>	<u>Illinois</u>		<u>Eastern</u>		
Analysis, wt %						
C	56.76	61.94		69.88		
H	4.24	4.36		4.90		
N	1.01	0.97		1.37		
S	0.67	4.88		1.08		
O	13.18	6.73		7.05		
Ash	22.14	19.12		13.72		
Moisture	2.00	2.00		2.00		
Gross heating value (Btu/lb)	9,888	11,388		12,696		
Oxygen (98% O <sub>2</sub> ) (lb/h)	1,298	1,408		1,634		
Steam (250°F, 14.7 psi) (lb/h)	272.9	541.3		587.4		
	<u>RESULTS</u>					
	<u>ASPEN</u>	<u>Koppers</u>	<u>ASPEN</u>	<u>Koppers</u>	<u>ASPEN</u>	<u>Koppers</u>
Gas production (SCFH)	51,665	51,783	57,752	59,489	64,473	66,376
Gas composition, mol % (dry)						
H <sub>2</sub>	33.3	32.86	35.0	34.62	35.7	35.39
CO	59.5	58.68	55.4	55.38	56.0	55.90
CO <sub>2</sub>	5.81	7.04	6.7	7.04	6.88	7.18
N <sub>2</sub>	1.07	1.12	0.98	1.01	1.11	1.14
H <sub>2</sub> S	0.27	0.28	1.80	1.83	0.36	0.35
COS	0.02	0.02	0.09	0.12	0.02	0.04
Carbon burnup, wt % (assumed)	99.5	-	97.0	-	97.0	-

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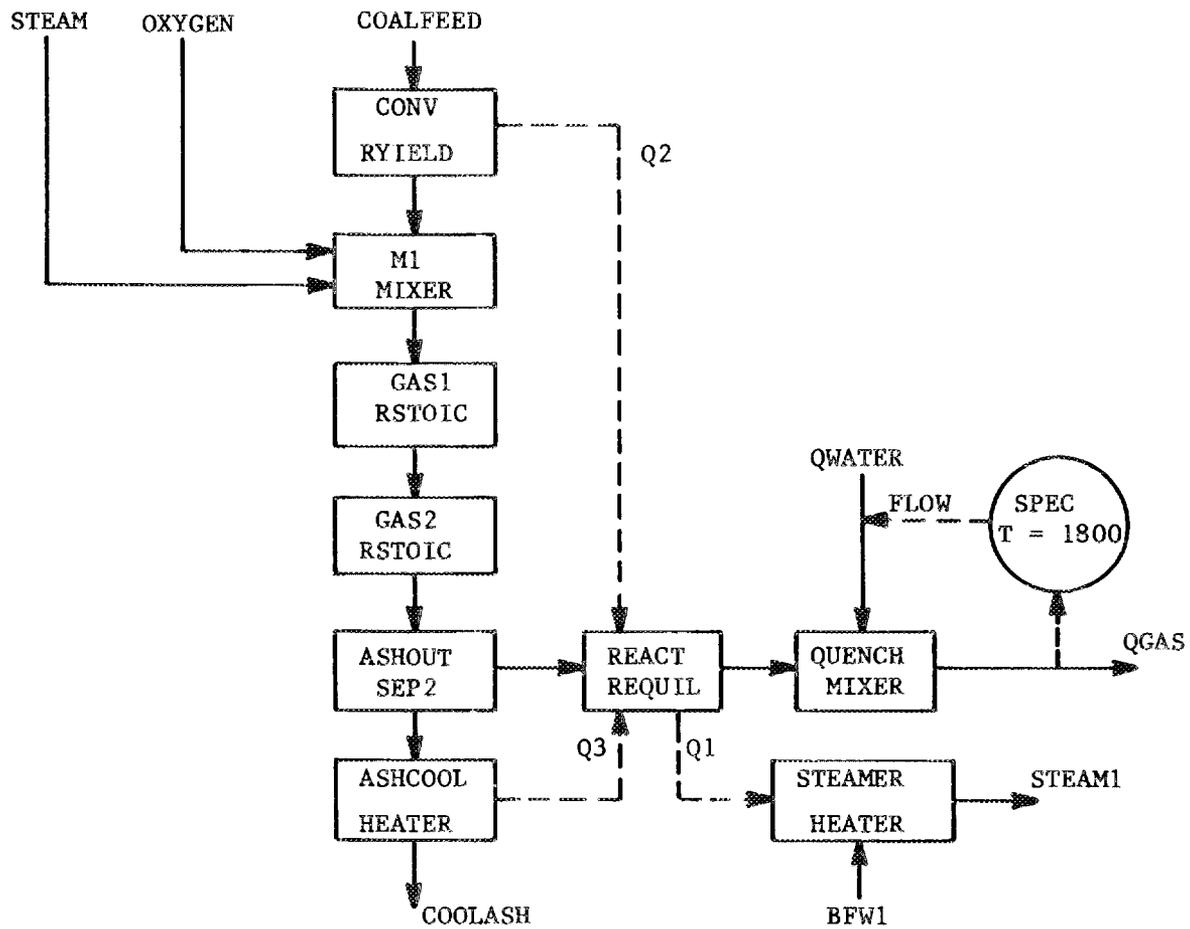


Fig. 3. ASPEN block diagram of entrained gasifier model with a solid coal feed.

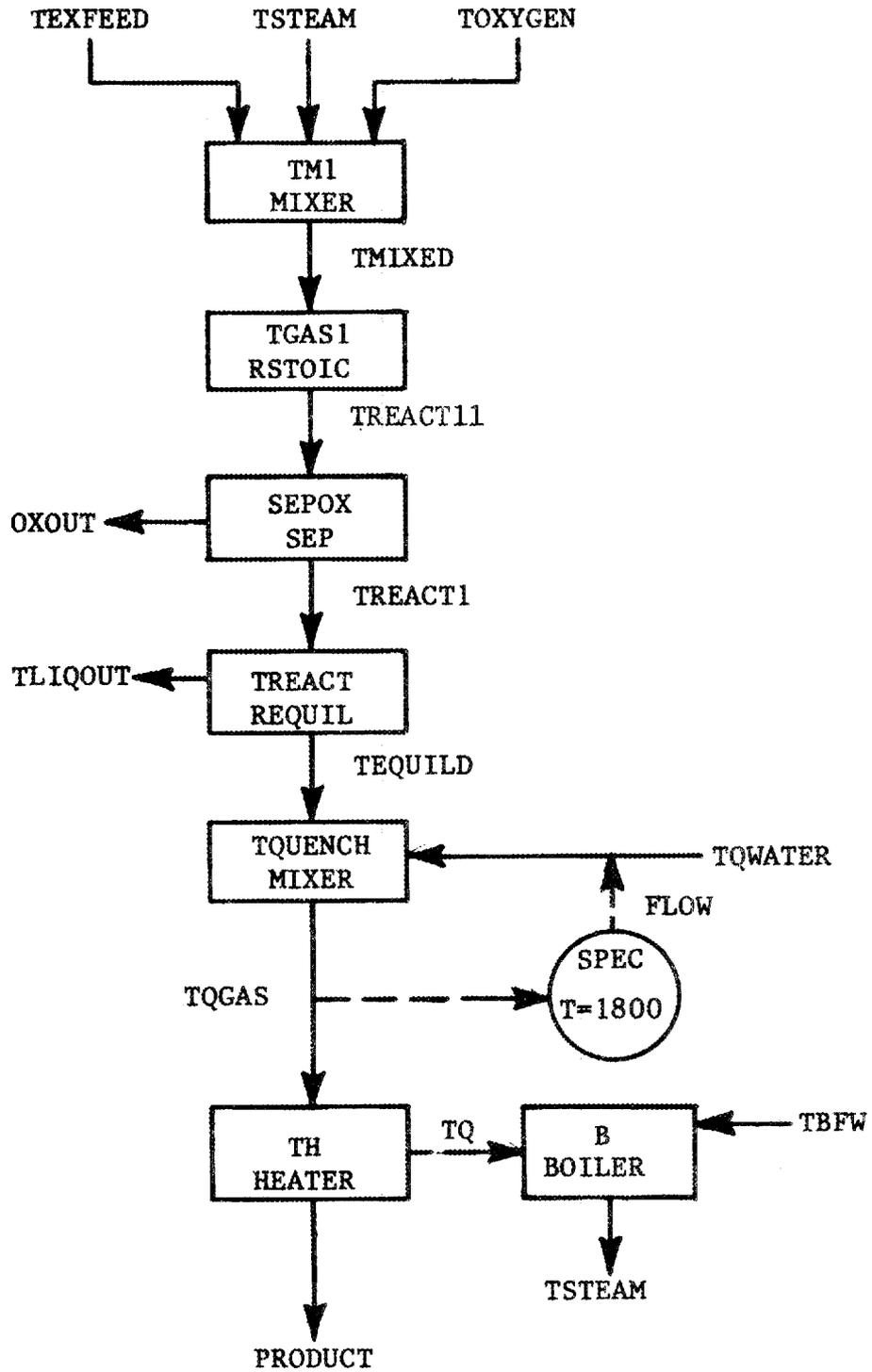


Fig. 4. ASPEN block diagram of entrained gasifier model with liquid feeds.

### 2.3 RAW-GAS COOLING

The Tri-State flowsheet calls for the raw synthesis gas to be cooled and sent to Rectisol, not using a raw shift as in some other proposed processes. The sensible heat in hot raw synthesis gas is a significant fraction of the heating value of the feed coal and, therefore, must be recovered efficiently. This recovery process is the function of the raw-gas cooling section.

The process flow diagram used for our gas cooling model is shown in Fig. 5. The details of this flowsheet were taken from Wham et al.<sup>6</sup> The gas cooling section cools the raw synthesis gas to the lowest practical temperature using water and air cooling. This maximum practical cooling reduces the refrigeration requirements in the Rectisol unit which follows.

The ASPEN block flow diagram for the gas-cooling model is shown in Fig. 6. The hot synthesis gas is first scrubbed with recycle condensate, block M1. The two-phase mixture from the scrubber is cooled in the first heat exchanger, block E301E3, generating medium-pressure steam. The gas from the first heat exchanger is fed to a knockout drum, with the condensate recycled to the scrubber. The gas from the knockout drum is cooled further in the second heat exchanger, block E303AE1, producing more medium-pressure steam and dirty condensate. The gas is then fed to the third heat exchanger to produce low-pressure steam. At this point, the gas stream is air-cooled and water-cooled and sent to the Rectisol unit. This model assumes a clean tar/water separation in block S9SPLIT, with the tar being fed to the Texaco gasifier. The Redlich-Kwong-Soave (SYSOP3) equation, which is excellent for light gases and hydrocarbons,

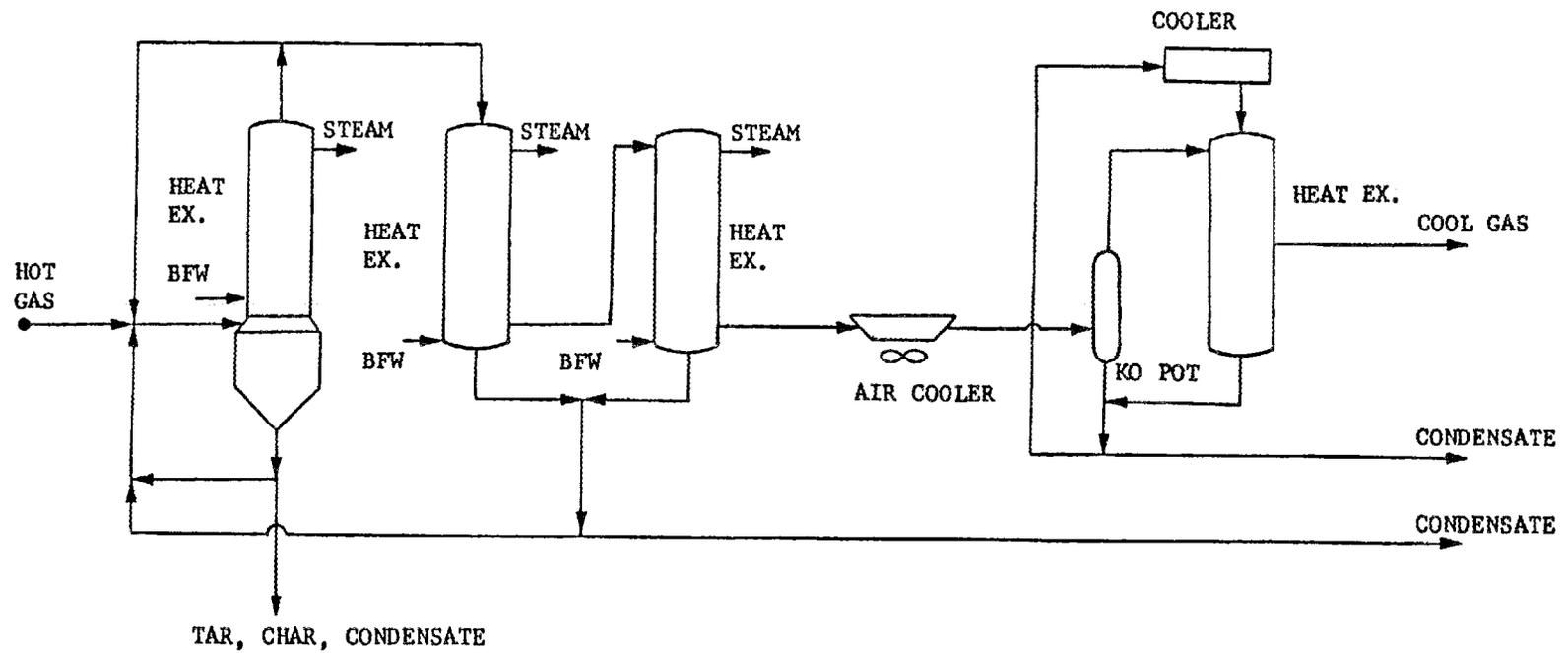


Fig. 5. Process flow diagram of gas cooling section.



is used for the calculation of physical properties for process streams; the ASME steam table correlations (SYSOP12) are used for steam and cooling water. The physical properties for the condensable hydrocarbons were obtained using the Wilson<sup>3</sup> correlation. When a rigorous ASPEN sour-water flash model has been developed, it should replace the present FLASH2 blocks.

