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Evaluation of the SYNTHOIL PROCESS

VOLUME II
STATUS OF DEVELOPMENT

MASTER

OAK RIDGE NATIONAL LABORATORY

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VOLUME II
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EVALUATION OF THE SYNTHOIL PROCESSVOLUME IISTATUS OF DEVELOPMENT

ABSTRACT

The Synthoil process for producing heavy desulfurized fuel oil from coal has been under development at Pittsburgh Energy Research Center since 1969. The status of development and technical feasibility of the process are reviewed. This is part of an engineering and economic evaluation based on the conceptual design of a 100,000-bbl/day commercial Synthoil facility. Experimental data are discussed with regard to their adequacy for the formulation of a basis for the process design of such a facility. Potential engineering and equipment problems are analyzed.

1. INTRODUCTION

This is the second of three volumes reporting the results of an economic and technical evaluation of the Synthoil process. The work was done for the Energy Research and Development Administration/Fossil Energy (ERDA/FE), Division of Major Facility Project Management. Under the terms of the agreement between ERDA/FE and Oak Ridge National Laboratory, the objectives of the evaluation were as follows:

1. to provide estimates of the costs of producing synthetic fuels from coal by the Synthoil process on a commercial scale, for comparison with the costs of other processes or of other sources of energy;
2. to assess the state of development of the Synthoil process in terms of the experimental data available, the adequacy of the data for design purposes, the possible areas of difficulty in process or equipment scale-up, and the status of the process as a candidate for commercial demonstration;
3. to provide recommendations for additional process or equipment research and development where needed.

The first objective was fulfilled by preparing a process design and economic evaluation of a complete 100,000-barrel per stream day (B/SD) "grass roots" facility charging 50,133 tons of Western Kentucky coal per day. This phase of the evaluation is reported in Volume I of this series of reports.

The second and third objectives are addressed in this volume. It includes an assessment of the status of development of the Synthoil process and of its technical feasibility. Also discussed are process design and scale-up, engineering and equipment design, adequacy of experimental data for design purposes, and additional process development needs.

Sources of process data and other information used in this study include Pittsburgh Energy Research Center, other process developers, and equipment vendors and manufacturers. Contacts in the petroleum refining industry provided much useful information regarding the design and operation of catalytic hydrocracking and hydrotreating units.

2. SUMMARY

Our main conclusions are briefly summarized below. A more complete discussion of each point is given in subsequent sections of the report. It should be emphasized that this study is based on process development information available as of July, 1976, and that process development studies are continuing. It is possible that further development may result in successful resolution of questions raised in this report.

1. The Synthoil process is at the experimental level of development. Data obtained from operation of the 1/2 ton per day (TPD) process development unit (PDU) at Pittsburgh Energy Research Center (PERC) at the time of this study were not adequate to form a firm basis for design of a large pilot or demonstration plant.

2. Catalyst life has not been adequately demonstrated. Some of the data indicate that the cobalt molybdate catalyst undergoes essentially complete deactivation in the first few weeks after startup. It is generally accepted that a catalyst life of at least four to six months is necessary for commercial feasibility. Efforts are being made to develop a more resistant catalyst.

3. Because development of a satisfactory catalyst may require considerable time, it may be desirable to conduct further investigation of the operation of the process in a noncatalytic (actually autocatalytic) mode. The optimal process configuration for the noncatalytic mode remains to be determined.

4. More experimental data are needed to provide a basis for selecting optimal process conditions. Among the process variables requiring further investigation are reactor pressure, hydrogen partial pressure, slurry space velocity, and slurry and gas mass velocities. Longer runs are needed to demonstrate process operability, product quality, and catalyst life. Short runs that are terminated with the product viscosity and sulfur content still changing do not form an adequate basis for projecting product quality over a six-month run.

5. The catalytic mode of development faces significant problems in reactor scale-up. If a deactivation-resistant catalyst can be developed, it still remains to be demonstrated that a fixed-bed catalytic reactor of large diameter can operate for long periods without plugging, excessive coke laydown, or flow maldistribution. Heat removal probably will not be a major problem if adequate flow distribution can be maintained.

6. Efficient recovery of heat from the reactor effluent is a difficult engineering problem. The inability to recover this heat economically would cause an appreciable reduction in overall thermal efficiency. The design in Volume I of this study was based on the use of effluent-feed heat exchangers, but the practicability of this operation remains to be proved.

7. Residue carbonization requires further development. Fluidized-bed carbonization work should be continued to demonstrate satisfactory feed-introduction techniques and operability of the fluidized bed without agglomeration and collapse.

8. Other engineering and equipment problems do not appear to be insurmountable. Feed slurry pumping, coking of the feed heater, and erosion-corrosion of piping, return bends, and letdown valves may present difficulties, but solutions to these problems are probably achievable with known engineering techniques.

9. Development work on solids-liquid separation should be continued. Separation of solid residue from the Synthoil reactor effluent by centrifugation or filtration appears to be feasible, but further development is needed to establish operating conditions and equipment sizes required and to reduce the cost of the operation. Investigation of antisolvents and agglomerating agents should be continued. Vacuum distillation also should be considered as a separation technique.

10. The gasification unit described in Volume I is based on operation of a large slagging entrained-bed gasifier at 245 psig. Further development of this system is required to demonstrate the capability for continuous operation at this pressure.

3. STATUS OF DEVELOPMENT

In this section, the experimental development of the Synthoil process is traced from 1969 to the present. The early work is only briefly summarized here, as it has been amply described elsewhere.¹⁻¹² Experimental work conducted in late 1975 and 1976 is covered here in relatively greater detail because of its importance in relation to the current status of the process. Referenced material is quoted directly in some cases.

3.1 Early Development

3.1.1 Initial studies in 5/16-in. reactor

Experimental work on the Synthoil process was started at Pittsburgh Energy Research Center (PERC) in 1969. The initial studies were conducted in a reactor made of 5/16-in.-ID stainless steel tubing with a total length of 68 ft. This was packed with 1/8- by 1/8-in. pellets of a commercially available catalyst consisting of cobalt molybdate on silica-promoted alumina. Coal, slurried with recycle oil, was passed through the reactor cocurrently with hydrogen. The capacity of this unit was 5 lb of slurry per hour. Five coals of various grades were processed successfully. Coals containing 3.0 to 4.6% sulfur were converted to oils containing 0.2 to 0.3% sulfur. No

sensible attrition of the catalyst or loss of its desulfurization activity was observed in continuous runs of up to 6 weeks duration (1000 hr).¹¹

3.1.2 One-half TPD process development unit

The 5/16-in. reactor was subsequently retired and replaced by a larger reactor consisting of two interconnected 14.5-ft sections of 1.1-in.-ID stainless steel pipe. The unit may be operated with one or both reactor sections packed with catalyst. Flow through each section is in the upward direction. This unit, which is customarily referred to as the 1/2-TPD PDU (process development unit), is still in operation and is the current source of experimental data on the process.

Before entering the reactor, the feed passes through an electrically heated preheater. This section originally consisted of a 3-in.-diam by 10-ft vessel packed with 3/4- by 3/4-in. ceramic pellets; the design has since been changed, as discussed in Sect. 3.4.1. The feed leaves the preheater at reaction temperature, which is generally about 450°C.

Table 3.1 summarizes the results of the most significant runs made on this unit through about July 1975. The successful run FB-39, made on western Kentucky 5.5% sulfur coal at 4000 psig, is discussed in detail in refs. 8 and 11. This run was the principal source of data for the process design basis of the 100,000-B/SD plant.

In considering the adequacy of FB-39 data for design purposes, however, it should be pointed out that in 200 hr of steady-state operation at 450°C, the viscosity of the product oil increased from 26 to 440 SSF at 77°F, and the specific gravity increased from 1.020 to 1.082. The increase in sulfur content was not stated.^{8,11} Because of the failure to reach stable product characteristics, the adequacy of these data for full-scale design is questionable.

3.2 Tabulation of More Recent Runs

Table 3.2 shows the feed and operating conditions for runs FB-48 through FB-56. As of August 1976, FB-56 was the latest run made on the 1.1-in. unit.

Runs FB-48, 49, and 51 are discussed briefly at this point, since they do not fall under the major classifications described later in this section.