#### 2.4 RECTISOL MODEL

The catalysts used for methanol synthesis and methanation are sensitive to poisoning by sulfur compounds. The Rectisol process is one of the more widely used processes for removing H<sub>2</sub>S from synthesis gas. The Rectisol process uses methanol as a solvent for the H<sub>2</sub>S. At the temperatures used (-70°F), H<sub>2</sub>S is more soluble in methanol than are the other major components of synthesis gas. The flowsheet used here is the standard five-column process designed for treating gases containing a significant concentration of naphtha.<sup>7</sup> The presence of naphtha complicates the processing because an azeotrope is formed between naphtha and methanol and two liquid phases can be formed in the naphtha/methanol/water system. To provide for these highly nonideal vapor-liquid equilibria, the version of the Soave-Redlich-Kwong equation of state that has been modified for polar components (Redlich-Kwong-ASPEN) was used. Fitted binary interaction parameters are used for all interacting species.<sup>4</sup> The data shown in the ASPEN input file are identical to the RKSKIJ insert used in the gasifier section.

The process flow diagram for the Rectisol model is shown in Fig. 7. The corresponding ASPEN block diagram is shown in Fig. 8. The raw gas

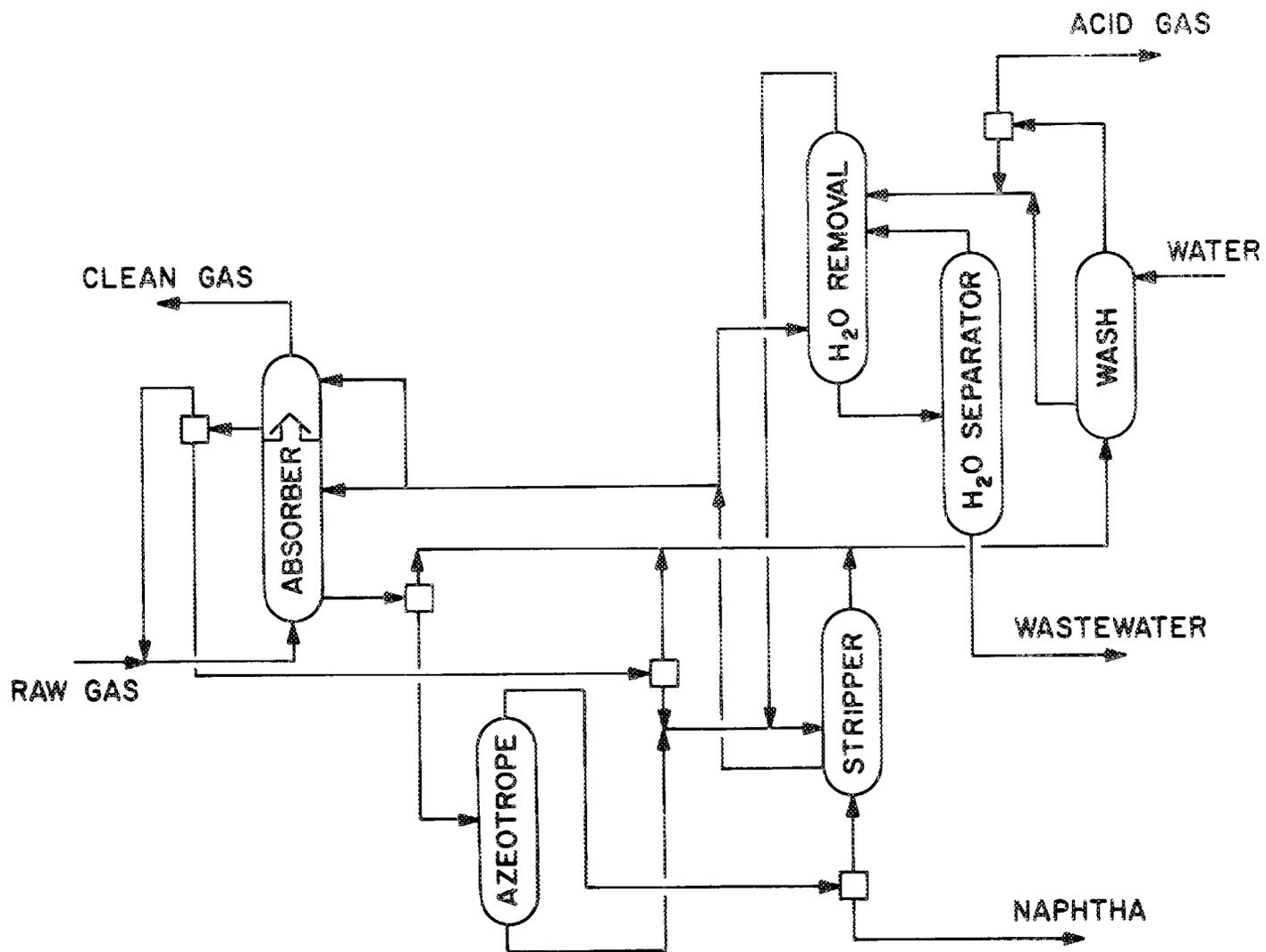


Fig. 7. Process flow diagram of Rectisol section.

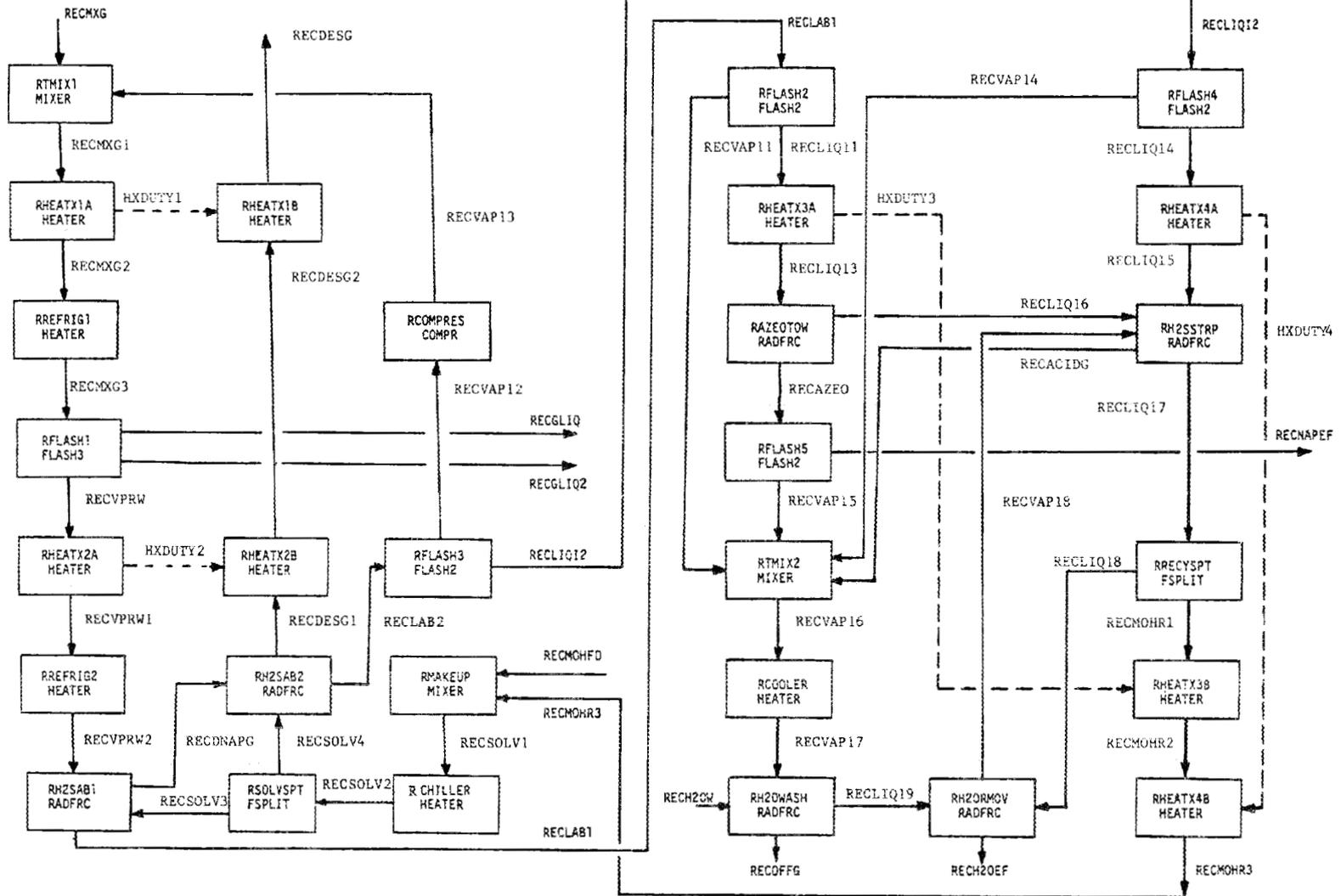
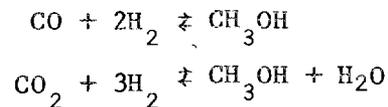


Fig. 8. ASPEN block diagram of Rectisol section.

from gas cooling is exchanged against the purified gas and with makeup refrigeration and fed to the prewash section of the absorber. The prewash is operated so that the naphtha is absorbed while allowing the lighter components to pass to the upper section of the absorber. The loaded solvent is sent to the azeotrope column to separate a clean naphtha product and a methanol-rich stream. The loaded solvent from the upper section of the absorber is flashed to release absorbed synthesis gas (which is recycled to the absorber inlet) and then fed to the stripper along with the methanol-rich stream from the azeotrope column. In the stripper the  $H_2S$  is stripped from the solvent forming a  $H_2S$ -rich vapor stream. The  $H_2S$ -rich stream is washed with water to recover the methanol. The water-methanol mixture is then distilled to obtain a lean methanol stream for recycle to the absorber. The bottom stream from the  $H_2S$  stripper is also recycled to the absorber.

## 2.5 METHANOL SYNTHESIS

The methanol synthesis model is based on the Lurgi tubular reactor concept.<sup>6,8-11</sup> In that scheme, the heat of reaction is used to make steam in the reactor shell, which is then available for use elsewhere in the process. Two methanol synthesis reactions are assumed to occur and to be at equilibrium at the reactor exit:



The flowsheet details have been taken from Wham et al.<sup>6</sup> The flowsheet used for the model is shown in Fig. 9. The synthesis gas is first compressed and mixed with the recycle. The mixture of fresh feed and

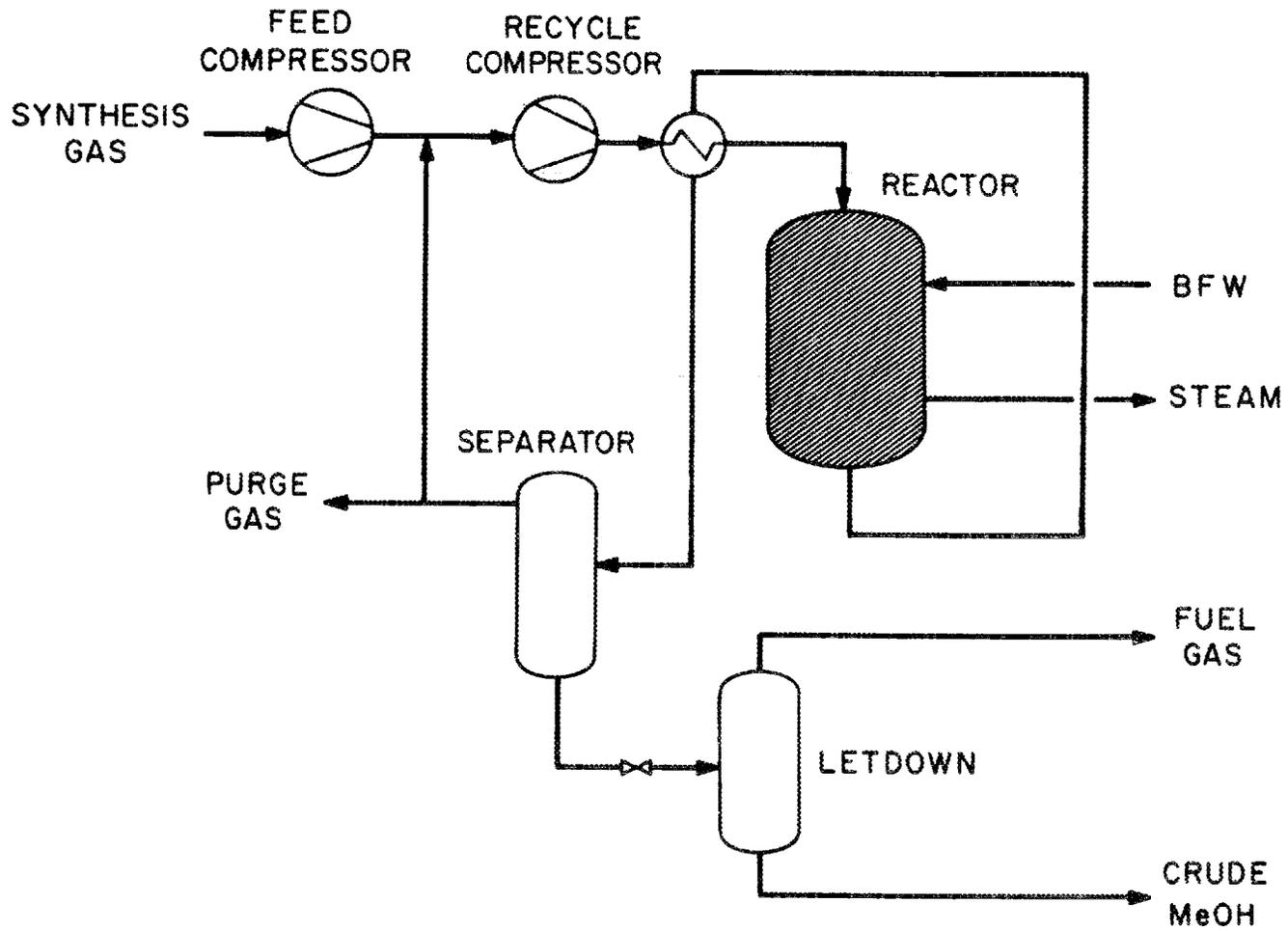


Fig. 9. Process flow diagram of methanol synthesis section.

recycle is then compressed to the desired reaction pressure. This stream is heated by heat exchange with reactor effluent before entering the reactor. After heat exchange with the reactor feed, the reactor effluent is cooled further in air- and water-cooled exchangers to condense the product methanol. The noncondensables are split, part recycled, and the rest purged to prevent buildup of inerts such as methane and higher hydrocarbons in the reactor loop. The purge gas is sent to the shift/methanation unit for further processing. The methanol product is further depressurized, vaporizing additional light gas, which can be used as fuel or sent to methanation. Part of the steam generated in the reactor jacket is expanded through a turbine to generate the power necessary to run the feed and recycle compressors.