Table 3 1 One-half-TPD Synthoil plant operations, runs FB-39 through FB-47

Common run conditions Reactor temp 450°C
 Preheater temp 450°C
 Paste concentration 35% coal + 65% recycle oil
 Gas recycle rate 1000 scfh
 Makeup H₂ rate 300 scfh

	Run No									
	FB-39	FB-40	FB-41	FB-42	FB-42-3	FB-43	FB-44	FB-45	FB-46	FB-47
Catalyst (Co/Mo)	5 5 lb	5 5 lb	5 5 lb	11 0 lb	11 0 lb	5 5 lb	5 5 lb	5 5 lb	4 5 lb Gulf 1/8 in extrud	4 5 lb Gulf 1/8 in extrud
Reactor dimension	1 in x 14 ft	1 in x 14 ft	1 in x 14 ft	1 in x 28 ft	1 in x 28 ft	1 in x 14 ft	1 in x 14 ft	1 in x 14 ft	1 in x 14 ft	1 in x 14 ft
Paste feed rate, lb/hr	25	25	25	30	50	25	25	25	25	25
Run pressure, psig	4000	2000	4000	4000	4000	4000	4000	2000	4000	2000
Feed coal	Homestead, Ky	Homestead, Ky	Clearfield Co, Pa	Illinois No 5 (Inland Steel)	Homestead, Ky	Indiana (Spencer Co)	W Va (Ireland Mine)	W Va (Ireland Mine)	W Va (Ireland Mine)	W Va (Ireland Mine)
Run duration, hr	500	500	36	30	300	20	500	300	500	250
Product oil assay	0 2% S 0 1% ash	0 55% S 1 75% ash			1 1% S 4 0% ash		0 5% S 1 0% ash	0 55% S 1 6% ash	0 7% S 1 6% ash	
Remarks	a	a	b	c	d	e	f	g	h	

^aVoluntary shutdown

^bRecycle oil too viscous to continue operations, shifted feed coal to Homestead, Kentucky, and continued run for oil production, operated an additional 400 hr

^cReactor plugged, had to be shut down, bad coal feed, assay showed 40% ash, drilled out catalyst and recharged for FB-42-3

^dVoluntary shutdown, ΔP on reactor at 300 psi and rising quickly Dropped paste feed rate to 30 lb/hr after losing preheater bottom heater, ran at 50 lb/hr for approximately 100 hr

^eReactor plugged, product oil very thin Shutdown, drilled out catalyst, recharged, started again, ran 8 hr and plugged again
 Recycle oil very thin, concluded that we had vapor phase in reactor depositing solids and plugging the reactor Coal had 10% ash, of which 40% was iron

^fVoluntary shutdown, ΔP on reactor averaged 35 psi for whole run, excellent operating conditions for this coal

^gVoluntary shutdown, ΔP on reactor 400 psi and rising, recycle oil very thick even though still operable, decided to terminate the run shutdown after batch No 59

^hVoluntary shutdown, average ΔP on reactor 50 psi, excellent operating conditions, shutdown after batch No 100, product oil was thicker than usual for 4000 psig

Table 3.2. One-half-TPD Synthoil plant operations, runs FB-48 through FB-56

	Run No.								
	FB-48	FB-49	FB-50	FB-51	FB-52	FB-53	FB-54	FB-55	FB-56
Feed coal ^a	WVI	b	WVI	c	WVI	HKY	HKY	HKY	HKY
Slurry rate, lb/hr	25	35	25	25	25	25	25	25	25
Pressure, psig	4000	4000	4000	4000	4000	4000	4000	4000	4000
Catalyst ^d	Akzo	H	glass	H	glass	H	H	H	H
Preheater type	3 in. x 10 ft	3 in. x 10 ft	3 in. x 10 ft	3 in. x 10 ft	3 in. x 10 ft	1.1 in. x 29 ft	1.1 in. x 29 ft	1.1 in. x 29 ft	1.1 in. x 43 ft
Reactor length, ft	14.5	14.5	14.5	29	14.5	14.5	29	29	29
Reactor temperature, °C	450	440-450	450	450	450	450	450	450-460	450
Total hours onstream	500		~200		700	279	169	425	367
Date completed						March 1976	April 1976	May 1976	July 1976

^aWVI = West Virginia, Ireland Mine, 3.8% sulfur, HKY = Homestead, Kentucky, 5% sulfur.

^bThere were three separate runs: feeds were SRC + solvent; solvent only; Synthoil.

^cSRC + solvent (50-50), followed by solvent only.

^dAkzo = Akzo Chemie 124-3P; H = 1/8- by 1/8-in. Harshaw 0402T, glass = 1/8- by 1/8-in. glass cylinders.

3.2.1 Test of Akzo Chemie catalyst

Run FB-48 was made to test the effectiveness of Akzo Chemie 124-3P cobalt molybdate catalyst. The results were slightly inferior to those obtained with Harshaw 0402T. It was decided to continue using the latter catalyst for subsequent work.¹³

3.2.2 Hydrotreating of coal-derived liquids

The efficacy of the Synthoil process for preparing petrochemicals by hydrotreating coal-derived liquids was tested in a short series of runs. Run FB-49 had three objectives:

1. to hydrotreat a solution of 60% SRC and 40% SRC solvent at 4000 psig and 440°C,
2. to hydrotreat SRC solvent alone at the same conditions, and
3. to hydrotreat the product Synthoil from run FB-48 at 4000 psig and 450°C.

Run FB-51 had two objectives:

1. to hydrotreat a solution of 50% SRC and 50% SRC solvent at 4000 psig and 450°C, and
2. to hydrotreat SRC solvent alone at the same conditions.

Analysis of the products from part 3 of run FB-49 showed that the feed had undergone only mild hydrogenation. The product contained no material distillable below 210°C. Results were not stated for parts 1 and 2 of either run. It was decided that the products of these runs would be evaluated by other ERDA contractors.¹⁴

3.3 Noncatalytic Operation

A discovery of major significance occurred with runs FB-50 and FB-52. In these runs, the cobalt molybdate catalyst was replaced by inert glass beads of the same size. Thus the only catalytic effect in the process was that due to the mineral constituents of the coal itself. For convenience, we will somewhat loosely refer to this as the noncatalytic mode of operation. West Virginia coal (Ireland mine) was run at 4000 psig and 450°C,

conditions identical to those used on the same coal in the successful catalytic run FB-44. By comparing the results of the "blank" runs FB-50 and -52 with those of FB-44, it was anticipated that quantitative conclusions could be drawn as to the efficacy of the cobalt molybdate catalyst and its rate of deactivation.

Run FB-50 was terminated prematurely at 200 hr; run FB-52, however, ran successfully for 700 hr. The product oil had an average sulfur content of 0.7 wt %.¹⁵ After the first 300 to 400 hr, the results of the non-catalytic and catalytic runs were almost identical, indicating that deactivation of the cobalt molybdate catalyst was essentially complete at that time. The results also indicated that catalyst deactivation was rapid during the initial period, and that a substantial amount of deactivation had occurred after the first 3 to 4 days of operation.¹⁶

Since the minimum feasible run length in a commercial plant is probably about 6 months, deactivation in the first 300 hr is obviously unacceptable. The conclusion that must be drawn is that either a better catalyst will have to be developed or a commercial plant, if built, must be designed for the noncatalytic mode of operation.

3.4 Effect of Preheater Residence Time

A series of runs aimed at investigating the effect of residence time in the preheater was started in March 1976. As a result of these runs, valuable new information was gained as to the role of the preheater in relation to the overall process.

3.4.1 Run FB-53 (March 1976)

The main objective of run FB-53 was to determine whether satisfactory conversion and operation could be obtained when using a short-residence-time preheater instead of the large 3-in.-diam by 10-ft preheater used previously in the 1/2-TPD unit. If the size of the preheater could be reduced substantially, this would result in a considerable cost reduction in the 10-TPD PDU and in future scaled-up plants. The possibility had been advanced that extended "soaking time" in the preheater might be necessary to liquefy most of the coal-oil slurry before it entered the

reactor; this was based on the premise that presolution is necessary because solid coal might be detrimental to the operation of the fixed-bed reactor. Run FB-53 was designed to test this hypothesis.¹⁷ The new preheaters consisted of two 14-ft sections of 1.1-in.-ID stainless steel pipe filled with 1/4-in. ceramic pellets to promote heat and mass transfer. Operating conditions and coal feed were the same as those used in the successful run FB-39. The catalyst used was Harshaw 0402T. Slurry residence time in the new preheaters was ~4 min as opposed to 20 min for the old 3-in. by 10-ft preheater.

The oil produced from this run showed much higher sulfur content and viscosity than the FB-39 product. Operation for at least 500 hr had been planned, but the run was terminated after 279 hr because the viscosity of the recycle oil was increasing so rapidly that it was becoming unmanageable. The sulfur content of the oil increased from 0.66 wt % at the start of the run to 1.10 wt % just before shutdown. The product oil viscosity increased from 25.1 SSF at 180°F at the beginning of the run to a viscosity too great to be measured on the Saybolt viscometer.¹⁸ The total pressure drop across the preheaters and reactor also increased with time, from ~70 psi at the start to 500 psi at the end.

This run marked a significant point in the development of the Synthoill process. By varying the preheater residence time, an indication was obtained as to the relative importance of the preheater and the reactor in the overall liquefaction-desulfurization process. The results strongly indicated that predissolution in the autocatalyzed preheater played an important part in the overall process.

3.4.2 Run FB-54 (April 1976)

Run FB-54 was made under the same conditions as FB-53 except that two reactor sections were used, which gave a total reactor length of 28 ft. The results again showed unsatisfactory desulfurization and excessive viscosity. The run was terminated after 169 hr because the recycle oil viscosity was increasing rapidly and becoming unmanageable, just as in run FB-53. Sulfur content of the centrifuged product increased from 0.3 wt % at the start to 1.0 wt % at shutdown. Viscosity increased from

a starting value of 19.3 SSF at 180°F to over 700 SSF at 180°F after 168 hr. Pressure drop across the reactor increased from 50 psi at the start to over 300 psi at the end of the run.¹⁹

The results of this run indicated that the increased reactor volume was not compensating adequately for the shorter preheat residence time.

3.4.3 Run FB-55 (May 1976)

Run FB-55 was a duplicate of run FB-54 except that only the slurry feed and the makeup hydrogen passed through the preheater. The recycle gas was preheated separately and was fed directly to the inlet of the reactor. The purpose of this arrangement was to permit a longer residence time for the slurry in the preheater, since the gas flow through the preheater was reduced by about 75%.

Shortly after startup, a plug was discovered in the 5/16-in.-ID tubing between the two reactor sections. This was remedied and the run was continued.

After 177 hr of coal feed, the viscosity of the recycle oil reached 436 SSF at 180°F, doubling every 24 hr. The sulfur content of the product oil had climbed to over 1.0%. Because of the continued rise in viscosity, sulfur content, and pressure drop, further operation at the specified conditions appeared to be impossible. However, it was decided to raise the preheater and reactor temperature from 450°C to 455°C to see what effect this would have on operability and product quality. It was found that this change caused a reduction in viscosity and pressure drop and permitted operation for an additional 172 hr, at which time the viscosity again began to rise rapidly. The temperature was then increased to 460°C, but this proved to be less effective than the first increase, and after another 72 hr the oil became too viscous for further operation. Sulfur content of the oil collected during operation above 450°C was too high to be acceptable.²⁰

3.4.4 Run FB-56 (July 1976)

In this run, preheater residence time was further increased by adding a third 1.1-in. diam by 14-ft-long preheat section. All other conditions

were the same as those of run FB-55 except that an initial preheater outlet temperature of 400°C was used. The recycle gas was heated separately to 470°C and was fed to the inlet of the reactor, which was operated at 450°C.

After 63 hr of operation, viscosity and sulfur content had become unacceptable, so the preheater temperature was raised to 450°C. This caused a marked improvement in the operation; viscosity decreased by a factor of 5 and sulfur content was reduced by one-half. The run was continued for a total of 367 hr and then was terminated voluntarily, although operating conditions were still satisfactory.

The following conclusions were drawn from this run:

1. Product quality is not acceptable with a preheater temperature of 400°C.
2. Preheater residence time at 450°C is a key factor in the process.
3. The 1.1-in. by 42-ft preheater, with the recycle gas bypassed, gives results equal to those of the old 3-in. by 10-ft preheater in which the recycle gas went through the preheater.
4. Three 8-in.-diam preheaters would be adequate for the 10-TPD PDU.²¹

3.5 Catalyst Development

A program of catalyst development is being carried out under ERDA sponsorship at PERC and other installations. It is a large program and no attempt will be made here to describe it completely.

At PERC, batch autoclave tests are being used as a preliminary screening operation to identify catalysts worthy of further testing in the 1/2-TPD PDU.¹³ Thus far, no catalyst has been found that is superior to Harshaw 0402T for use in the Synthoil process. At PERC and other locations, investigations are underway to identify the causes and mechanisms of catalyst deactivation, with the objective of developing catalysts of longer life for coal applications.

A small continuous catalyst life-test unit was constructed at PERC. Initially, the reactor consisted of 1/8-in.-ID tubing packed with 12 x 14-mesh catalyst particles. Subsequent modifications were made to increase

the diameter of the tubing and to improve operating reliability. As of June 1976, ten runs had been made. Reactor plugging continues to be a problem.²⁰

In coal processing operations, a small life-test unit such as that described here cannot precisely duplicate the process conditions and the flow regime of a large-scale reactor. Catalyst life for full-scale design purposes must, therefore, be proved in a reactor large enough to simulate the flow conditions encountered in the full-scale case.

3.6 Future Operations

3.6.1 10-TPD PDU

The 10-TPD PDU is under construction and is expected to be completed in late 1977. The present design calls for three 6-in.-diam by 15-ft reactors and two 8-in.-diam by 15-ft preheaters. Provision is made for bypassing any of these vessels as desired.

3.6.2 Synthoil II

Synthoil II is the name given to the second 1/2-TPD process development unit, which is to be built adjacent to the first 1/2-TPD unit at PERC. At present, the unit is in the design approval stage, and no firm schedule has been set for its construction.

3.6.3 Operation of Synthoil I

At the time of this writing (September 1976), no indications are available regarding plans for the next run on the 1/2-TPD Synthoil I unit. Since the two main points of current interest are the short-residence-time preheater and the noncatalytic mode of operation, there has been some discussion of further study of one or both of these in the next run.

3.7 Additional Data Requirements

In obtaining experimental bench-scale or PDU data for the preparation of a process design basis for a commercial-scale unit, it is important to focus attention on those process variables that have a substantial impact on the overall economics of the process; this will facilitate the selection of optimal conditions. The principal needs for additional data are as follows:

3.7.1 Reactor pressure

Runs on the design feedstock at several different pressures are needed to determine the optimal pressure for process design, and to determine the minimum pressure at which the process will give acceptable conversion and product characteristics.

3.7.2 Hydrogen partial pressure

The effect of hydrogen partial pressure on yields and run length at constant total pressure should be determined. For example, the minimum hydrogen purity that will give satisfactory operation at a given hydrogen recycle rate and at a pressure of 4000 psia needs to be established.

3.7.3 Slurry mass velocity

The maximum slurry mass velocity chosen for design purposes must be supported by the available experimental data. This variable has a considerable impact on the cost of the process. In establishing the process design basis for the 100,000-B/SD plant, it was decided that the mass velocity of the slurry should be the same as that used in the successful run FB-39 (i.e., 3785 lb/hr per square foot of reactor cross-sectional area). Based on this decision, the total reactor cross-sectional area required was 1950 ft². It was also decided to make the slurry space velocity the same as that used in run FB-39 (i.e., 261 lb of slurry per hour per cubic foot of reactor volume). This fixed the total reactor volume requirements. The effect of these two decisions was to make the total catalyst bed depth the same as that used in the bench-scale unit (i.e., 14.5 ft). The number of reactors required was then determined from structural considerations that limited the maximum internal diameter of the reactor to ~8.8 ft. This led to a requirement for 32 reactors.

From a cost point of view it would be highly desirable to reduce the number of reactors. One way of doing this would be to use a higher slurry mass velocity. Assuming that the slurry space velocity is unchanged, doubling the slurry mass velocity would permit the use of 16 reactors, each with the same diameter as before but twice as long. This would substantially reduce the capital investment in reactors and associated piping and equipment. Further, if the assumption is made that the recycle-gas mass velocity is the same as that used in the bench-scale run, the change described would permit a 50% reduction in the total recycle gas flow.

Clearly, process design decisions such as these must be based on strong experimental evidence. Run FB-39 was made at a slurry feed rate of 25 lb per hour and a catalyst bed depth of 14.5 ft. To support the change mentioned above, successful runs would be required at a slurry feed rate of 50 lb per hour, which would correspond to a mass velocity of $7570 \text{ lb hr}^{-1} \text{ ft}^{-2}$.

3.7.4 Hydrogen/slurry ratio

The effect of varying the ratio of hydrogen to coal slurry needs to be determined independently of the effect of varying the hydrogen mass velocity.

3.7.5 Reactor length/diameter ratio

The effect of the reactor L/D ratio on yields, product characteristics, and run length also needs to be investigated because of the possible effect of backmixing on conversion.

3.7.6 Run length

Bench-scale runs thus far have not been of sufficient duration to establish product yields and quality under commercial conditions. In our design we assumed a run length of 6 months. In a commercial plant, because of the time and expense involved in shutting down and replacing the catalyst, the run length is a major factor in determining the economic viability of the process. Bench-scale and PDU runs of at least 4 months duration are needed to confirm design conditions, yields, and catalyst behavior.

3.7.7 Reactor pressure drop

In view of the complex flow regime in the reactor and the coke-forming nature of coal-derived liquids, a large amount of PDU data will be needed before we can confidently predict the pressure drop through a large reactor. This variable is of major importance in determining the process design. It affects the paste pumps, the recycle and makeup compressors, and the reactor design itself. It is necessary to know the rate of increase of pressure drop at various points throughout the run, since this will be an indication of the rate of fouling and will help to establish the maximum run length that can be expected.

3.7.8 Design runs

In the preceding paragraphs, the process variables have been discussed separately. The process design basis must consider all of these variables simultaneously. Because of the complex interactions of major variables (e.g., pressure, temperature, space velocity, H_2 /oil ratio, reactor pressure drop, run length), it is almost impossible to assemble a credible process design basis without having a successful series of runs at the conditions contemplated in the design. In other words, the design runs should duplicate the conditions of the process design basis. The process yields during the design runs will be used to establish the design material balance. The reproducibility of such runs will determine the degree of confidence that the process will operate as expected.

Data taken throughout the design runs should be adequate to show the changes in yields, product quality, and operating conditions that take place as the run progresses. For design purposes, it is necessary to have the appropriate data at start of run, middle of run, and end of run conditions. Data should include yields of all products (including gases), hydrogen consumption, product characteristics (e.g., density, boiling range, sulfur content, viscosity), and pressure drops across the feed preheaters and reactors.

3.7.9 Demonstration of coke burn-off

Coke burn-off needs to be demonstrated in the 1/2-TPD or in the 10-TPD PDU so that the feasibility of using this technique as a means of aiding

catalyst removal can be evaluated. If it can be shown that burning off the coke permits the catalyst to flow freely out of the reactor, a major potential operating problem will have been solved. On the other hand, if the catalyst cannot be made to flow even after burning, the problem of catalyst removal becomes much more difficult.

3.8 Conclusions

Our conclusions as to the status of development of the Synthoil process are given below, along with some recommendations:

1. The process is at the experimental level of development. Recent exploratory work has uncovered important basic questions requiring further investigation. Construction of the 10-TPD unit can best be justified on the grounds that it will be a highly flexible and versatile experimental tool, capable of investigating several alternative process configurations.

2. With regard to the design of a large-scale plant, the experimental data available as of July 1976 were not adequate to permit optimization of major process variables such as pressure, slurry space velocity, and slurry and gas mass velocities. Also, run lengths with steady product characteristics were not sufficient for design purposes. Extrapolation of experimental runs of 10 to 20 days duration to the 180-day length required for commercial operation is not practicable because of the rapid changes in product quality occurring near the end of the experimental runs. Longer runs will be needed to prove the feasibility of the process for commercial application.

3. A major question still to be resolved is whether the process should be developed along catalytic or noncatalytic lines. At present, it appears desirable to pursue both lines of investigation. It should be clear, however, that these represent two different end processes. Resolution of this question is needed before the process can be scaled up further.