The ASPEN block diagram for the methanol synthesis simulation is shown in Fig. 10. The simulation uses the ASPEN COMPR block to simulate the two compressors and the turbine. ASPEN HEATER blocks have been used to simulate the heat exchangers, with the two sides of the feed/effluent exchanger connected by a heat information stream, Q1. The reactor is modeled by an ASPEN REQUIL block and is assumed to operate isothermally. The heat of reaction from the reactor is passed to the boiler user model via heat stream Q2. The steam produced in the boiler is split, with part of the steam sent to the turbine. The turbine block accepts the work information streams from the compressors, W1 and W2, and calculates an "excess" work information stream, W3. An ASPEN DESIGN-SPEC varies the split of the steam stream so that the excess work from the turbine is zero. The product condensation and letdown operations are simulated with the ASPEN FLASH2 block. The fitted binary interaction

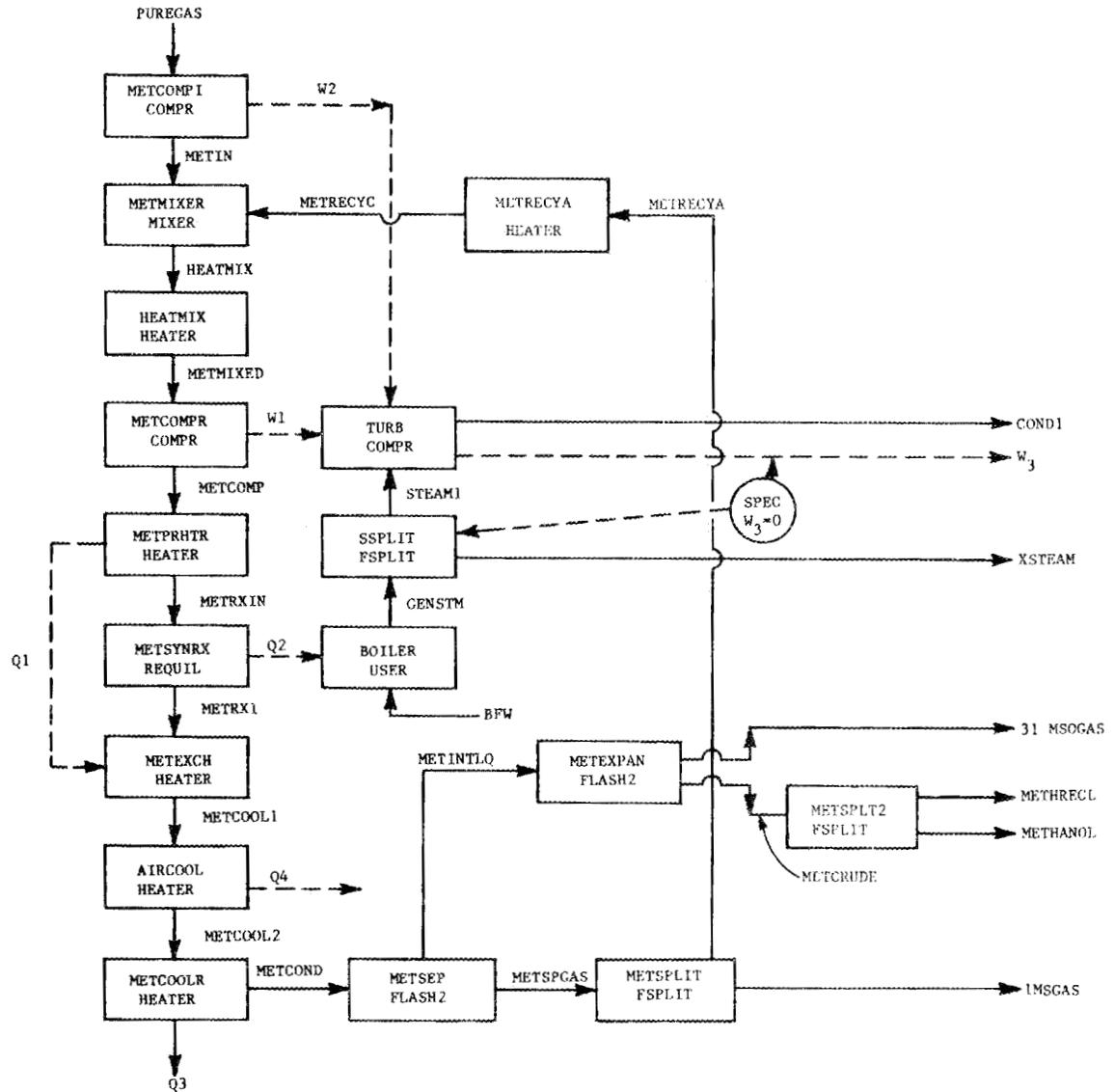


Fig. 10. ASPEN block diagram of the methanol synthesis section.

constants discussed in the Rectisol model are used for the vapor-liquid equilibrium calculations.

The methanol synthesis model has four primary independent variables: (1) feed composition and state, (2) reactor temperature, (3) reactor pressure, and (4) recycle ratio. Other variables, usually considered constant (e.g., pressure drops through the equipment, temperature and pressure of the product separators, steam pressure, etc.), can also be varied.

Table 2 shows the results of varying the reactor pressure and recycle ratio, holding the synthesis temperature constant (500°F) and using the feed composition from the Tri-State design report.<sup>12</sup> The feed composition and conditions are shown in Table 3. The results in Table 2 indicate that using recycle ratios greater than about 1.0 increases the equipment size and compressor horsepower, with little increase in methanol production. In the case of Tri-State, where the purge gas is to be shifted and methanated to produce SNG (assuming that the SNG can be sold), there is little incentive to use a recycle ratio greater than 1.0.

Table 3. Synthesis gas feed to methanol synthesis model

Component	Flow rate (lb-mol/h)
H <sub>2</sub>	57,241
CO	28,630
CO <sub>2</sub>	1,528
CH <sub>4</sub>	13,594
C <sub>2</sub> H <sub>6</sub>	388
C <sub>2</sub> H <sub>4</sub>	92
N <sub>2</sub>	541
H <sub>2</sub> O	0
CH <sub>3</sub> OH	0
Feed temperature	100°F
Feed pressure	608 psia

Table 2. Results from methanol synthesis model

Pressure (atm)	Recycle ratio	Feed compressor (hp)	Recycle compressor (hp)	Purge gas H/CO	MeOH production (lb-mol/h)	Purge gas production (lb-mol/h)
100	0	64,500	2,270	2.00	18,795	44,458
100	1	64,500	3,860	1.92	24,444	29,537
100	2	64,500	5,500	1.80	25,281	23,321
100	4	64,500	8,500	1.58	26,113	20,553
100	6	64,500	11,600	1.44	26,448	19,424
75	1	40,000	4,800	1.95	22,352	28,523
75	2	40,000	7,000	1.86	24,396	28,118
75	4	40,000	11,000	1.69	25,206	23,933
75	6	40,000	15,000	1.55	25,770	22,250
50	2	9,300	9,700	1.93	20,566	38,575
50	4	9,300	16,000	1.81	22,957	28,656
50	6	9,300	22,000	1.71	23,932	28,182

## 2.6 MTG MODEL

The basis for producing gasoline from synthesis gas via methanol is the Mobil methanol-to-gasoline (MTG) process. This proprietary process uses a zeolite catalyst to convert methanol to light liquid fuels (lighter than about  $C_{10}$ ) and some light gases. Because of the proprietary nature of the process, very little is known about the MTG synthesis reactor itself. A product yield structure for the reactor was taken from Schreiner.<sup>9</sup> Other process details were taken from Kam and Lee<sup>13</sup> and from Selover.<sup>11</sup>

The process flow diagram used for the simulation of the MTG, fractionation, and alkylation section is shown in Fig. 11. The feed to the unit is heated against the reactor effluent, mixed with light-gas recycle, and fed to the reactor. The reactor is assumed to be the Lurgi-tubular type, and the heat of reaction is used to generate steam. The reactor effluent is cooled to produce a three-phase mixture of gasoline, water, and light gases: (1) the gases are recycled to the reactor; (2) the water is sent to wastewater treatment; and (3) the gasoline is sent to the gasoline fractionation section.

The fractionation section is of the standard two-column design, producing light gases ( $C_2^-$ ), a stabilized gasoline ( $C_5^+$ ), and an alkylation feed ( $C_3-C_5$ ). The gasoline can be sent to gasoline blending without further treatment. The alkylation feed is mixed with the isobutane recycle stream and fed to the alkylation reactor. The alkylation step reacts unsaturates with isoalkanes to produce high-octane gasoline, by the reactions:

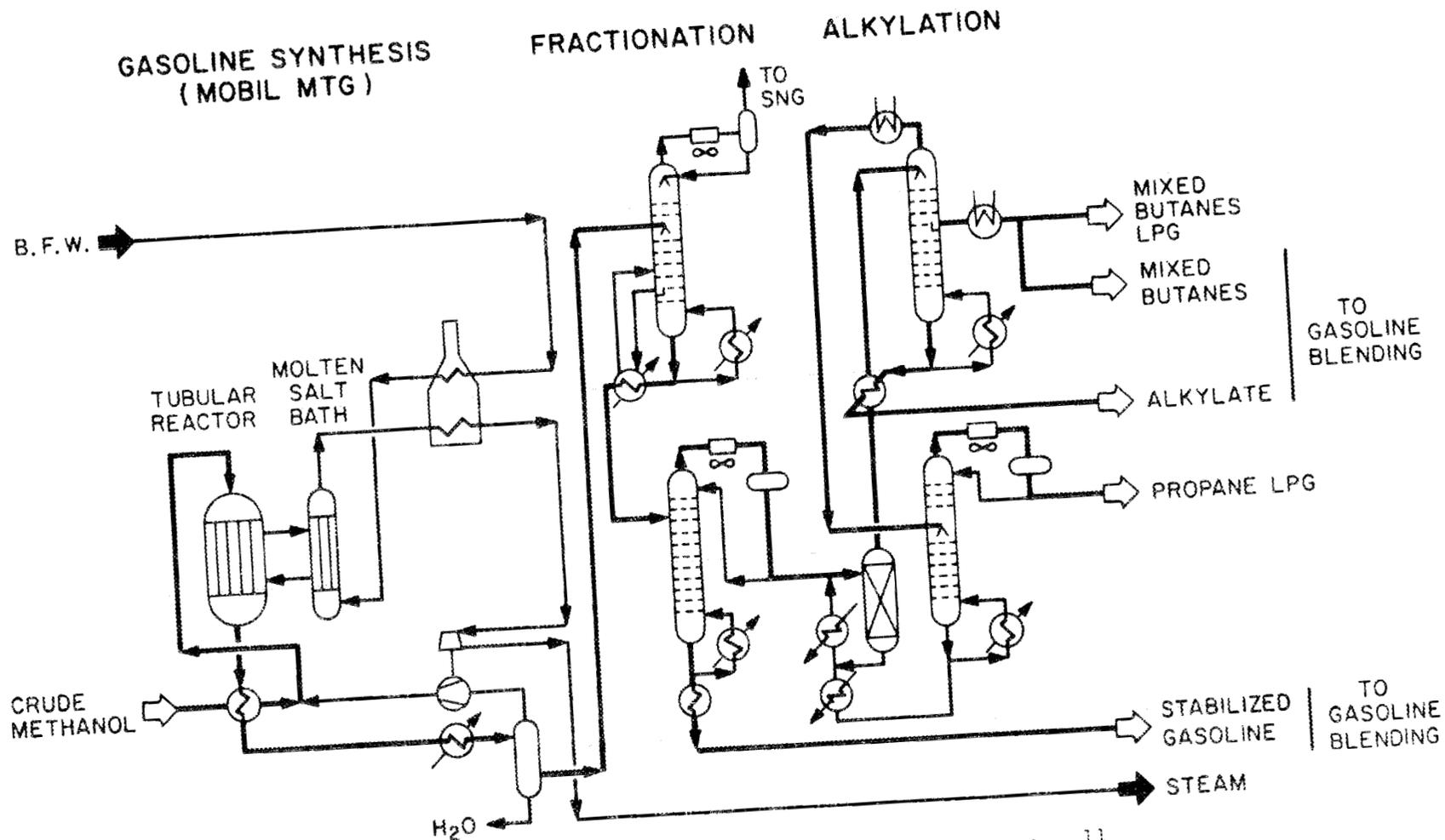
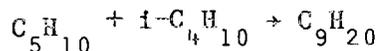
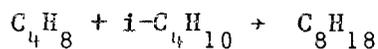
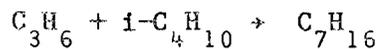


Fig. 11. Process flow diagram of MTG section.<sup>11</sup>



It is common practice<sup>14</sup> to recycle large amounts of isobutane to prevent polymerization and to ensure complete conversion of the unsaturates.

The alkylation product is sent to a two-column fractionation system to recover the unreacted isobutane for recycle, the alkylate for gasoline blending, as well as C<sub>3</sub> and C<sub>4</sub> product streams.

The ASPEN block diagram for this simulation is shown in Fig. 12. The overall section contains reactors, heat exchangers, and distillation columns. The Grayson-Streed correlation (SYSOP2) is used for vapor-liquid equilibria calculations. Grayson-Streed is adequate for this unit since the compounds handled are primarily light liquid hydrocarbons. The ASPEN reactor model RYIELD is used to simulate the MTG synthesis reactor, based on yield data from Schreiner.<sup>9</sup> An equilibrium reactor model could not be used because the actual reactions have not been published; in addition, a shape-selective zeolite catalyst which skews the product slate has been used in the process. The RYIELD model quantitatively converts the feed methanol to gasoline and lighter products using the final product distribution as published by Mobil. A serious limitation of this model is that the reactor is based on a single product distribution, obtained at Mobil's "preferred" operating conditions. Therefore, varying reactor temperature and pressure may give erroneous results. The model is adequate for calculating heat duties, product recoveries, etc.