4. Further progress along the fixed-bed catalytic route must await the development of a catalyst that is much more resistant to deactivation than those presently available.

5. In both the catalytic and noncatalytic modes of operation, more complete data are needed regarding the amount of conversion and desulfurization taking place in each section of the preheater and reactor.

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4. ENGINEERING ASSESSMENT

Engineering problems associated with the Synthoil process are discussed in this section. The emphasis is on mechanical design problems, but there is some unavoidable overlap with process design considerations.

4.1 Feed Slurry Pumping and Heating

In the design of the 100,000-B/SD facility, the high-pressure slurry feed pumps were assumed to take suction on a nitrogen-blanketed slurry storage tank maintained at 300 to 350°F. The high-pressure pumps, discharging at 4300 psig, pump the slurry through reactor-effluent heat exchangers; the slurry exits at 600°F and subsequently goes through a gas-fired heater from which it exits at 810°F. Recycle and makeup hydrogen join the slurry at the inlet to the fired heater; provision was also made to have part of the hydrogen join the slurry upstream of the reactor effluent heat exchanger.

Major questions were raised during the design of the slurry pumping and heating system in regard to the formation of a highly viscous gel-like mixture as the coal-oil slurry is heated through a temperature zone of about 450 to 700°F. The increase in viscosity in this region has been noted by several investigators. The possibility of excessive pressure drop in the preheat exchangers or in the fired heater was considered to be a potential problem.

Another question was whether the hydrogen should be added upstream of the fired heater. If it could be added downstream, the discharge pressure of the hydrogen compressors could be reduced, thus saving a considerable amount of horsepower.

Conversation with SRC process development personnel convinced us that the hydrogen should be added upstream of the fired heater.^{1,2} Tests conducted at the SRC pilot plant located at Wilsonville, Alabama, showed that coking of the heater tubes will occur when the hydrogen partial pressure in the heater is too low, especially at temperatures approaching heater outlet conditions (about 775 to 825°F). Apparently, the tendency of the liquefaction products to polymerize and degenerate to coke is retarded by

the presence of a high partial pressure of hydrogen. Based on these considerations, both SRC plants add their hydrogen upstream of the fired heater, and coking is not a problem in either plant.

Another point brought out in these conversations was that the pressure drop through the fired heater was much less than had been anticipated on the basis of the viscosity exhibited in the gel region. The plant at Wilsonville, Alabama, experiences a pressure drop of only 30 to 40 psi, compared with a calculated (design) drop of 350 psi. The possibility was advanced that the gel may be thixotropic, in which case its viscosity could be markedly reduced under turbulent conditions.

In the design of the Synthoil unit reported here, the reactor outlet pressure was 4000 psia, and the maximum pressure drops through the reactor and the fired heater were 100 psi and 120 psi, respectively. The maximum pressure at the heater inlet was 4220 psia. The hydrogen recycle and makeup compressors were designed for a discharge pressure of 4265 psia, thus providing for a pressure drop of 45 psi in the heat exchangers of the preheat system. The slurry feed pumps were designed for a maximum discharge pressure of 4290 psia to provide an extra margin of safety.

Experience with coal slurry pipeline charge pumps indicates that high-pressure motor-driven reciprocating plunger or piston pumps can be obtained that will be adequate for this service. Replacement of rods, pistons, and valves will probably be more frequent than is customary in most oil refining applications. Black Mesa pipeline piston pumps have shown a rod life of about 1000 hr, a piston life of about 2000 hr, and a valve life of about 2500 to 3000 hr.

Operation of the Hygas pilot plant also provides data on high-pressure coal-slurry feed pumps.³ To obtain an adequate suction condition, the high-pressure reciprocating charge pump is fed by a low-speed centrifugal pump that takes suction from the slurry mix tank. The centrifugal pump has a Ni-Hard casing and flushed mechanical seals. The reciprocating pump has valves of Colmonoy-6 and valve seats of Stellite-coated alloy steel. The valves are replaced every 1000 hr.

The Synthoil-fired heater design is based on a fairly low heat absorption rate ($7000 \text{ Btu hr}^{-1}\text{ft}^{-2}$) and uses tubes of Incoloy 800. The low heat absorption rate is designed to reduce the tubewall temperature and to avoid any possibility of flame impingement on the tubes, in view of the coking tendency of the feed and the dangers of metal softening and rupture. Erosion of return bends is expected to be a problem; the suggested solution is to provide extra thickness to allow for wear and to plan on replacement every 3 to 5 years, or as necessary. For safety reasons, the arrangement of parallel passes in the fired heaters must be such that positive flow is absolutely assured in every tube pass. In the 100,000-B/SD design, this was done by providing a slurry feed pump for each heater pass.

Operation of the feed slurry tanks at 300 to 350°F does not appear to present any problems. Two factors that could cause difficulty at higher temperatures are (1) viscous gel formation, and (2) polymerization with sludge or coke formation. The tanks are kept agitated by pump-around loops and by side-mounted propeller-type mixers. These techniques are used in SRC operations with satisfactory results.

The avoidance of coke deposition and fouling in the reactor effluent-reactor feed heat exchangers is expected to be a major problem. This is discussed in another section.

With the above exception, the feed slurry pumping and heating system does not appear to offer any insurmountable problems, and it appears that design of an adequate system is within the grasp of currently available technology. If a decision had to be made today, the effluent-feed heat exchangers would probably be omitted, and the owners would accept the loss of thermal efficiency that this entails. This is discussed further in Sect. 4.3.

4.2 Synthoil Reactor Design

4.2.1 The reactor as a pressure vessel

As described in the section on the process design basis, the commercial plant design was based on the same gas and slurry mass flow rates and the same gas-slurry ratio as were used in the 1/2-TPD PDU runs. Also, the same slurry space velocity was used. As a result of these assumptions, the total reactor cross-sectional area for the 100,000-B/SD plant is about 1950 ft². The total catalyst bed depth of each reactor is 14.5 ft, which is the same as in the 1/2-TPD PDU.

Many factors are involved in determining the required number of reactors. It was assumed that the applicable code requirements would be ASME Boiler and Pressure Vessel Code Section VIII Division 2. Physical constraints of vessel fabrication limit the maximum wall thickness to about 13 in. This refers to monowall or monoblock construction; multiwall construction does not have such a constraint. Design temperature limits the allowable design stress of the metal; the design temperature is itself a function of the type of vessel design, that is, hot wall or cold wall. The combination of allowable design stress and maximum metal thickness puts an upper limit on the vessel diameter. Use of refractory linings (cold wall design) reduces the temperature experienced by the load-carrying steel wall and thus increases the allowable design stress. Hydrogen-induced cracking and embrittlement must be considered in the selection of materials; suitability of material is a function of the pressure and temperature of operation.

Both hot wall and cold wall designs were considered, and the required number of reactors was calculated in each case. Maximum operating and design conditions for the hot wall vessel are as follows:

Pressure, maximum operating, psig	4150
Pressure, design, psig	4400
Temperature, maximum operating, °F	860
Temperature, design, °F	885
Hydrogen partial pressure, psig	3520

At these conditions, according to the Nelson⁴ curves, 2.25 Cr - 1 Mo steel is not adequate; a higher alloy such as 3 Cr - 1 Mo (SA387 Grade 21, Class 1 or 2) is required. Division 2 of the ASME Code Section VIII gives an allowable stress intensity of 19,000 psi for this material at 850°F, but it does not specify allowable stress intensities at temperatures above 850°F. An approximate estimate of the allowable stress at 885°F was made by using the same percentage reduction from 850°F to 885°F as is shown for the SA387 Grade 22 Class 2 material, that is, 21,800 psi to about 18,500 psi, or about 15%. Applying this percentage reduction to 19,000 psi, an approximate allowable stress of 16,000 psi was obtained for SA387 Grade 21 Class 2 at 885°F. Using this as the assumed allowable stress, the wall thickness limit of 13 in. gives a maximum reactor inside diameter of ~6.75 ft. With this diameter, about 55 reactors would be needed to give the total required cross-sectional area of 1950 ft.

For monowall construction, the above considerations indicate that a cold wall design should be examined. The first step is to decide on the amount and type of refractory lining desired. The highly turbulent mixture of coal, ash, coal oil, and gases is expected to be quite abrasive; hence, at least the innermost layer of refractory lining (closest to the inside environment) should be abrasion resistant. A high-alumina content refractory similar to Harbison-Walker "Castolast G" would be desirable. Alternatively, a corrosion- and erosion-resistant stainless steel liner (type 347 or comparable) could be installed over a lower strength, higher insulating refractory. By reducing the temperature experienced by the load-carrying wall, the use of 2 1/4 Cr - 1 Mo is permitted by the Nelson curves.⁴ The lower price of 2 1/4 Cr - 1 Mo, as compared to that of 3 Cr - 1 Mo, will result in a lower vessel cost.

To find the design temperature of the metal wall, and hence the design stress, the overall heat transfer rate through the various films and materials into the ambient atmosphere must be calculated. Numerous assumptions as to heat transfer coefficients, film thicknesses, convective effects, thickness and conductivity of insulation (inside and outside the vessel), etc., are needed to solve for the heat transfer rate. The solution for the overall heat transfer rate simultaneously gives the temperature drops through the various layers.

Some simplifying assumptions must be made in order to provide a preliminary estimate of the heat transfer rate. It will be assumed that the wall will be covered first by 4 in. of an insulating refractory (Harbison-Walker Lightweight Castable Low Iron or comparable material) to provide a high degree of insulation. A 4-in.-thick abrasion-resistant refractory (Harbison-Walker Castolast G or comparable) is then applied to provide erosion protection. In the presence of high concentrations of hydrogen, the conductivity of such refractories will increase by as much as 2 1/2 times. The thermal conductivity of an abrasion-resistant refractory under design conditions is at most $32.5 \text{ Btu ft}^{-2} \text{ hr}^{-1} (\text{°F/in.})^{-1}$ while the insulating refractory has a conductivity of no more than $4 \text{ Btu ft}^{-2} \text{ hr}^{-1} (\text{°F/in.})^{-1}$. If the reactor is assumed to be uninsulated on the outside and exposed to air at 80°F, the total temperature drop across the refractory is sufficient to reduce the maximum metal temperature to below 300°F when the inside temperature is 885°F. Under these conditions, a heat loss of about $600 \text{ Btu ft}^{-2} \text{ hr}^{-1}$ is experienced through the reactor wall. At 300°F, with a maximum vessel wall thickness of 13 in. of low-alloy steel (SA387 Grade 22 Class 2), the maximum inside diameter is 9.3 ft, taking into account 8 in. of refractory. At this diameter, 29 reactors are required to handle the specified throughput. To provide for four identical trains, 32 reactors of slightly smaller diameter and wall thickness were used.

It was decided to protect the base metal of the vessel shell by a 3/8-in. weld overlay of type 347 stainless steel. This gives protection against corrosion from hydrogen sulfide and from any aqueous-phase condensation that might occur behind the refractory.

It is not advisable to attempt to reduce the heat loss by using external insulation. This adversely affects the temperature distribution, causing the metal wall of the vessel to operate at a higher temperature. For example, with 1.5 in. of external insulation, the metal wall temperature would increase from 280°F in the bare wall case to almost 700°F in the insulated case. Although the heat loss is reduced to one-fourth that of the bare wall case, the vessel is now much more vulnerable to any temperature excursions, since most of the temperature drop occurs outside the metal wall. In addition, the lower available design stress decreases

the maximum diameter attainable, thereby increasing the required number of vessels. Last, and most important, is the safety aspect. Outside insulation prevents the direct observation of hot spots on the vessel shell. By using a bare wall design, a heat-sensitive paint can be used which changes color above a certain temperature. This provides the additional safety factor required for the cold wall design where refractory failure with hot spot production is a constant hazard.

Once the preliminary design of the vessel shell has been determined, the structural design and attachment of internal parts must be considered. Distributor plates, catalyst support screens, and catalyst withdrawal pipes are needed. Because the pressure drop across an individual catalyst bed may reach 30 psi, the support structure for each bed must be capable of carrying a load of about 120 tons, and the cumulative load for all three beds is about 360 tons. Direct metal attachment to the vessel wall raises the problem of hot spots caused by heat conduction through the supports. The structural problems are therefore quite difficult. The final design may transmit additional loads to the heads of the vessel. A complete stress analysis will be required to take localized loads into account.

For corrosion resistance, the internals are of type 347 stainless steel.

If the number of reactors is to be reduced, some method must be found to either circumvent the wall-thickness limitation or to increase the available inside diameter. Multiwall design, which is more common abroad than in the United States, is one such possibility. Although the ASME Code Section VIII Division 2 covers the design considered for monowall construction, the code does not extend to multilayer design. For hot wall design of multilayer vessels in hydrogen service, the highest design temperature that has been considered is about 860°F, which is sufficient for petroleum hydrocracking but somewhat low for the Synthoil system. Again, the recommendation of refractory lining is valid. A calculation by McDowell, Milligan, and Korin⁵ in a similar situation (870°F hydrocracker) showed that for a given inside diameter, the weight of the cold wall design was about one-half of that of the hot wall design. In a multiwall design, metal directly exposed to the hydrogen environment can

be selected on the basis of the Nelson⁴ curves. Additional layers can be of less expensive, stronger steels. Problems resulting from exposure to hydrogen are avoided in the outer layers principally by venting those layers to the atmosphere. Further investigation of multiwall vessels should be considered, although many of the designs available are of proprietary materials, which makes it difficult to establish a common basis for evaluation.

An alternate way to increase the available inside diameter is to use internal water cooling. Much of the heat that would be lost through the walls in the refractory-lined design can be recovered in the water-jacketed design. Cooling water at reactor operating pressure would be circulated through an annulus formed by a stainless steel liner. It would then be sent to a flash drum at some lower pressure (e.g., 800 psig) to recover heat as high-pressure saturated steam. The water jacket acts to reduce the temperature rise across the reactor more efficiently than a refractory lining. The number of reactors required would be reduced because a water jacket requires less cross-sectional area than does a refractory lining. Assuming that water jacketing reduces the metal wall temperature to 300°F or less, 24 reactors would be required. However, the hazards associated with water jacketing, where a break in the inner lining could result in shutdown of the entire unit, would dictate very careful design and instrumentation. Also, the internals would have to be attached to the jacket.

After consideration of the possibilities mentioned, a refractory lined, cold wall, monowall design was selected for purposes of cost estimation. The potential cost savings offered by other alternatives are not large, and the designs of these alternatives are too tentative at this time to attempt to evaluate and take advantage of such savings.

4.2.2 Removal of heat from the reactor

The exothermic heat of reaction is estimated at about 6000 to 10,000 Btu/lb of hydrogen consumed, or about 600 to 1000 MM Btu/hr for the 100,000-B/SD plant.⁶

Two ways of handling the heat removal problem suggest themselves:

(1) use of an adiabatic reactor, which would have about a 50°F temperature rise from inlet to exit, and (2) an internal reactor cooling system with a circulating coolant.

In the adiabatic concept, all of the heat generated is carried out as sensible heat in the reactor effluent stream. Quench hydrogen may be added to control the overall temperature rise.

A reactor equipped with a circulating coolant system offers possible advantages, but the cooling system would be expensive and difficult to maintain. The danger of leaks would be a constant operating problem. If a leak occurred, the reactor could depressure into the coolant system, forcing an immediate shutdown of the plant. Also, such an incident would be hazardous because of the release of flammable material into the coolant system. Because of this, the coolant system would have to be protected by a closed blowdown system to carry flammable materials to a flare located at a safe distance from the plant. Finally, the internal coolant piping could interfere with flow paths, causing flow distribution problems and localized coking. Similar problems have been observed in connection with the design of internals for petroleum hydrocracking reactors.

After consideration of the advantages and disadvantages of these methods, it was decided to use the adiabatic reactor concept for this study. All of the heat of reaction is removed in the reactor effluent stream. Inlet and outlet design temperatures are 810°F and 860°F, respectively. To limit the exothermic temperature rise, the catalyst in the reactor is divided into three separate beds, each of which is ~4.8 ft deep. Provision is made for introducing quench hydrogen between successive beds. This can be used as a means of controlling temperature rise under upset conditions. It is expected that quench will not be needed under normal operating conditions. Provisions also are made for rapid depressurizing of the reactor system in the event of an uncontrollable temperature runaway. The reactors are depressurized into a blowdown header which leads to a liquid collection vessel and a flare for gaseous material. Strong support structures are provided to absorb the forces generated during blowdown.

This method of controlling reaction temperatures and of protecting against temperature runaways has been used in oil refinery hydrocracking units since the early 1960's. It might be argued that the Synthoil process will require a more elaborate in-reactor cooling system, because the hydrogen consumption (4 wt % of feed) is greater than that in typical hydrocrackers (2 wt % of feed). But the gas recirculation rate in the Synthoil process is correspondingly greater, and the overall temperature rise of about 50°F is less than that encountered in many hydrocracking units.

In the present state of knowledge of the Synthoil process, it seems reasonable to assume that the adiabatic multibed reactor with quench injection will be adequate. To require an internal coolant system would impose an additional financial penalty upon the process. This seems unwarranted without clear evidence that such a system is necessary.

Regarding the danger of upsets, plugging, and hot spot formation, it seems evident that this will be a greater problem for Synthoil than for petroleum hydrocracking, for two reasons: (1) the solid-slurry nature of the Synthoil feed would appear to aggravate plugging tendencies, and (2) the coke-forming tendency of the liquids formed from coal is much greater than those derived from petroleum. However, it seems unlikely that this situation can be ameliorated by using cooling coils within the reactor. If plugging starts, it will probably become progressively worse at a rapid rate, because the coked area tends to grow by hydrogen starvation. This will lead to accelerated maldistribution of flow and generally unsatisfactory reactor operation. Thus, if severe coking and plugging are encountered in the Synthoil process, it is difficult to believe that the use of a cooling system in the reactor would eliminate the problem. If plugging is not encountered, the heat-removal problem can probably be handled adequately by the adiabatic reactor design.

Operation of the 10-TPD pilot plant at PERC should help to demonstrate whether the adiabatic reactor concept is feasible, and whether coke laydown will be a severe problem.

The mathematical analysis of the temperature profile of an internally cooled exothermic reactor and its possible implications in regard to the maximum diameter of the Synthoil reactor are discussed further in Appendix B.

4.2.3 Flow distribution in the reactor

The problem of achieving and maintaining adequate flow distribution in the reactor is one of the major difficulties anticipated in the scale-up of the Synthoil process. The problem actually consists of several inter-related problems. First, the gas and slurry phases must be thoroughly mixed before they enter each catalyst bed. Second, they must be distributed uniformly across the cross section of the bed. Finally, the natural tendency of the gas and liquid phases to separate and form independent flow paths within the bed must be discouraged.

The problem of achieving adequate mixing and flow distribution at the inlet to each bed is difficult. It was assumed that two internal distributor plates, constructed of stainless steel, would be installed below each bed. Because of the presence of the coal slurry, however, it may be difficult to get proper flow distribution across the cross section of the reactor without getting into problems of plugging and excessive pressure drop.