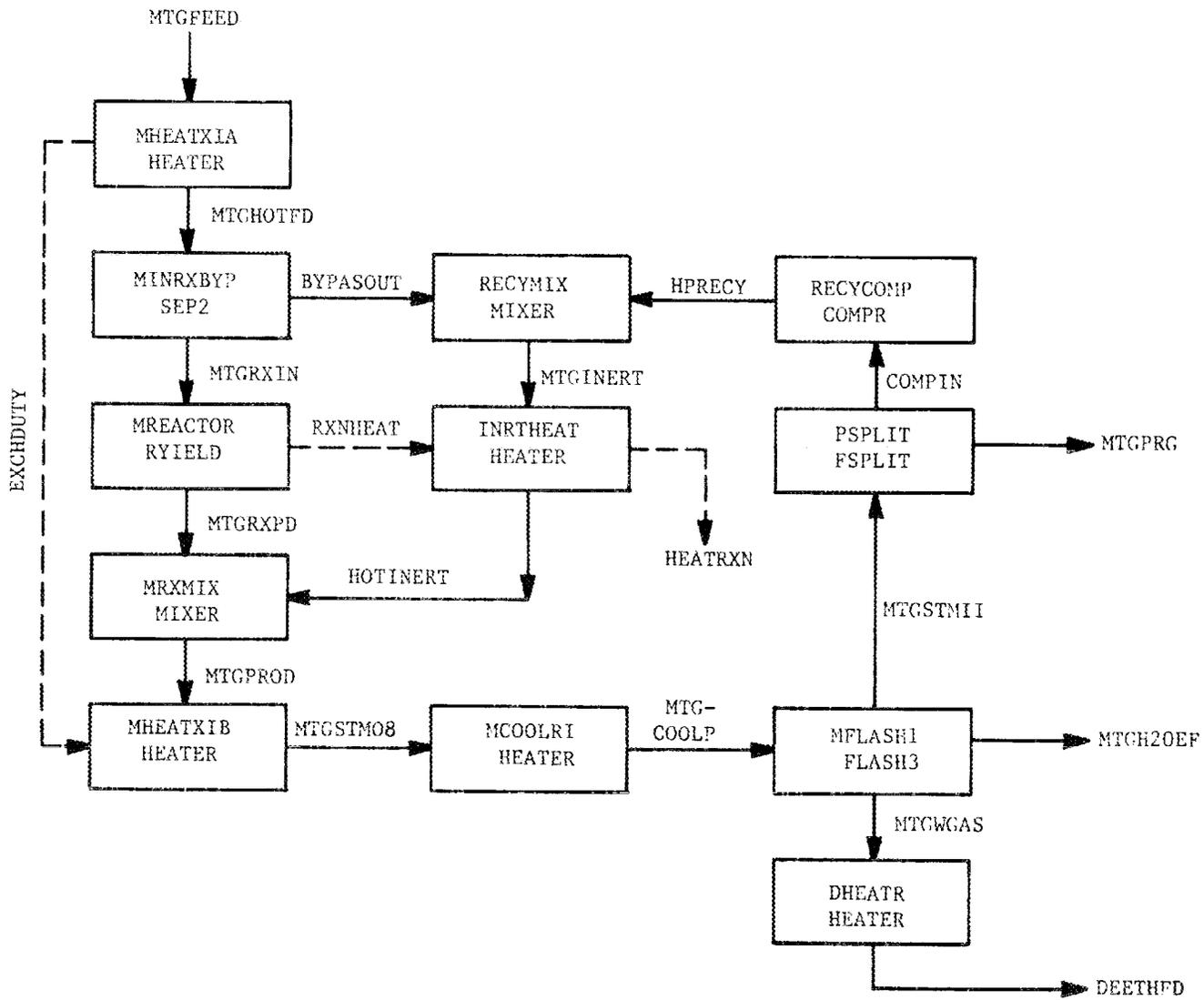


Fig. 12. ASPEN block diagram of MTG section.

The distillation columns in the fractionation section are simulated using the ASPEN rigorous distillation model, RADFRC, as shown in Fig. 13. The alkylation reactor is modeled using the ASPEN stoichiometric reactor RSTOIC, as illustrated in Fig. 14. The heat exchangers are modeled using the ASPEN single-sided heat exchanger model, HEATER. For heat transfer between process streams, the HEATER blocks are connected by an information heat stream.

## 2.7 SHIFT/METHANATION SECTION

The purge gas from methanol synthesis and various other smaller gas streams in the process contain a significant fraction of the energy value of the feed coal. For that reason these streams must be properly used to maintain an acceptable process efficiency. If a market for SNG is available, the most efficient use of these gases is to produce pipeline-quality gas. This option was the one chosen in the Tri-State design.

Details for the flowsheets used in this simulation were obtained from Wham,<sup>6</sup> Selover,<sup>11</sup> and Irvine.<sup>15</sup> The process flowsheets used for this simulation are shown in Figs. 15 and 16. Most of the gas sent to the shift/methanation unit is purge gas from the methanol synthesis area. The amount of gas sent to the shift unit, which increases the hydrogen content, is determined by the amount of hydrogen needed by the methanation processes or other processes. In the shift area,  $H_2O$  and  $CO$  are reacted to form  $CO_2$  and  $H_2$ . Some of the  $H_2$ -rich stream is treated for  $H_2$  recovery for subsequent use in the hydrotreater. The remaining gas is remixed with the rest of the purge gas and fed to the methanation

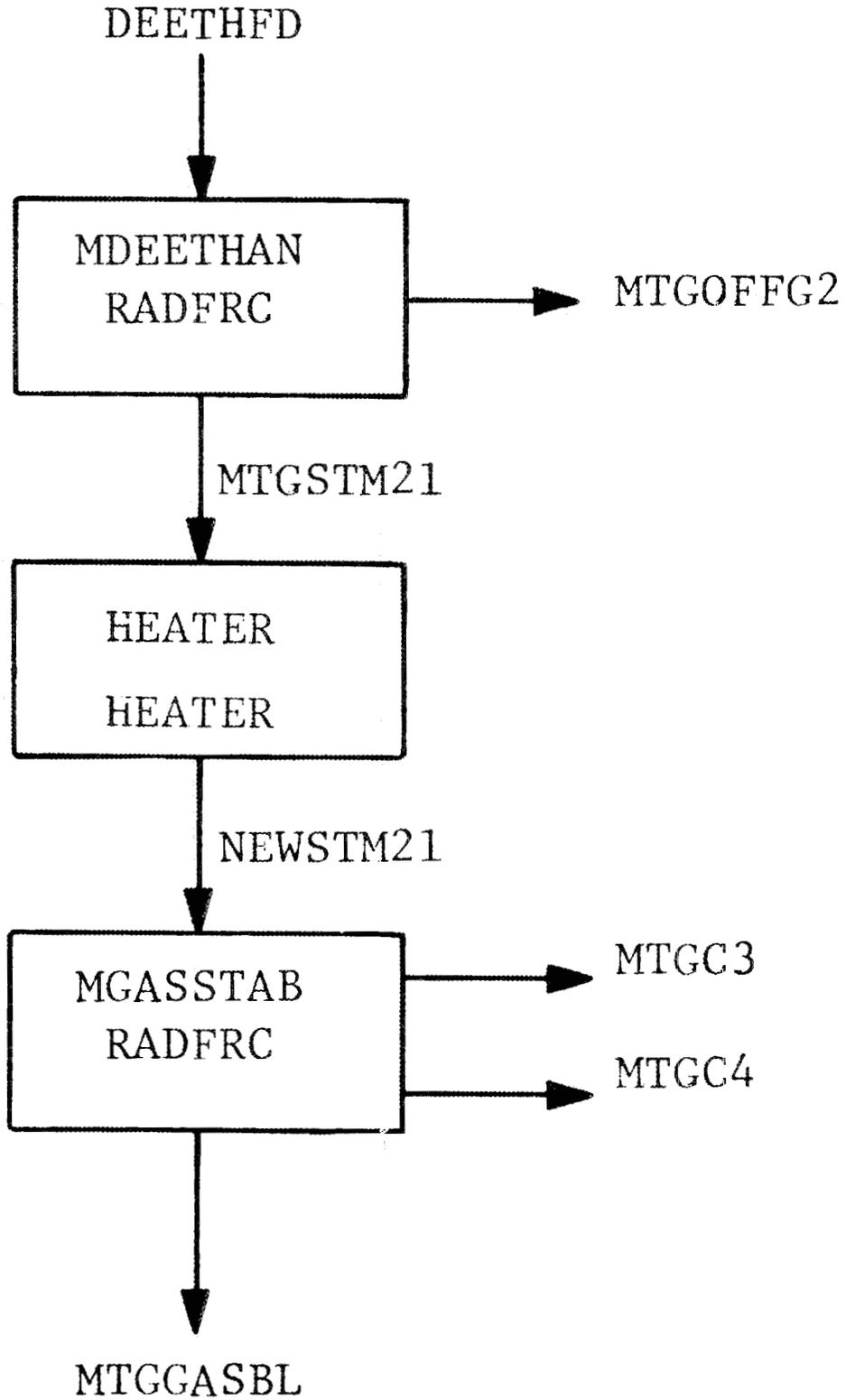


Fig. 13. ASPEN block flow diagram of fractionation section.

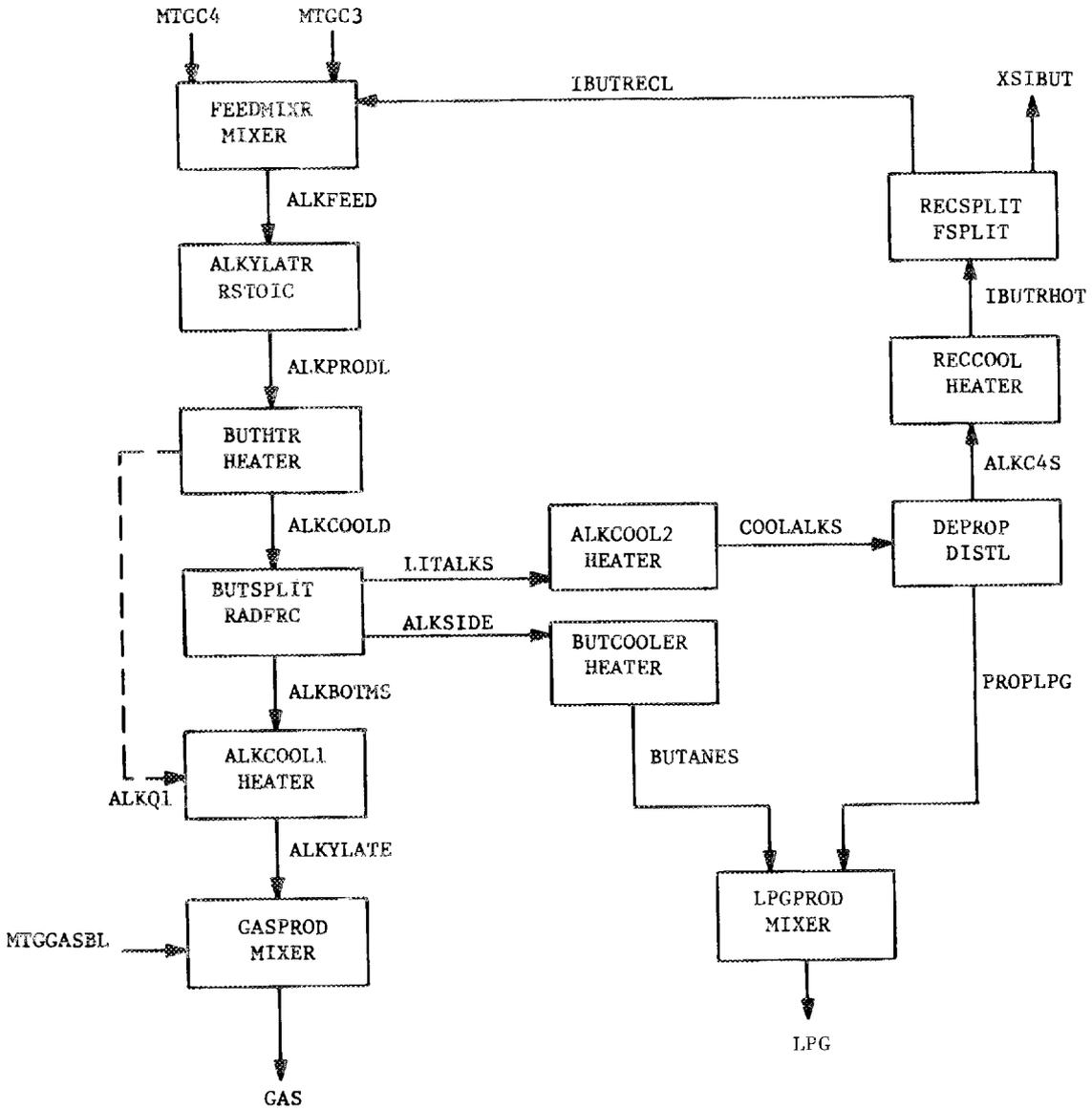


Fig. 14. ASPEN block diagram of alkylation section.

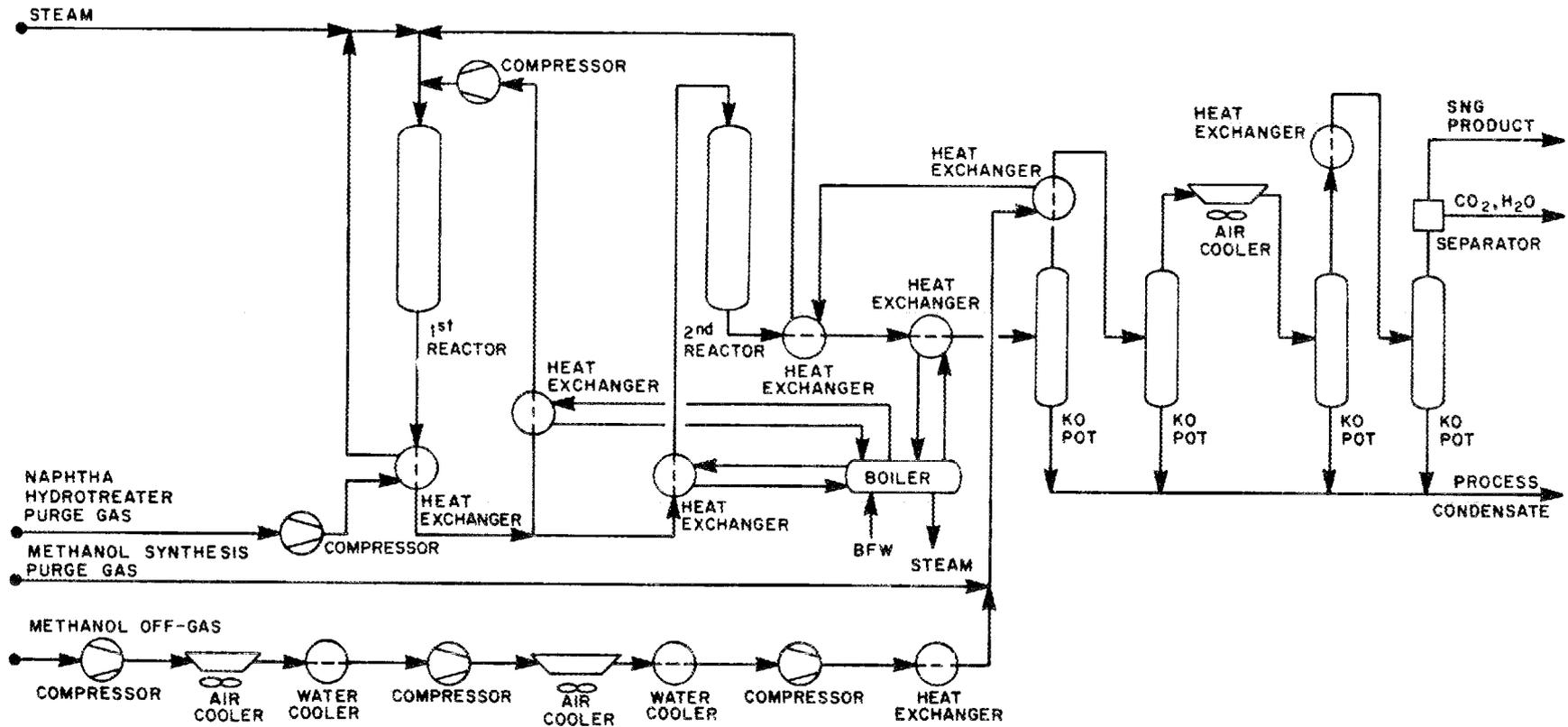


Fig. 15. Process flow diagram of methanation section.