The pressure drop across the catalyst bed introduces a mechanical load that adds to the difficulty of the problem. As mentioned earlier, the pressure drop across the beds imposes a load of about 120 tons on the support plates of each bed. Possibly the structural arrangement could be worked out so that this load is transmitted to the head of the reactor, in which case the head would receive the total force of 360 tons. To do this would require substantial support members between beds, and this could interfere with the flow redistribution arrangement. If the choice is made to support each bed individually, then the support beams of each bed would have to carry the full load of 120 tons. In this case, the size of the beams themselves could cause appreciable problems with respect to flow distribution.

Separation of the gas and liquid phases within the bed with formation of independent flow paths has been experienced in petroleum hydrocracking. When this occurs, there is a tendency for the liquid phase to hydrocrack more rapidly, resulting in an excessive temperature rise in the portion of the reactor occupied by the liquid flow channel. This causes accelerated coke laydown, which tends to increase the pressure drop in that portion of the bed and thus aggravate the flow maldistribution problem. Problems of

this type have generally been solved by improving the design of the flow distributor plates.

It is likely that the presence of coal in the reactor will greatly intensify the flow distribution problem because of the extreme coke-forming tendency of the coal-derived liquid, and because of the tendency of the solid material to plug up the small interstices between catalyst pellets.

No attempt has been made to make detailed designs of the flow-distribution plates and bed-support structures for the Synthoil reactor. This would be beyond the scope of this report. These problems, however, remain to be solved before any substantial scale-up of the reactor beyond the 10-TPD PDU size can be achieved. Further, it appears that for large reactor diameters, it may be necessary to build a mock-up to demonstrate adequate flow distribution and to test the effectiveness of various distributor designs.

4.2.4 Removal of spent catalyst

It is assumed that each Synthoil train is shut down twice a year for replacement of the catalyst. To avoid excessive shutdown time between runs, it is essential to be able to remove the spent catalyst from the reactors without undue difficulty. Preferably, the catalyst pellets should flow out smoothly when the reactor is depressurized and opened. To make this possible, it is assumed that a decoking operation will be necessary before opening the reactor. After the process is shut down and depressurized, the first step is to blow the reactors with steam to remove as much oil as possible. Hot inert gas is then circulated through the reactor. A small amount of air is bled in and the coke is gradually burned off. The progress of the burning wave is followed by thermocouples. The amount of air is gradually increased until burnoff is complete, at which point the reactor is cooled and purged. The catalyst withdrawal nozzle in the bottom head is then opened. In some cases it has been found necessary to do this under water to avoid spontaneous ignition. An internal standpipe connects the catalyst beds to the withdrawal nozzle. The standpipe also connects to a nozzle in the top head, permitting the introduction of a steel rod for clearing the pipe if necessary.

Any small amounts of catalyst remaining can be swept out manually when the reactor is opened for inspection. Fresh catalyst is then loaded into each bed, and the reactor is ready for the next run.

It is not expected that the procedure described will regenerate the catalyst activity sufficiently so that it can be used again. However, this is a point that needs to be verified experimentally.

4.3 Heat Recovery

4.3.1 Synthoil reactor effluent heat recovery

The Synthoil reactor effluent consists of gases, liquids, and solids at 860°F and 4000 psig. The mixture must be cooled to about 550°F for the initial phase separation in the high-pressure high-temperature separator. The amount of heat available from 860°F to 550°F is about 3885×10^6 Btu/hr. Failure to recover this heat usefully would severely impair the overall thermal efficiency of the process. Since the total coal input to the facility represents $43,638 \times 10^6$ Btu/hr, the heat in the reactor effluent (to 550°F) represents 8.9% of the heat input to the facility, or 14.9% of the heating value of the products. If this heat were not recovered, the overall thermal efficiency would drop from 59.6% to 50.7%.

The main problem in the recovery of this heat is the polymerizing and coking tendency of the effluent. It appears likely that ordinary shell and tube heat transfer surfaces would quickly become fouled with deposits of coke-like residues. Under these conditions, heat transfer rates would drop to such an extent that the exchanger would be virtually useless. The exchangers could be cleaned during periodic shutdowns. However, it appears likely that the exchangers might have to be taken out of service more frequently than the 6-month schedule contemplated for catalyst replacement. Unless spare lines of exchangers were provided, this could reduce onstream time to an unacceptable degree.

The capital expenditure involved in providing spare lines of exchangers would be very great. In addition, each line would have to be provided with valves. The mechanical problems in valving off a hydrogen-containing system at 4000 psia and 860°F, with coal solids present, are formidable.

Double block valves with bleed valves between would have to be provided before a group of heat exchangers could be safely removed from service. Even then, the danger of leakage and valve failure would be a continual problem, and the consequences of such a failure while removing an exchanger could be catastrophic. In all probability, good safety practice would dictate that the entire unit be shut down before attempting to remove a tube bundle.

For these reasons, it appears preferable to omit these exchangers entirely if they cannot be kept reasonably clean over operating periods of about 6 months.

In the design and economic evaluation described in Volume I, it was assumed that effluent-feed exchangers could be used and that they would remain in service throughout the 6-month operating period. The use of reactor feed slurry on the cold side, of course, presents additional problems. The experience of commercial hydrodesulfurization units operating on heavy feedstocks is that effluent heat exchangers are not advisable. The assumption that these exchangers can be used should be kept in mind when evaluating the overall thermal efficiency reported in Volume I.

If effluent heat exchangers are not used, the Synthoil reactor effluent might have to be quenched by injecting a stream of cool recycle liquid. A possible source for this liquid might be the distillate collected in the high-pressure low-temperature separator. This material has a low boiling range and would tend to be largely vaporized at the conditions of the initial separation. This would permit recovery of a large amount of heat by condensing the vaporized material. However, the thermal efficiency of heat recovery starting at 550°F would be considerably less than when starting at 860°F. Nevertheless, such a process configuration might turn out to be the best available alternative.

4.4 Other Equipment

4.4.1 High-pressure centrifugal compressors

High-pressure centrifugal compressors suitable for recycle gas and makeup gas services are available at the present time. The makeup gas service requires several units in series, but this presents no problems.

4.4.2 Slurry letdown valves

The high-pressure slurry letdown valve controls the level in the high-temperature high-pressure separator, operating on slurry at about 550°F with a pressure differential of about 3800 psi. Severe erosion problems are anticipated. This item requires further development. Ways of reducing the total pressure drop, such as a restriction orifice or choke ahead of the valve, might be considered.

4.5 Overall Reliability

The 100,000-B/SD Synthoil facility consists of 15 major process units and their related utility and auxiliary systems. This is somewhat similar to an oil refinery, which also consists of a number of interconnected process units. However, there is an important difference which makes the operating characteristics of the Synthoil facility much more critical than those of an oil refinery. In a typical oil refinery, it is usually possible to shut down several of the process units without forcing the shutdown of the entire refinery. In the Synthoil facility, virtually none of the process units can be shut down without causing the immediate shutdown of the whole facility. This is because of the extreme degree of interdependence among the units and the absence of storable intermediate products. For example, if the gasifier or any of the gas-treating units goes down, the Synthoil unit must also shut down because it is not economically feasible or practical to store large amounts of hydrogen. Conversely, if the Synthoil unit is shut down for any appreciable period, the hydrogen production train must shut down because there is no place to use the hydrogen.

With this kind of process arrangement, some increase in reliability can be afforded by providing several parallel lines of equipment in the critical process units. In this way, the facility can be kept running at partial capacity even though some of the parallel trains are down. This was the design philosophy used in the study reported here. It must be pointed out that this philosophy is expensive, since it tends to negate economies of scale. However, the alternative philosophy of using single trains and risking the shutdown of the entire facility appears even less attractive for a facility of this size.

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5. ANCILLARY PROCESSES

The status of development of the ancillary processes used in the overall facility is discussed below.

5.1 Solids-Liquids Separation

The problem of separating fine ash-char-catalyst solids from the liquid products of coal hydroliquefaction is one of the most difficult technical problems facing the development and application of processes for the hydroliquefaction of coal. A similar problem, but of lesser degree, exists in liquefaction processes based on pyrolysis. The problem is especially challenging for processes such as Synthoil that produce boiler fuels by relatively low-severity hydrogenation, because this type of hydrogenation produces the most viscous product streams. The solids must be removed, at least to some degree, for a variety of reasons. Removal of solids from the Synthoil process is necessary to meet sulfur and ash specifications. Other factors of possible significance are erosion of downstream equipment, fouling and poisoning of catalysts in downstream processing, and sludge formation in storage or during transportation.

The reactor effluent from the Synthoil process is a mixture of gases, liquids, and undissolved solids at a temperature of $\sim 860^{\circ}\text{F}$ and a pressure of ~ 4000 psig. After multistage high- and low-temperature flash separation and removal of the vapor phase, the remaining liquid contains the desired heavy-oil product plus undissolved coal solids, ash, and possibly some catalyst fines. For use as boiler fuel, the product must meet specifications on both sulfur and ash content. The solids are high in sulfur and ash, and must be largely eliminated in order to meet specifications. It is estimated that solids content must be kept below $\sim 3\%$ in order to give a satisfactory product.¹ This would correspond roughly to 2% ash and 0.4% sulfur for the western Kentucky coal used as the design feed.

The solids are finely divided, with a large percentage in the 1- to $5\text{-}\mu$ size range. The separation of these solids from heavy coal-derived oils is extremely difficult. The very small particles rapidly plug most filtration media. The high viscosity of the oil makes the separation slow

and increases the size of the equipment needed. The driving force available for centrifugal separation is small because the density of the organic sulfur-containing solids is not greatly different from that of the liquid, although the inorganic solids are somewhat more dense.