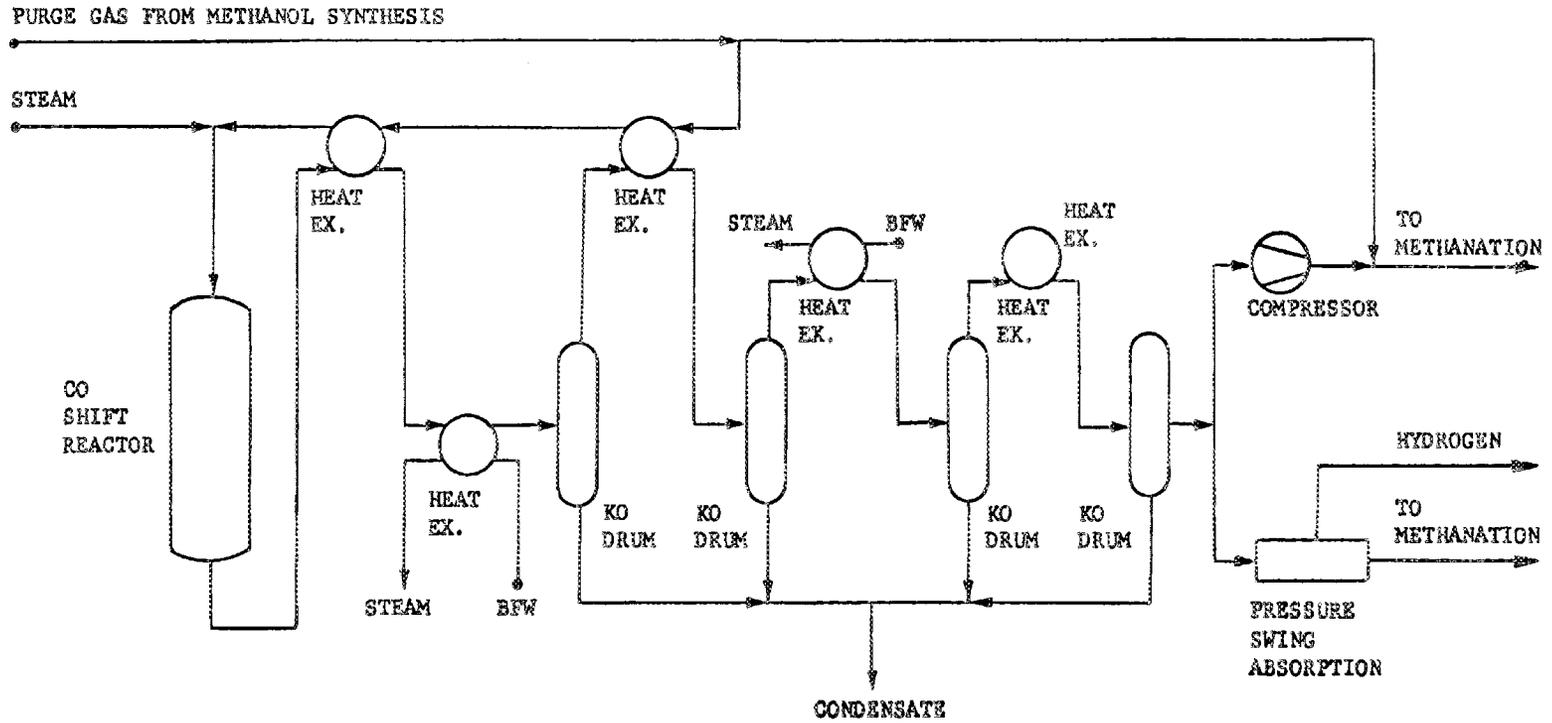
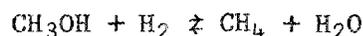
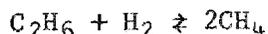


Fig. 16. Process flow diagram of CO-shift section.

unit. In the methanation unit, CO, CO<sub>2</sub>, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>6</sub> are reacted with hydrogen to form CH<sub>4</sub> and water in two reactors as follows:



The first reactor reacts most of the CO, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>6</sub> with hydrogen, and the second reactor essentially completes these reactions and reacts CO<sub>2</sub> with the remaining hydrogen. In both the shift and the methanation sections, condensers remove water from the reactor effluent.

The ASPEN block flow diagram for the shift unit simulation is shown in Fig. 17. The purge gas from the methanol synthesis is split between the shift area and the methanation area. A split of 35% to the shift unit has been assumed for this stage of development of the detailed models. The amount of gas sent to the shift area will depend on how much hydrogen is needed and will be determined concurrent with the overall plant mass balance. The gas to the shift unit is heat exchanged with reactor effluent using ASPEN heat streams. The gas is then mixed with steam via a FORTRAN design statement to achieve a H<sub>2</sub>O-to-CO ratio of 3:1. The steam-gas mixture is reacted in an adiabatic REQUIL reactor to achieve the CO and H<sub>2</sub>O conversion to H<sub>2</sub> and CO<sub>2</sub>.

The reactor effluent is heat exchanged with the reactor feed in a HEATER block. The reactor effluent is cooled further by heat exchange with boiler feed water to produce steam. The user subroutine BOILER determines how much boiler feed water is required to produce saturated steam at a given pressure. The gas is cooled further in a series of

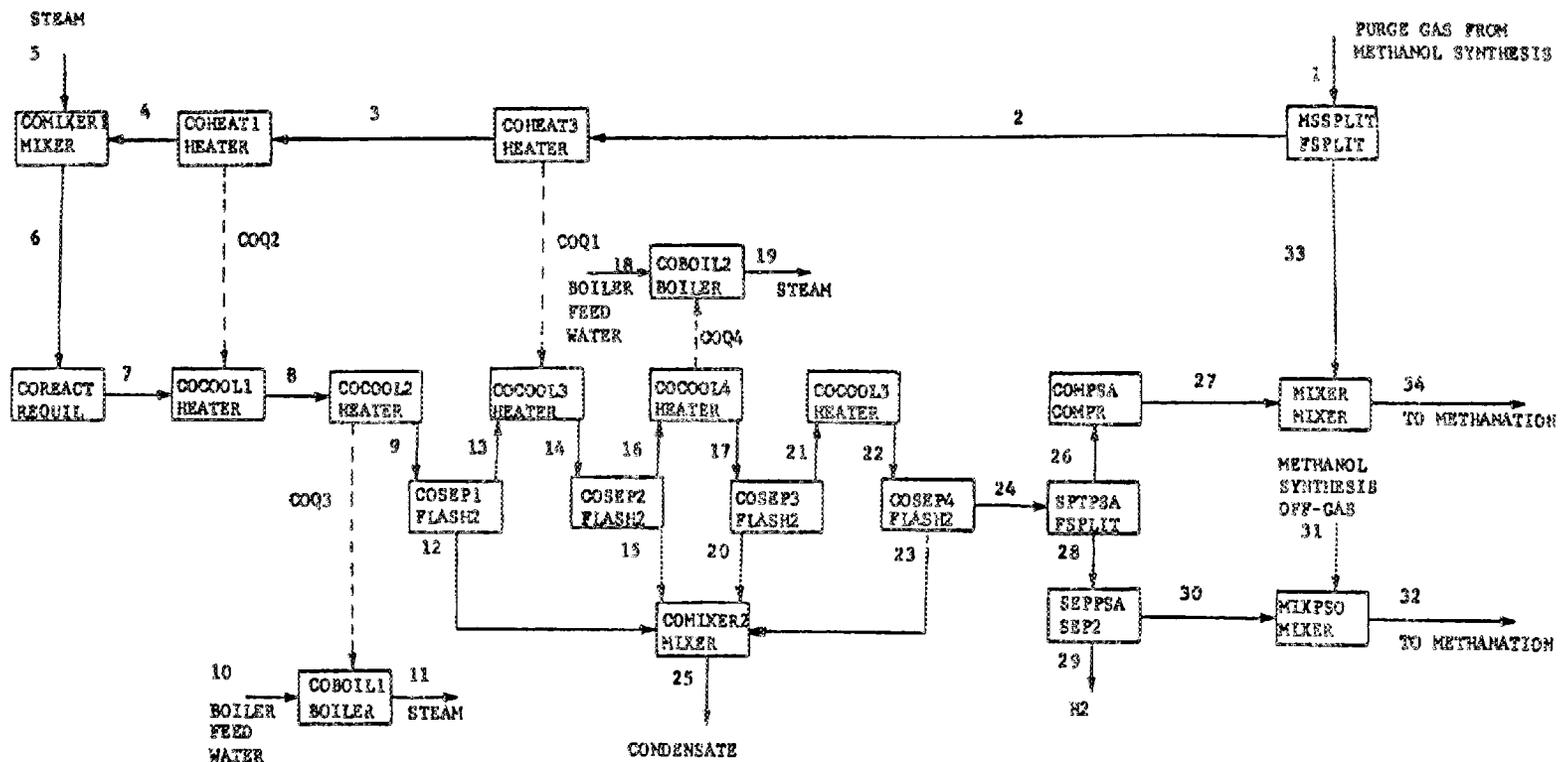


Fig. 17. ASPEN block diagram of CO-shift section.

ASPEN HEATER and FLASH2 blocks, and the condensed water is removed. Some hydrogen is removed from part of the gas stream for use in areas other than the methanation unit. The remainder of the gas is sent to the methanation area.

The ASPEN block diagram for the methanation section is shown in Fig. 18. In the methanation area two adiabatic reactors are used to react the CO, CO<sub>2</sub>, and the other hydrocarbons with H<sub>2</sub> to form methane and water. The first reactor is an adiabatic ASPEN REQUIL reactor. The effluent from the reactor is cooled and then split in order to recycle some of the cooled effluent to maintain a specified temperature of 850°F for the reactor effluent. The amount of split is determined by an ASPEN design specification that samples the effluent stream temperature and then varies the amount recycled accordingly by varying the amount split in BLOCK SPLIT1.

The second reactor is modeled by an ASPEN RGIBBS block made adiabatic by a design specification. The design specification samples the stream leaving the reactor and adjusts the temperature in the RGIBBS block to set the heat stream to a small relative value. The reactor effluent is then cooled by HEATER blocks, and the condensate (which is mostly water) is separated by using ASPEN FLASH2 units. Two reactors have been used in this simulation because of the nature of the methanation reactors. Since carbon monoxide is an inhibitor to the catalyst as far as carbon dioxide is concerned, no CO<sub>2</sub> reacts until all of the CO has been reacted. The ASPEN REQUIL model treats this situation well, since any species not mentioned in the stoichiometry specification is treated as an inert component.

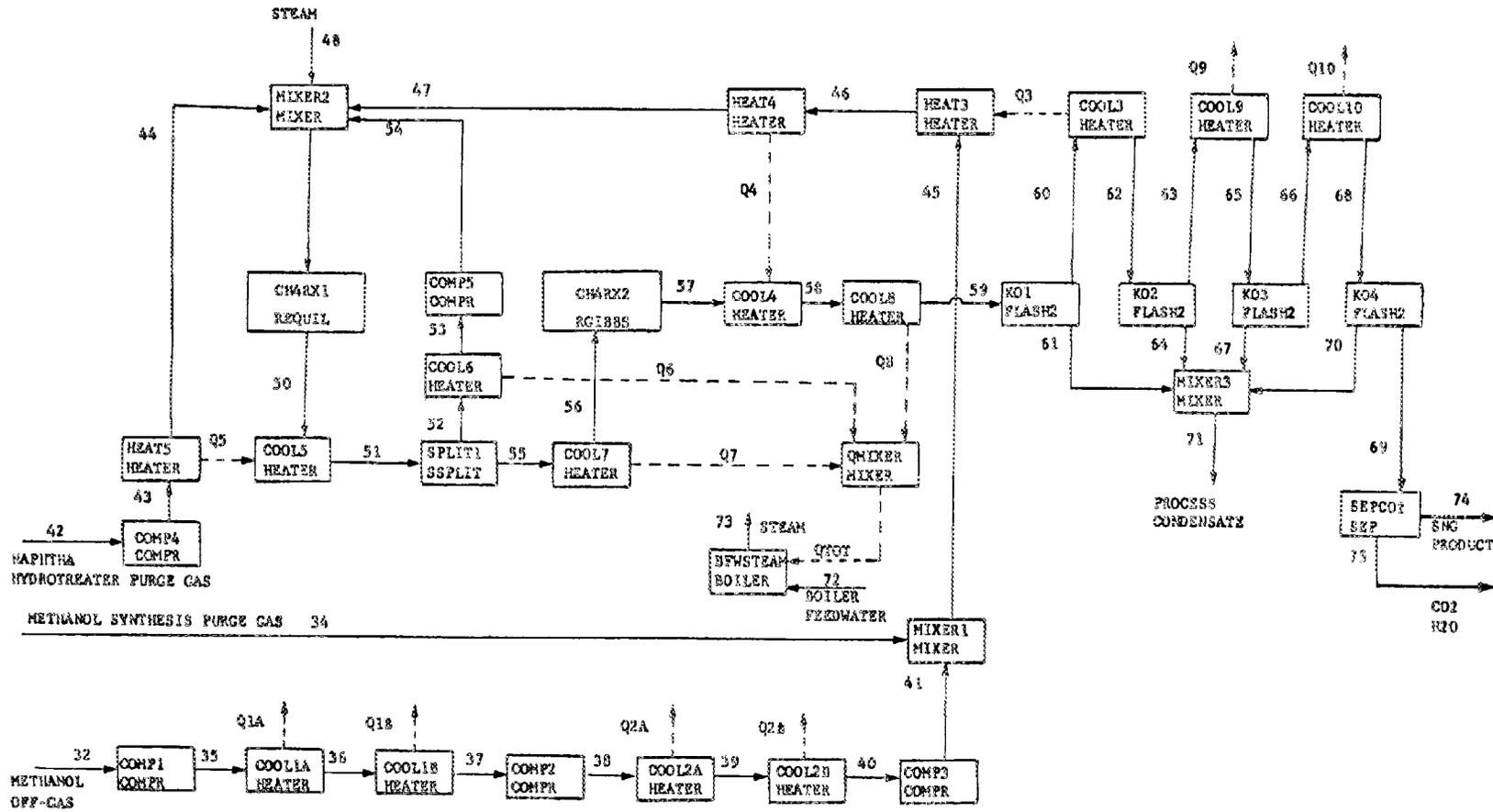


Fig. 18. ASPEN block diagram of methanation section.