The two separation methods most likely to be effective and economically feasible in this application are rotary-drum filtration and centrifugation. Where vacuum distillation can be used, it is undoubtedly one of the most economical separation methods. We believe that vacuum distillation should be investigated further for this application. Possible difficulties that might be encountered are (1) coking of the distillation column preheater if a fired heater is used, and (2) inadequate yield of distillate. Other methods of separation, and analyses of their capabilities, are given in recent reviews of solid-liquid separation in coal conversion processes.¹⁻³

Bench-scale batchwise centrifugations of the Synthoil product oil at PERC have shown that centrifugation can produce an oil that meets EPA guidelines for ash and sulfur.⁴ However, these runs were performed on a small-diameter batch-type centrifuge operating at a speed much higher than would be feasible on a commercial-scale continuous machine. The 4-in.-diam Sharples Supercentrifuge gave an effective separation force of ~13,000 g at 15,000 rpm. On a commercial scale, it is essential that a machine capable of continuous removal of solids, such as the Sharples Super-D-Canter, be used. However, large-scale continuous machines cannot achieve rotating speeds and g-forces as high as those of the laboratory-scale machines. Tests performed on a Sharples Super-D-Canter showed that adequate separation could not be achieved at 200°F.⁵ Operation at a higher temperature is a possibility; this would lower the viscosity and improve the separation.

The upper limit of the operating temperature for Synthoil product centrifugation is not well established. The temperature must be held below the point at which thermal cracking is encountered. Also, it is probable that lighter fractions of the oil would be vaporized at high temperatures unless a high-pressure shell (150 psig or more) is used to enclose the centrifuge. A suitable machine of this type is not available commercially. One might possibly be developed, but there are difficult design problems.

The possibility pursued in the design presented in Volume I is to flash off the lighter fractions at about 540°F and 16 psia, and centrifuge the resulting oil at atmospheric pressure. This requires a high-temperature centrifuge, but the difficulty of high-pressure operation is eliminated. The objection to this scheme is that after flashing off the low-boiling distillates, the viscosity of the remaining oil is increased. However, the effect of operating at a higher temperature could more than compensate for this. To assess this possibility more thoroughly, data are needed on the boiling ranges and viscosity vs temperature characteristics of various fractions of the product oil. Once the necessary data are obtained, various methods are available for estimating the viscosity of the oil remaining after flashing off a given fraction of light material.

In the bench-scale Synthoil runs conducted at PERC, solids separation was performed on the recycle oil as well as on the net product oil. It is not known whether operation with a solids-containing recycle oil is feasible. Conceivably, this could lead to pressure-drop buildup in the reactor. It is possible that a partial separation of solids from the recycle stream will be adequate, and this has therefore been selected as the basis for the Synthoil conceptual design. The centrifuge overflow is lower in solids concentration and is recycled to the slurry feed tank. The underflow, containing the partially concentrated solids, goes to rotary-drum filters. Some limited experimental data⁵ are available for design, but more experimental work is needed on the Synthoil product stream to determine the relative amounts of solids contained in the centrifuge overflow and underflow when a 75%/25% split is performed.

Proposals by Gulf Research and Development Company (in their Catalytic Coal Liquids process)⁶ and by Hydrocarbon Research Incorporated (in their H-Coal process)⁷ have included hydroclones as a partial separation process prior to rotary drum filtration. Hydroclones are relatively inexpensive, and high throughputs can be attained in units of small physical size. Operating costs are low since there is no heat requirement. An overall economic balance would be required to determine whether the total costs of such an arrangement would be lower than those of filtration alone, or of centrifugation followed by filtration. Such a balance would depend on

the specific process characteristics and the required sharpness of separation. There is no way to anticipate the results until more experimental data are available.

Design of the rotary drum filtration unit of the solids-containing Synthoil product stream was based on information obtained through meetings and correspondence with vendors and operators of current experimental filtration units.^{2,8-13} It has been shown in other coal conversion processes that pressure precoat rotary drum filtration can reduce solids concentrations to below 0.1 wt %, which is well below the level required for the Synthoil product. Rotary-drum precoat filtration has been carried out at high temperatures (to 600°F) and high pressures (about 150 psig) on coal-derived streams.

The filtration rates achieved thus far on coal-derived oils in laboratory and pilot plant tests are rather low, typically not more than 10 to 15 gal of filtrate per hour per square foot of filter area.^{2,8} To determine the filter surface area required in a commercial plant, the filtration rate is reduced to allow downtime for precoating, cleaning, and maintenance. If an average overall rate of $11 \text{ gal hr}^{-1} \text{ ft}^{-2}$ can be achieved, a Synthoil plant producing 100,000 B/SD of oil will require about $13,500 \text{ ft}^2$ of filter surface, assuming that only the net product is filtered. The largest design for a commercial rotary drum precoat filter is about 500 ft^2 .¹⁰ Thus about 27 filters are required for the net product only. If the recycle oil also requires filtration, the number of filters required would be approximately quadrupled. Hence, the design shown in Volume I of this report saves considerable capital cost by using centrifugation followed by filtration rather than filtration alone. Assuming this is feasible, the use of 27 centrifuges at about \$275,000 each (based on the Sharples Super-D-Canter model P-6800 modified for high-temperature operation)⁵ would eliminate the need for an additional 81 rotary drum filters at \$600,000 each (based on a conceptual 500-ft^2 Goslin-Birmingham precoat rotary-drum filter modified for high-temperature and high-pressure operation).¹⁰ Including installation and required ancillary equipment, the saving is at least \$75 million. However, it should again be pointed out that extensive experimental verification is required. For example, filtration of the

thickened slurry from the centrifuges may present serious problems not found in the more dilute filtrations.

The cost of higher electrical consumption of the centrifuges (200 hp each vs 20 hp for filters) is negligible compared to the reduction in diatomaceous earth precoat consumption. Consumption of precoat is reduced from ~48 TPD to 12 TPD, and precoat costs are reduced by \$4500/day. This is based on the conceptual design used in Volume I, where an effort has been made to minimize precoat usage, and on an expected mix of Johns-Manville filter aids.¹⁴

Maintenance of the high-speed rotating centrifuges is expected to result in a sizable downtime requirement. The 27 centrifuges represent 20% overcapacity to allow for such outages.

Even with the savings resulting from centrifugation prior to filtration, there is still considerable room for improvement in the economics of solid-liquid separation. The total capital cost of the separation section of the Synthoil plant is a significant portion of the overall cost of the facility. Also, the separation section represents an area in which difficult mechanical design problems must be solved in order to achieve satisfactory operation. Much additional work in methods of improving or eliminating filtration is required. For example, recent work has shown that it may be possible to replace diatomaceous earth with sized coal as the precoat material.¹⁵ Such innovations could substantially reduce the total cost of filtration, which is currently expected to be at least \$1 per barrel of product oil.¹⁶

5.2 Low-Temperature Carbonization

More experimental work is needed on the fluidized-bed carbonization of the filter cake residues from the filtration of the Synthoil product.

Carbonization of residue from a combined solvent extraction--catalytic coal hydrogenation process was successfully accomplished at the 20-TPD pilot plant at Cresap, West Virginia.¹⁷ Planned reactivation of the 1700-lb/hr fluidized-bed carbonizer at Cresap will provide further pilot-scale information on this process, and a concurrent bench-scale

experimental program at ORNL¹⁸ will permit rapid testing of a variety of feedstocks and provide data for scale-up. PERC is also constructing a 50-lb/hr fluidized-bed solvent recovery facility to operate on-Synthoil sludge (residue).¹⁹

The PERC facility will consist of a feed system, a fluidized-bed reactor, and a gas and liquid recovery system. The feed will be a 50-wt % solids slurry, and the fluidizing gas will be nitrogen. The configuration of the fluidized-bed reactor closely resembles that of the Cresap carbonizer, except that the gas cyclones are mounted externally because of headroom limitations. The reactor consists of a section of 10-in. pipe about 7 ft tall, with a 4-in. pipe draft tube. A disengaging section of 18-in. pipe about 4 ft tall is joined to the top of the reactor. The recovery system contains a tar separator and a tar receiver, a condenser, and a condensate decanter. A gas sampling station is also included.

Reliable methods need to be developed for avoiding agglomeration in the fluidized bed. At present, the most practicable method seems to be to mix the feed as quickly as possible with a larger circulating stream of hot char. However, this procedure has not yet been developed to the point where reliability can be predicted. The exact geometry of the feed injection and mixing devices needs further study and experimentation. Both external and internal char circulation should be considered.

5.3 Gasification

The Babcock and Wilcox entrained flow, slagging gasifier has been demonstrated in a semicommercial unit and in other pilot-scale units. Operating data on a pilot unit built at Morgantown, West Virginia, were generated at 100 psig, and to a lesser extent at 300 psig during the 1950's and 1960's.²⁰ The capacity of the unit was about 2.5 TPD at 100 psig and 12 TPD at 300 psig. Continuous slagging and lock hopper discharge of slag under pressure were demonstrated. A total of 300 hr of operation was logged, but the duration of each run was limited by the capacity of the batch feeder to approximately 8 hr.

Babcock and Wilcox have projected the design of a commercial unit to gasify ~850 TPD of coal at 50 psig. Another unit is projected that would gasify ~3000 TPD of coal at a pressure of 175 psig.

Each of the two gasifiers in the Synthoil facility is designed to gasify about 9000 tons of material per day (6000 TPD of coal plus 3000 TPD of char from the low-temperature carbonizer) at 245 psig. In order to demonstrate capability for continuous operation at this pressure, and because design scale-up factors are empirically determined, an extensive gasifier development effort may be required.

Due to the high ash content of the char, the total ash content of the gasifier feed material (coal and char) is about 37 wt %. This factor may require additional investigations to determine its effect on gasifier design, gasification reactions, refractory performance, and slagging properties.

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APPENDIX A. PHYSICAL DATA

A.1 Vapor-Liquid Equilibrium Data

From the standpoint of process design, vapor-liquid equilibrium data are more important than other types of physical data because they enter directly into the calculation of the process material balances where the process calls for the separation of vapors and liquids. In processes such as Synthoil, these separations occur at critical locations. As a result, errors in equilibrium relationships can have a much greater relative effect on the plant design than errors in other physical properties such as viscosity and thermal conductivity.

Design calculations in the reactor effluent letdown and high-pressure gas recycle systems require the estimation of vapor-liquid equilibrium relationships in multicomponent mixtures at pressures up to 4000 psig and temperatures to 550°F or higher. These calculations are an important part of the process design, because they are needed to determine the purity of the recycle gas and the amount of hydrogen makeup required. This sets the size of the entire hydrogen production train, which comprises a large part of the total capital investment in the facility.

The amount of uncertainty in these calculations is rather large, because adequate experimental equilibrium data are not available on mixtures of the type encountered here at the pressures and temperatures mentioned. The designer is therefore obliged to use available correlations based on data at lower pressures. The design calculations for this report made use of the Chao-Seader¹ and Grayson-Streed² methods. Use of these correlations beyond 2500 psia is not a recommended procedure, but at the present time there is no generally available alternative that can be demonstrated to be superior.

For coal liquefaction work, an experimental data base of vapor-liquid equilibria is needed covering a wide range of mixtures and temperatures, and extending up to at least 4000 psia. The mixtures should include hydrogen, nitrogen, hydrogen sulfide, methane, and intermediate and heavy hydrocarbons, especially aromatic and polynuclear aromatic hydrocarbons such as are found in coal-derived liquids. A temperature range

up to 800°F should be covered. Given a data base of this scope, investigators would probably be able to develop satisfactory predictive correlations, and process calculations based on such correlations would be adequate for equipment design purposes.

A.2 Viscosity and Boiling Range

The need for data on the viscosity and boiling range of the product oil from the Synthoil process was mentioned earlier in connection with the solids-liquid separation problem. The capacity and efficiency of centrifugation and filtration equipment depend largely on the viscosity of the liquid phase. For satisfactory design of such equipment, it is essential to have viscosity data as a function of temperature. At elevated temperatures (400 to 600°F), some of the lower boiling fractions of the product oil may be vaporized. Hence it becomes necessary to be able to estimate the amount vaporized and the viscosity of the remaining oil. Methods are available for making such estimates, provided that the boiling range and viscosity of the various fractions of the product oil are known.

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APPENDIX B. MATHEMATICAL ANALYSIS OF REACTOR-TEMPERATURE PROFILE

A mathematical analysis of the temperature profile of an internally cooled exothermic reactor has been made by Dr. G. J. Quarderer. A copy of his analysis was sent to ORNL from ERDA in the form of unpublished notes. An abridged version of Dr. Quarderer's analysis is included here because it has been interpreted as raising questions as to the thermal stability of the Synthoil reactor. Briefly, it has been used to lead to the conclusion that, because of thermal stability considerations, the maximum diameter of a Synthoil reactor will be about 2 ft. We do not agree with this conclusion, for reasons that will be explained later.

The abridged version of the analysis is given in Sect. B.1, and our comments as to its interpretation are given in Sect. B.2.

B.1 Abridged Version of Dr. Quarderer's Analysis

Assume a cylindrical plug flow, fixed-bed reactor with mass flow in the axial direction. Assume an exothermic reaction with heat being removed by radial transfer to a circulating cooling system.

An energy balance, assuming heat flow in the radial direction only, with simplifying assumptions, gives the equation:

$$G C_p \frac{\partial T}{\partial Z} = (-\Delta H_r)R - \frac{2h (T_m - T_c)}{a(1 + \frac{ha}{4k_r})} \quad (1)$$

Differentiating with respect to the axial dimension yields:

$$G C_p \frac{\partial^2 T}{\partial Z^2} = (-\Delta H_r) \frac{\partial R \partial T}{\partial T \partial Z} - \frac{2h}{a(1 + \frac{ha}{4k_r})} \frac{\partial T}{\partial Z} \quad (2)$$

Assuming that the criterion for stability is $\frac{\partial^2 T}{\partial Z^2} \leq 0$, the critical point at which this is just satisfied occurs when $\frac{\partial^2 T}{\partial Z^2} = 0$. Applying this condition to the previous equation gives:

$$-\Delta H_r \frac{\partial R}{\partial T} = \frac{2h}{a(1 + \frac{ha}{4k_r})} \quad (3)$$

Assuming that R can be expressed as

$$R = A e^{-E/R_g T} f(\text{concentration}), \quad (4)$$

Then

$$\frac{\partial R}{\partial T} = A f(\text{concentration}) \frac{E}{R_g T^2} \quad (5)$$

and, using Eq. (4),

$$\frac{\partial R}{\partial T} = \frac{R E}{R_g T^2} . \quad (6)$$

Substituting this in Eq. (3) gives

$$-\Delta H_r \frac{R E}{R_g T^2} = \frac{2h}{a(1 + \frac{ha}{4k_r})} . \quad (7)$$

Rearranging

$$\frac{1}{h} + \frac{a}{4k_r} = \frac{2 R_g T^2}{a(-\Delta H_r) R E} . \quad (8)$$

To simplify this, it is estimated that in practice $\frac{1}{h}$ is small compared to $\frac{a}{4k_r}$. The $\frac{1}{h}$ term on the left side is dropped and the equation becomes

$$\frac{a}{4k_r} = \frac{2 R_g T^2}{a(-\Delta H_r) R E} . \quad (9)$$

The critical value of the radius is found by rearranging:

$$a = \left[\frac{8 R_g T^2 k_r}{(-\Delta H_r) R E} \right]^{0.5} . \quad (10)$$

This is the value of the radius when $\frac{\partial^2 T}{\partial Z^2} = 0$. It is clear from Eq. (2) that a decrease in the value of the radius will cause a decrease in $\frac{\partial^2 T}{\partial Z^2}$. The criterion $\frac{\partial^2 T}{\partial Z^2} \leq 0$ will therefore be satisfied if

$$a \leq \left[\frac{8R_g T^2 k_r}{(-\Delta H_r) RE} \right]^{0.5} \quad (11)$$

The maximum allowable radius of the reactor for thermal stability is the value of a given by Eq. (10).

Notation

G	= mass flow rate, g-mole/cm ² sec
C_p	= heat capacity, cal/g-mole, °C
T_m	= temperature, mean fluid, °K
Z	= axial location, cm
R	= reaction rate, g-mole sec ⁻¹ cm ⁻²
h	= heat transfer coefficient, cal cm ⁻² sec ⁻¹ , °C
a	= radius of reactor, cm
k_r	= thermal conductivity, radial, cal cm ⁻¹ sec ⁻¹ , °C
T_c	= coolant temperature, °K
ΔH_r	= heat of reaction, cal/g-mole
R_g	= gas constant
E	= activation energy
T	= reactor temperature, °K

B.2 Interpretation of the Analysis

By substituting numerical values typical of the Synthoil process into Eq. (10), the maximum value of the radius of the reactor can be calculated to be about 1 ft. The conclusion has therefore been drawn that the maximum allowable diameter of a Synthoil reactor is about 2 ft.

We believe that this conclusion misinterprets Dr. Quarderer's analysis. First, it should be pointed out that Eq. (10) was derived on the basis that the reactor is equipped with a cooling system that removes the heat of reaction in a radial direction. If it is assumed that there is no cooling system (i.e., that the reactor is adiabatic), then Eq. (1) becomes

$$G C_p \frac{\partial T}{\partial Z} = (-\Delta H_r) R ,$$

and Eq. (2) becomes

$$G C_p \frac{\partial^2 T}{\partial Z^2} = (-\Delta H_r) \frac{\partial R}{\partial T} \cdot \frac{\partial T}{\partial Z} .$$

Since an adiabatic exothermic reactor necessarily has a positive value of $\partial T / \partial Z$, the preceding equation shows that $\partial^2 T / \partial Z^2$ will also be positive. Therefore, the criterion $\partial^2 T / \partial Z^2 \leq 0$ cannot be satisfied, regardless of the diameter of the reactor. Thus, if it is accepted that $\partial^2 T / \partial Z^2 \leq 0$ is the criterion for determining whether a reactor can be built, then it must be concluded that no adiabatic exothermic reactor can be built, regardless of its diameter.

However, the analysis does not attempt to offer proof that a positive value of $\partial^2 T / \partial Z^2$ means that the reactor is unsafe to operate. Misinterpretation arises when this is assumed without proof. The criteria of operational safety are much more complex than $\partial^2 T / \partial Z^2 \leq 0$, and are not easily susceptible to mathematical analysis. The successful operation of dozens of commercial hydrocracking and hydrotreating reactors, all of which violate the criterion $\partial^2 T / \partial Z^2 \leq 0$, is ample evidence of this point.

To summarize, the word "unstable" has been used only to denote the condition $\partial^2 T / \partial Z^2 > 0$. There is no evidence that this condition alone is sufficient to rule out the feasibility of a reactor. If it were, no adiabatic exothermic reactor could be built. Many such reactors have been built and operated successfully.

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