## 2.8 NAPHTHA HYDROTREATER

The naphtha produced from Lurgi gasification is a potentially valuable product. Before the naphtha can be used, however, it must first be treated to reduce its sulfur and nitrogen content. The commercially available technology for this function is catalytic hydrotreating. Details of the hydrotreating flowsheet used for this simulation were obtained from Schreiner.<sup>9</sup>

The process flow diagram for the hydrotreater model is shown in Fig. 19. The gasifier naphtha is pumped to reaction pressure, mixed with hydrogen, heat exchanged with the reactor effluent, and heated further to reaction temperature by a fired heater. Conditions in the catalytic reactor are chosen to saturate the double bonds with as little carbon-bond cracking as possible and little aromatic-ring hydrogenation. After the reaction, the effluent is cooled, and three phases are formed. The gas phase is separated and amine-washed to remove hydrogen sulfide and then is split into recycle- and purge-gas streams. The aqueous phase is sent to water treatment, and the organic phase is stabilized by removing water, light hydrocarbons, and dissolved gases in a distillation unit.

The ASPEN block diagram for this model is shown in Fig. 20. The equipment names in the ASPEN diagram shown in Fig. 20 are either mnemonic or correspond with the equipment names on Schreiner's flowsheet. Input and product stream values for temperature, pressure, and flow rates of components are given by Schreiner, but all internal values were developed for this study.

In the ASPEN simulation, ASPEN HEATER blocks are used to simulate heating or cooling processes. The ASPEN PUMP block is used for the

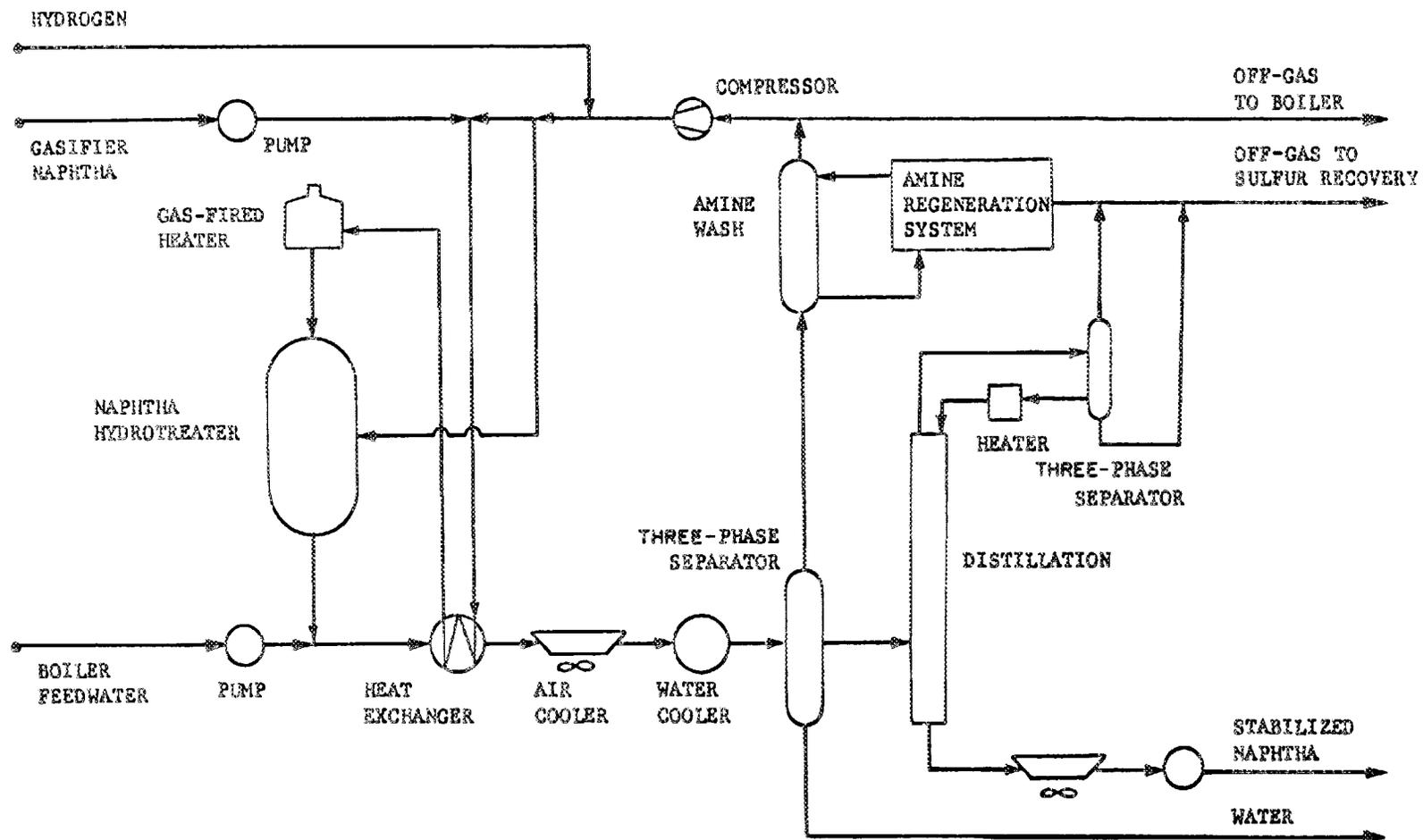


Fig. 19. Process flow diagram of naphtha hydrotreating section.

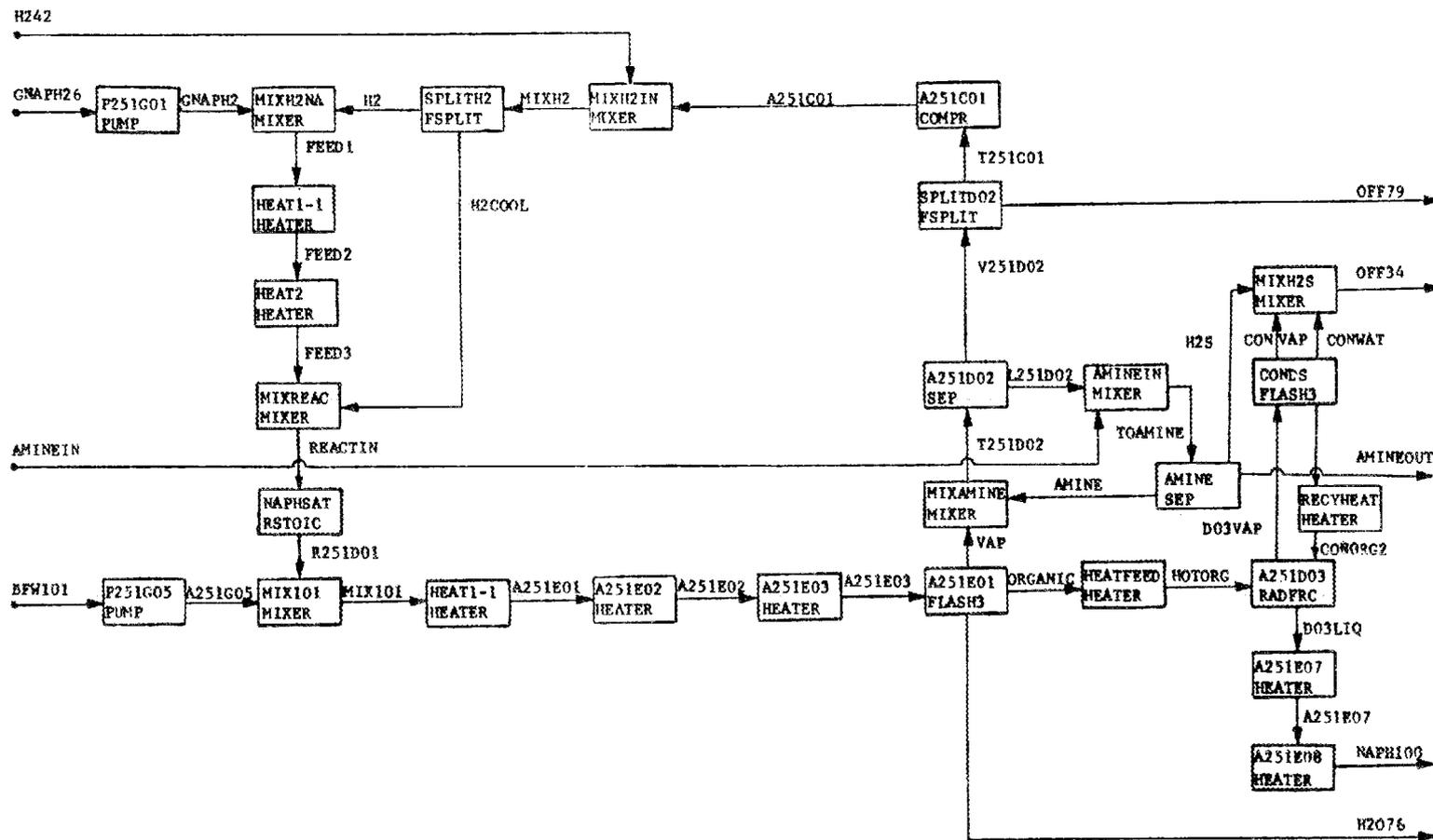
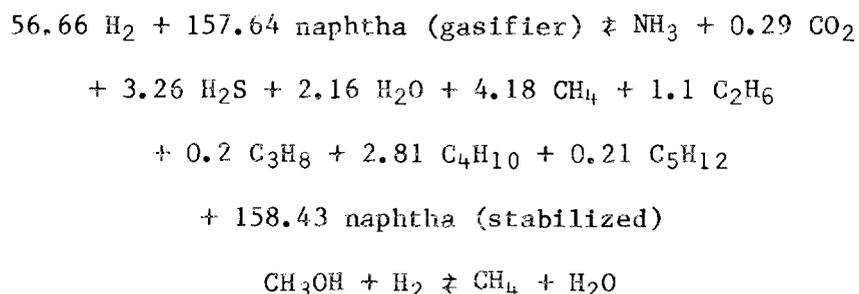


Fig. 20. ASPEN block diagram of naphtha hydrotreating section.

gasifier naphtha feed and the water feed pumps. An ASPEN compressor (COMPR) is used to compress the recycle hydrogen stream to reaction pressure. Three-phase flash options are used for the streams after the injection of water into the reactor effluent and are used until the three-phase flash separator is reached in the stream. Since no specific details are known about the reactor, an equilibrium model cannot be utilized; hence, the ASPEN RSTOIC reactor is used. The reaction stoichiometry is deduced from the inputs and products of the gasifier hydrotreating section in Schreiner. The two reactions used in RSTOIC are given as follows:



The separation of the three-phase mixture containing the reactor product and the cooling water is simulated with ASPEN's FLASH3 block. The split of the hydrogen-containing gas stream to recycle or to purge gas is arbitrary and may be changed if further information becomes available on the recycle stream or on the dependency of the hydrogenation reaction(s) in the reactor on the concentration of hydrogen. The split is presently set to recycle 70% of the gas stream.

The naphtha stabilizer that treats the organic phase from the FLASH3 block is modeled as a 30-tray distillation routine using the RADFRAC block of ASPEN. The column is kept hot enough so that there is only one liquid phase (organic). No condenser is used in the RADFRAC

block; a FLASH3 ASPEN block is used as a condenser, and only the organic phase is refluxed after being heated by a HEATER block.

The hydrotreated naphtha was given a molecular weight of 97.3 by Schreiner, but no molecular weight was assigned to the gasifier naphtha. In this study, a molecular weight of 100 was assigned to the gasifier naphtha and may be adjusted if more information is obtained. The gasifier naphtha and hydrotreated naphtha are entered as user-defined components. Except for the molecular weight, the physical properties are those of toluene but may be adjusted as further information dictates. The Redlich-Kwong-Soave equation of state was used for vapor liquid equilibrium and enthalpy calculations.

## 2.9 FORTRAN SUBROUTINES

In the course of developing the ASPEN simulations, it was found necessary (or convenient) to write some FORTRAN subroutines to perform some simple, repetitive tasks and to enhance the flexibility and utility of the models. Two of these subroutines, user-~~yield~~ routines DEVOL and DECOMP, were described in the Lurgi gasifier section. The gasifiers also call three other user subroutines (developed by a previous study<sup>4</sup>): (1) ENYHLU, which calculates the enthalpy of ash at any temperature; (2) ASH11, which calculates the enthalpy of ash solids at a given temperature, and (3) SAVMWU, which calculates the average molecular weight of a stream. User unit operation subroutine BOILER and the enhancements to the coal enthalpy model HCOALGEN are discussed in this section.

Maintaining an accurate steam balance is very important if useful simulations are to be produced. User unit operation model BOILER was

written for this purpose. In many places in the Tri-State process, waste heat is used to make steam. The mechanism for this in ASPEN is for the HEATER or FLASH2 block that is simulating the cooling of the process stream to calculate the heat duty and store the result in a heat information stream. In order to model the waste heat boiler, it is necessary to adjust the flow of feed water to the boiler so that saturated steam is produced with no heat or water "left over." This function can be accomplished with an ASPEN DESIGN-SPEC; however, the input language is clumsy, and its use requires iterative calculations. User unit operation model BOILER performs this function rapidly.

Simply put, BOILER accepts an input heat stream and calculates the water flow rate necessary to obtain the desired steam conditions. The desired steam pressure and degrees superheat (default = 0.0) are passed via the REAL vector in the ASPEN input language. BOILER performs the necessary units conversion.

The ASPEN physical property system provides several methods for estimating the heat of combustion of a coal. Provision was not made, however, for the direct input of a known value of a coal's heat of combustion. The model HCOALGEN has been modified to allow this option. To use the direct input option, two steps are necessary: (1) to specify option six for the heat of combustion (first option code) in HCOALGEN, and (2) to put the desired heat of combustion (Btu/lb, dry) in the first location of the component attribute COALMISC.

The modifications to HCOALGEN are quite simple. The heat-of-combustion monitor subroutine ENTHCC was modified to accept an option code of 6. When an option code of 6 is encountered, ENTHCC will call

the new subroutine ENT445. Subroutine ENT445 merely obtains the heat of combustion from the component attribute vector, converts the units to SI, and returns the value to ENTHCC.

### 3. INTEGRATION OF MODELS

As can be seen in Fig. 1, most of the unit operations present in the Tri-State project flowsheet have been modeled using ASPEN. [Unit operations not modeled include head-end processing steps (such as coal preparation and the oxygen and steam plants) and cleanup processes (such as ammonia and sulfur recovery.)] In order to perform overall plant material and energy balances, it would now be desirable to couple appropriately all of the developed models into a single simulation. Plant output streams could then be checked for various input feed and internal process conditions. In this way, the process efficiency and/or product slate desired could be optimized for a particular coal and overall flowsheet.

The coupling of all of these ASPEN models into a single simulation program yields, however, a computer program that is quite complex and one that requires a considerable amount of core. This problem has been circumvented by dividing the overall flowsheet into subsets. As shown in Fig. 21, the various ASPEN models have been combined into five major groups: (1) Lurgi gasifier, gas cooling, gas-liquor separation, and Texaco gasifier; (2) Rectisol; (3) methanol synthesis, CO-shift, methanation, and SNG purification; (4) naphtha hydrotreater; and (5) Mobil MTG, fractionation, alkylation, and gasoline blending. Sequential execution of these major groups should allow overall plant balances to be achieved in essentially a single pass.

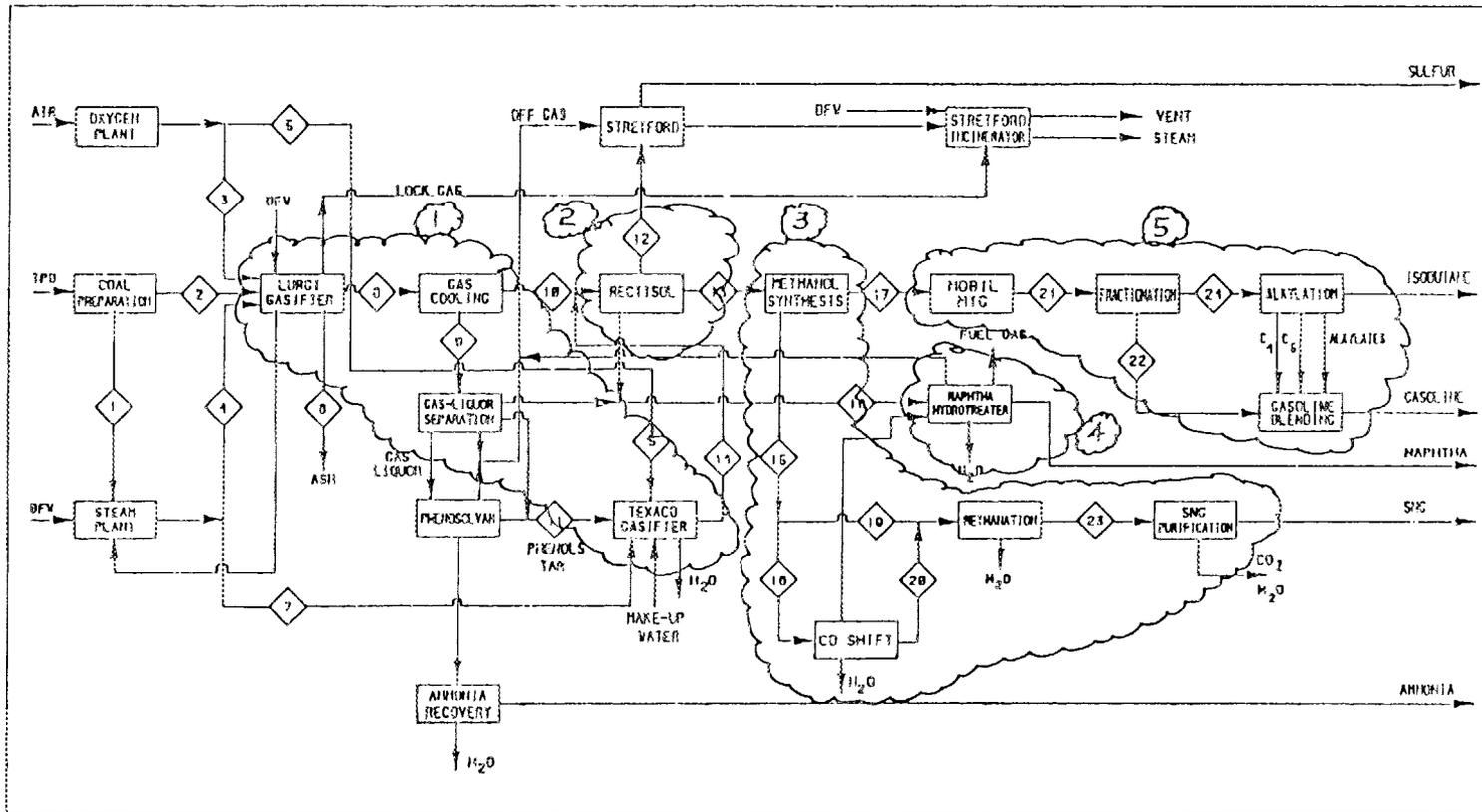


Fig. 21. Major groupings of the Tri-State process ASPEN models.

#### 4. RESULTS

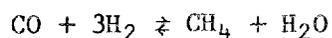
The final Tri-State Synfuels Project block flow diagram, entitled "Case 13 - Coal to Gasoline - Quarter Size Plant,"<sup>12</sup> was used as the baseline Tri-State case for checking the developed ASPEN models in an overall simulation performed by sequential execution of the major groups. To demonstrate the range of operability of these models, overall simulations were also performed using feed of Illinois No. 6 coal and the original full-scale feed rate of Kentucky No. 9 coal to the plant.

##### 4.1 BASELINE TRI-STATE CASE

In the baseline Tri-State case, 240 tons/h of Kentucky No. 9 coal would be converted to transportation fuels and chemicals. The chemical and physical characteristics of this coal are given in Table 4. It should be noted that the hydrogen and oxygen values listed in Table 4 include contributions from the moisture in the coal, so that the ultimate analysis is on an "as-received" basis. This form of the ultimate analysis is required by the ASPEN model. Before a simulation could be performed, it was necessary to match the ASPEN predicted Lurgi gasifier output results with the experimentally determined output of the Lurgi gasifier used in the SASOL test of Kentucky No. 9 coal<sup>1</sup> (see Appendix). This was accomplished in two steps: (1) by varying the REAL vector specified in the ASPEN input file and used by the subroutine DEVOL to form the volatile products, and (2) by varying the temperature at which the following first two reactions of the REQUIL block took place:

Table 4. Chemical and physical characteristics of Kentucky No. 9 coal.

Ultimate analysis (as received coal)	%
Ash	15.4
Carbon	59.6
Hydrogen	5.3
Nitrogen	1.2
Sulfur	3.5
Oxygen	15.0
	100.0
Proximate analysis	%
Moisture	8.2
Fixed carbon	43.4
Volatile matter	33.0
Ash	15.4
	100.0
Heat of combustion = 12,475 Btu/lb (dry coal)	



A comparison of the experimental and predicted gasifier results (using 1620 and 1410°F, respectively, for the two reactions above) is shown in Table 5. The agreement is quite good; further refinement of the REAL vector and/or the reaction temperatures could make it even better. From the SASOL coal test, the amount of tar, C<sub>2</sub><sup>+</sup>, and phenol formed were known. Since these components are only formed in the subroutine DEVOL, their vector values were easily determined. In addition, the water vector value was set to account for the amount of water indicated by the coal proximate analysis. The remaining vector values (for H<sub>2</sub>, CH<sub>4</sub>, CO,

Table 5. Lurgi gasifier output using Kentucky No. 9 coal

	Model	SASOL coal test
Clean tar produced, as % MAF coal fed:	5.6	5.6
Dry gas composition, %		
Hydrogen	41.4	40.8
Carbon monoxide	15.4	15.9
Carbon dioxide	30.8	30.6
Methane	9.1	9.4
C <sub>2</sub> +	0.9	0.9
Nitrogen	1.0	0.9
Hydrogen sulfide	1.4	1.5
	100.0	100.0

and CO<sub>2</sub>) were set to make the total vector sum to unity while simultaneously they were manipulated, along with the reaction temperatures, to match the coal test data. The final vectors obtained were 0.0072, 0.2863, 0.3400, 0.0131, 0.0849, 0.0915, 0.0036, and 0.1734 for the formation of H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CO, C<sub>2</sub>+, CO<sub>2</sub>, phenol, and tar, respectively.

Intermediate results of sequential execution of the major groups shown in Fig. 21 are given in Table 6. The output of the first major group consists of the cooled gases from the Lurgi and Texaco gasifiers and is the input to the Rectisol model. The COS, NH<sub>3</sub>, and C<sub>2</sub>-C<sub>4</sub> output streams were not inputted to the Rectisol model because they have not yet been incorporated into that model (i.e., binary interaction parameters for these species were not available). The C<sub>6</sub>H<sub>6</sub> entry represents the amount of naphtha entering the second major group. Since (1) the SASOL coal tests did not indicate the formation of any naphtha, and (2) the

Table 6. Intermediate simulation results for baseline Tri-State case

Component	Gasifier and cooling output, Rectisol input (lb-mol/h)	Rectisol output, MeOH synthesis input (lb-mol/h)	MeOH synthesis output, MTG input (lb-mol/h)
H <sub>2</sub>	16,583	16,532	0.4
CO	7,660	7,551	0.7
CO <sub>2</sub>	11,823	1,441	120
CH <sub>4</sub>	3,460 <sup>a</sup>	3,306	13
C <sub>2</sub> -C <sub>4</sub>	333 <sup>b</sup>	-	-
C <sub>6</sub> H <sub>6</sub>	100	-	-
N <sub>2</sub>	418	412	0.2
H <sub>2</sub> S	511	0.7 <sup>a</sup>	-
COS	6 <sup>a</sup>	-	-
H <sub>2</sub> O	173	-	284
NH <sub>3</sub>	61 <sup>a</sup>	-	-
CH <sub>3</sub> OH	-	-	6,944 <sup>c</sup>

<sup>a</sup>Output stream component, but not used in input stream.

<sup>b</sup>Used as an input stream only.

<sup>c</sup>MeOH synthesis = (6944 lb-mol/h)(32.042 lb/lb-mol) (24 h/d)/(2000 lb/ton) = 2670 tons/d; MeOH synthesis from Case 13 Flowsheet = 2670 tons/d.

Case 13 flowsheet shows naphtha from the Rectisol unit being fed to the Texaco gasifier, the fourth major group, naphtha hydrotreating, has been omitted in this overall simulation.

The six RADFRAC blocks in the ASPEN Rectisol model are shown in Fig. 8. The first two of these distillation units are used to remove the H<sub>2</sub>S impurity, while the remaining units are used primarily to recover naphtha from the synthesis gas stream. In actual ASPEN simulations, all of these RADFRAC blocks converged individually, but overall convergence of the entire flowsheet was very difficult to obtain. Numerous attempts were made to achieve convergence of the right half of the flowsheet (Fig. 8) by (1) breaking the ties between the two halves

of the flowsheet (e.g., streams RECLAB1, RECLIQ2, and RECMOHR3), and (2) replacing the RADFRC blocks by simple SEP blocks, individually and in varying combinations. Unfortunately, neither of these approaches aided the convergence problems. There were some indications, however, that the convergence difficulties could be traced to two inner loops in the right half of the flowsheet. These inner loops are defined by the following: (1) streams RECACIDG, RECVAP16, RECVAP17, RECLIQ19, and RECVAP18; and (2) streams RECLIQ17, RECLIQ18, and RECVAP18. Tearing stream RECVAP18 might confirm if these loops are indeed the source of the convergence problems.

The number of iterations was not increased above the default values because the history file did not indicate that the maximum number of iterations was being approached. However, more iterations and/or the use of different convergence schemes could be tried to see if any improvement could be made. For this simulation, only the first two RADFRC blocks were used. This was reasonable since all of the H<sub>2</sub>S is removed from the gas stream by these first two blocks, while the remaining blocks are primarily used to recover naphtha. Since the SASOL coal test did not indicate the formation of any naphtha, the use of the remaining RADFRC blocks was not considered essential. The entire ASPEN language is included in the input file, but the right half of the flowsheet shown in Fig. 8 has been commented out. These could be used by anyone desiring to check the recovery of the naphtha in the synthesis gas stream.

The output from the Rectisol unit, with its much reduced content of H<sub>2</sub>S and CO<sub>2</sub>, is fed into the third major group: methanol synthesis, shift, and methanation. The predicted amount of methanol produced,

2670 tons/d, was forced to agree closely with the 2670 tons/d shown on the Case 13 flowsheet by varying the recycle ratio in the methanol synthesis model. To obtain agreement, a recycle ratio of 1.63 was used. The predicted composition and rate of SNG production are shown in Table 7, along with the outputs of the fifth major group (MTG, fractionation, and alkylation).

The ASPEN block diagrams shown in Figs. 13 and 14 for the fractionation and alkylation sections, respectively, use several RADFRC distillation blocks. As was the case for the Rectisol model, these RADFRC blocks can be made to converge individually, but are very difficult to converge when part of the overall flowsheet. Thus, in these

Table 7. Predicted outputs for baseline Tri-State case

Production	Model	Case 13 Flowsheet
SNG, MMSCFD	39.5	37.0
LPG, lb/h	4,300	4,300
Isobutane, lb/h	4,760	4,750
Gasoline, lb/h	85,400	85,600
<u>SNG</u>		
<u>Component</u>	<u>lb-mol/h</u>	<u>%</u>
H <sub>2</sub>	30.7	0.71
N <sub>2</sub>	205.7	4.73
CO	1.2	0.03
CH <sub>4</sub>	<u>4,104.2</u>	<u>94.53</u>
Total	4,341.8	100.00
Heat of combustion (HHV) = 956 Btu/SCF		

simulations the RADFRC blocks have been replaced by simple SEP blocks which require no iterative calculations. These blocks were calibrated using the results obtained when the appropriate individual RADFRC block was used. The ASPEN input file developed in this work, however, contains both the SEP blocks and the original RADFRC blocks, with the latter being commented out. If desired, a user could remove the comments and use all or part of the RADFRC blocks, along with two special FORTRAN blocks (ETSPEC and GSSPEC) useful for setting the product flowrates from blocks MDEETHAN and MGASSTAB (see Fig. 13).

The simulation predicts that 39.5 MM SCFD of SNG, containing 94.5% methane, will be produced. This value compares favorably with the 37 MM SCFD shown on the Case 13 flowsheet. The models predict that 4760 lb/h of isobutane is formed (stream XSIBUT on Fig. 14), which is 0.2% higher than the flowsheet value of 4750 lb/h. The predicted gasoline value (stream GAS on Fig. 14) of 85,400 lb/h is 0.2% less than the flowsheet value of 85,600 lb/h. The predicted LPG production is identical to the flowsheet value of 4300 lb/h. These predicted product rates were obtained by modifying the yield structure used for the MTG reactor so that the LPG, isobutane, and gasoline product rates would match the Tri-State flowsheet. This Tri-State yield structure is shown in Table 8. When the yield structure given by Schreiner<sup>9</sup> and shown in Table 9 was used, the production rates predicted by the models were changed considerably, as shown in Table 10. It should be noted that a slight error will occur in the atom balance around the reactor when either of these yield structures are used. This error is caused by lumping all of the products beyond C<sub>5</sub> into a single-term labeled gasoline and then

Table 8. Tri-State MTG reactor yield structure

Basis: 1 lb pure methanol in feed

Product	lb-mol
Hydrogen	0.00001240
Water	0.03141444
Carbon monoxide	0.00000536
Carbon dioxide	0.00001670
Methane	0.00023524
Ethene	0.00000567
Ethane	0.00006086
Propene	0.00002018
Propane	0.00028053
<i>1</i> -Butene	0.00001783
<i>n</i> -Butane	0.00012767
<i>i</i> -Butane	0.00042703
Cyclopentane	0.00001468
<i>1</i> -Pentene	0.00001426
<i>n</i> -Pentane	0.00008450
<i>i</i> -Pentane	0.00084042
Gasoline	0.00311861

Table 9. MTG reactor yield structure of Schreiner

Basis: 1 lb pure methanol in feed

Product	lb-mol
Hydrogen	0.00001260
Water	0.03135000
Carbon monoxide	0.00000536
Carbon dioxide	0.00001670
Methane	0.00023525
Ethene	0.00000568
Ethane	0.00006086
Propene	0.00002018
Propane	0.00046480
<i>1</i> -Butene	0.00008514
<i>n</i> -Butane	0.00020970
<i>i</i> -Butane	0.00067960
Cyclopentane	0.00001482
<i>1</i> -Pentene	0.00013720
<i>n</i> -Pentane	0.00008451
<i>i</i> -Pentane	0.00074200
Gasoline	0.00277500

Table 10. Predicted outputs for baseline Tri-State case using the MTG reactor yield structure of Schreiner

Production	Schreiner yield structure	Tri-State yield structure
SNG, MMSCFD	39.5	39.5
LPG, lb/h	7,120	4,300
Isobutane, lb/h	5,630	4,760
Gasoline, lb/h	81,500	85,400

assigning this pseudocomponent the properties of *n*-heptane. If these higher molecular weight products were not combined, however, an additional 31 components would have to be used in the remainder of the simulation. Using Schreiner's yield structure, the predicted amount of gasoline produced is considerably reduced, while the predicted amount of isobutane and LPG produced are larger. Thus the basic difference between the two yield structures has been to shift product formation toward the higher carbon (i.e., gasoline) end of the product slate.

#### 4.2 FULL-SIZE TRI-STATE CASE

In the full-size Tri-State case, 960 tons of coal per hour would be fed to the Lurgi gasifier. This case was simulated to ensure that the models developed could operate over a range of flow rates. The intermediate simulation results are shown in Table 11. Comparison with Table 6 shows that each component of the gasifier output streams have been increased by a factor of 4, the same factor that the coal feed rate has been increased. Similarly, the Rectisol output streams have been increased by a factor of 4 as compared to Table 6. The H<sub>2</sub>S content of

Table 11. Intermediate simulation results for full-size Tri-State case

Component	Gasifier and cooling output, Rectisol input (lb-mol/h)	Rectisol output, MeOH synthesis input (lb-mol/h)	MeOH synthesis output, MTG input (lb-mol/h)
H <sub>2</sub>	66,334	66,131	1.6
CO	30,641	30,204	2.8
CO <sub>2</sub>	47,292	5,764	481
CH <sub>4</sub>	13,840	13,222	54
C <sub>2</sub> -C <sub>4</sub>	1,333 <sup>a</sup>	-	-
C <sub>5</sub> H <sub>6</sub>	400 <sup>b</sup>	-	-
N <sub>2</sub>	1,671	1,647	0.9
H <sub>2</sub> S	2,044	2.8 <sup>a</sup>	-
COS	25 <sup>a</sup>	-	-
H <sub>2</sub> O	693 <sup>a</sup>	-	1,138
NH <sub>3</sub>	245	-	-
CH <sub>3</sub> OH	-	3 <sup>a</sup>	27,781 <sup>c</sup>

<sup>a</sup>Output stream component, but not used in input stream.

<sup>b</sup>Used as an input stream only.

<sup>c</sup>MeOH synthesis = (27,781 lb-mol/h)(32.042 lb/lb-mol)(24 h/d)/(2000 lb/ton) = 10,680 tons/d.

the gas stream has been reduced by 99.86% so that the total gas stream contains only 24 ppm H<sub>2</sub>S. The amount of methanol produced, 10,680 tons/d, is also a factor of 4 times the baseline case value of 2670 tons/d.

The predicted product rates for this case are shown in Table 12. As would be expected, since methanol is being converted to gasoline, the predicted gasoline production rate of 341,600 lb/h is 4 times the baseline value of 85,400 lb/h. The estimated isobutane, SNG, and LPG rates are also 4 times the baseline values. Thus the change in coal feed rate proportionally changed all the output product rates, showing the rangeability of the ASPEN models developed in this study.

Demonstrating such versatility and range of operability is very important for any process simulation since it shows if the models

Table 12. Predicted outputs for full-size Tri-State case

Production	Model	
SNG, MMSCFD	158	
LPG, lb/h	17,200	
Isobutane, lb/h	19,040	
Gasoline, lb/h	341,600	

Component	SNG	
	lb-mol/h	%
H <sub>2</sub>	118	0.68
N <sub>2</sub>	822	4.74
CO	5	0.03
CH <sub>4</sub>	16,376	94.55
Total	17,321	100.00

Heat of combustion (HHV) = 956 Btu/SCF

developed have been sufficiently generalized. In this case, specific values for certain feeds, splits, and outputs were replaced with ratios, often using FORTRAN blocks to set initial estimates. Similar tests of any new models that are developed should be made to assure generality.

#### 4.3 ILLINOIS No. 6 FEED

In order to demonstrate the versatility of the ASPEN models developed in this study, the baseline Tri-State case (i.e., 240 tons of coal fed per hour) was simulated using Illinois No. 6 coal as feed to the Lurgi gasifier. The chemical and physical characteristics of this coal, shown in Table 13, were taken from test data.<sup>16</sup>

Table 14 shows that the composition of the dry gas produced using the Illinois No. 6 coal, using the same REAL vector and reaction temperatures

Table 13. Chemical and physical characteristics of Illinois No. 6 coal

Ultimate analysis (as received coal)	%
Ash	9.0
Carbon	64.3
Hydrogen	5.5
Nitrogen	1.2
Sulfur	2.8
Oxygen	17.2
	100.0
Proximate analysis	%
Moisture	10.3
Fixed carbon	46.0
Volatile matter	34.7
Ash	9.0
	100.0
Heat of combustion = 12,770 Btu/lb (dry coal)	

Table 14. Lurgi gasifier output using Illinois No. 6 coal as compared to Kentucky No. 9 coal

	Ill. No. 6 coal	Ky. No. 9 coal
Clean tar produced, as % MAF coal fed:	5.9	5.6
Dry gas composition, %		
Hydrogen	40.3	41.4
Carbon monoxide	16.0	15.4
Carbon dioxide	30.7	30.8
Methane	10.0	9.1
C <sub>2</sub> +	1.0	0.9
Nitrogen	1.0	1.0
Hydrogen sulfide	1.0	1.4
	100.0	100.0

as previously, is very similar to that predicted for the Kentucky No. 9 coal. Higher percentages of carbon monoxide and methane are predicted for the Illinois coal, while a slightly lower percentage of hydrogen is expected. Because of its lower sulfur content, the amount of H<sub>2</sub>S predicted is considerably less than that predicted using the Kentucky No. 9 coal.

The intermediate simulation results are shown in Table 15. A comparison with Table 6 shows that the gasifier outputs are very similar and that the Rectisol unit again removes over 99% of the H<sub>2</sub>S from the gas stream. The fact that some H<sub>2</sub>S is predicted to remain in the synthesis gas stream for each of these simulations indicates that zinc oxide guard beds should probably be used prior to methanol synthesis to avoid poisoning of its catalyst. The predicted amount of methanol produced, 2772 tons/d is 3.8% greater than the baseline case value.

The estimated outputs are given in Table 16. Comparison with Table 7 shows that more SNG, LPG, isobutane, and gasoline would be produced using Illinois No. 6 coal, as compared to the use of Kentucky No. 9 coal. The SNG produced is again composed of 95% methane, with the major impurity being nitrogen. The major reason for the increased product rates using the Illinois coal is its lower ash content (9.0% as opposed to 15.4% for the Kentucky coal).

## 5. CONCLUSIONS

The ASPEN process simulator has been used to model the Tri-State indirect coal liquefaction process. Individual components of the Tri-State flowsheet were developed in modular form so that they will have application to a number of different process alternatives. Models developed in this study include the following: Lurgi gasifier, Texaco

Table 15. Intermediate simulation results using Illinois No.6 coal

Component	Gasifier and cooling output, Rectisol input (lb-mol/h)	Rectisol output, MeOH synthesis input (lb-mol/h)	MeOH synthesis output, MTG input (lb-mol/h)
H <sub>2</sub>	16,949	16,897	0.4
CO	8,399	8,279	1
CO <sub>2</sub>	12,379	1,448	124
CH <sub>4</sub>	3,940	3,764	15
C <sub>2</sub> -C <sub>4</sub>	374 <sup>a</sup>	-	-
C <sub>6</sub> H <sub>6</sub>	100 <sup>b</sup>	-	-
N <sub>2</sub>	427	421	0.2
H <sub>2</sub> S	407	0.5 <sup>a</sup>	-
COS	6 <sup>a</sup>	-	-
H <sub>2</sub> O	189	-	196
NH <sub>3</sub>	63	-	-
CH <sub>3</sub> OH	-	-	7,211 <sup>c</sup>

<sup>a</sup>Output stream component, but not used in input stream.

<sup>b</sup>Used as an input stream only.

<sup>c</sup>MeOH synthesis = (7211 lb-mol/h)(32.042 lb/lb-mol)(24 h/d)/(2000 lb/ton) = 2772 tons/d

Table 16. Predicted outputs using Illinois No.6 coal

Production	Model
SNG, MMSCFD	44.3
LPG, lb/h	4,460
Isobutane, lb/h	4,940
Gasoline, lb/h	88,600

Component	SNG	
	lb-mol/h	%
H <sub>2</sub>	13.0	0.27
N <sub>2</sub>	210.2	4.32
CO	0.4	0.01
CH <sub>4</sub>	4,640.4	95.40
Total	4,864.0	100.00

Heat of combustion (HHV) = 964 Btu/SCF

gasifier, synthesis gas cooling, Rectisol, methanol synthesis, methanol-to-gasoline, CO-shift, methanation, and naphtha hydrotreating. In addition, an enhancement has been made to ASPEN to allow for the direct input of coal heat of combustion values, and three FORTRAN programs were developed to handle the devolatilization and decomposition of coal in a gasifier and the handling of boiler feed water.

Simulations were made of three cases: (1) the baseline Tri-State flowsheet with Kentucky No. 9 coal fed in at 240 tons/h; (2) a full-size Tri-State case with Kentucky No. 9 coal fed in at 960 tons/h; and (3) the baseline Tri-State case with Illinois No. 6 coal fed at 240 tons/h. Prediction of the synthesis gas composition produced by the Lurgi gasifier was calibrated using the SASOL coal test data. For the first case, the simulation was forced to match the production rates of methanol, LPG, isobutane, and gasoline as indicated by the Tri-State Case 13 flowsheet. This was accomplished by (1) using a recycle ratio of 1.63 in the methanol synthesis model, and (2) modifying the MTG reactor yield structure. Quadrupling the coal feed rate of the first case, the second case indicated that exactly four times as much SNG, LPG, isobutane, and gasoline would be produced. The use of Illinois No. 6 coal in the third case resulted in outputs slightly higher than those predicted by Kentucky No. 9 coal. The anticipated isobutane, LPG, and gasoline production rates are 3.8% higher for the Illinois coal, while the SNG production would be expected to be 12% higher.

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## 7. APPENDIX: SASOL COAL TEST DATA

A brief summary of the SASOL coal test data<sup>1</sup> is shown in Table 17. These data represent a very small part of the overall report and should not be interpreted as representing the design conditions of the Tri-State project. Extensive data and discussion of the coal test are included in the DOE report,<sup>1</sup> and interested readers are referred to it.

The data presented in Table 17 were used to determine the flow rates of oxygen, steam, and water to the Lurgi gasifier in this simulation. In addition, the average gasifier outlet temperature of 1030°F was used in the simulation. Further coal test results (i.e., product gas composition and amount of clean tar produced) were presented earlier in Table 5.

Table 17. Feed rates used in SASOL coal test and Lurgi gasifier simulation of baseline Tri-State case

	SASOL Coal Test		Simulation	
	Flowrate ton/h	Ratio to AR coal	Flowrate lb/hr	Ratio to AR coal
Coal (MAF)	15.9	0.764	366,226	0.764
Ash	3.2	0.154	73,676	0.154
Moisture	1.7	0.082	39,137	0.082
Total as received coal	20.8		479,039	
Oxygen	8.6	0.413	197,741	0.413
Steam	34.6	1.663	796,864	1.663
Water	7.7	0.370	177,337	0.370
Gasifier outlet temperature, °F	1000~1060		1030	



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