favorable performance of the Kolbel system. The results of the work of the IIT and the University of Tokyo come closest to confirming this favorable performance.

The DSIR catalyst experienced a fairly rapid decline in activity (and selectivity change) throughout the run period necessitating reactor temperature increases to try to regain activity. In addition, catalyst attrition occurred so that very small particles ($\simeq$ 1 micron) were produced. They followed the change in composition of the catalyst with time and noted that raising the temperature increased "free carbon" formation. This increased the slurry viscosity and drastically decreased the gas hold up. Eventually the run was terminated because of gelation of the slurry.

The USBM also experienced catalyst deactivation but neither the Germans nor the IIT workers addressed the issue of catalyst deactivation. Kolbel estimated that his catalyst life was approximately 400-500 kg hydrocarbons/kg catalyst. Regeneration was cited as being easily achieved.

6.4.2 Operational Results

Table VI-2 shows the main process parameters used by the four groups to study the performance of the slurry reactor. The temperature and pressure regimes were similar and the space velocities again were comparable except for the lower GHSV used by the workers at the IIT. The longest run time was achieved by the USBM. The DSIR experiment was terminated after 19 days because of slurry gelation.

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TABLE VI-2

PROCESS PARAMETERS FOR F-T SLURRY REACTORS

	KOLBEL	DSIR**	USBM	IIT*
Temperature (^{o}C) Average	268	272	259	260
Pressure (BAR)	12	10.25	10-14	10
Gas Rate (Nm^3/h)	2700	65	3.4	0.6
GHSV (liters inlet gas/ liter expanded slurry/h)	270	200	240	100
Total Run Time (Days)	~ 38	19	52	–

*Indian Institute of Technology
**Department of Scientific and Industrial Research

TABLE VI-3

PERFORMANCE DATA FOR F-T SLURRY REACTORS

	KOLBEL	DSIR		USBM	IIT
Hours on Stream	Run Average	126	402	504	(Run No. 10)
CO Conversion %	91	50.5	47.3	73	93.9
CO + H$_2$ Conversion %	89	46.3	45.1	59	91.5
H$_2$/CO Usage Ratio	0.63	0.53	0.65	0.62	0.80
Rate Constant*	21.5	4.61	4.84	7.74	10.7
Space-Time Yield C$_3$+ In 24h (kg/m^3 reactor volume)	930	425	381	~720	418
Space-Time Conversion (1 converted gas/gFe/h)	3.0	2.57	2.61	0.47	0.61
Catalyst Yield (kg hydrocarbons/kgFe/h)	0.51	0.58	0.55	~0.1	~0.11

* Rate Constant = $\dfrac{SV}{P} \log_{10}\left(\dfrac{1}{1-c}\right)$

Table VI-3 shows the performance data obtained by these workers. The Kolbel data taken at the Rheinpreussen-Koppers pilot plant are an average of the 38-day run. The other data were obtained after a certain number of hours on stream.

Kolbel and IIT achieved high single pass conversions of synthesis gas, DSIR never obtained high activity and the conversions remained low throughout the run. The USBM maintained an activity between these extremes with a $CO + H_2$ conversion of approximately 60%. Kolbel obtained by far the highest space-time yield of 930. This compares with 1250 for the Arge reactor and probably double that for SYNTHOL reactor.

The rate constant concept was used by the DSIR to assess the catalytic activity of their slurry (first order chemical reaction assumed). The relative activity of the slurry was almost five times higher in Kolbel's case than in the DSIR experiment.

Although the scale of the reactors used for this comparison is very different, Kolbel has shown that little difference in overall performance results from bench scale to pilot plant, a scale up factor of 1:1666.[25] The bench scale reactor that Kolbel used for his comparison had the same slurry volume as the IIT reactor.

6.4.3 Operating Differences

Table VI-4 lists the main operating differences between the four groups of workers. The most notable of these are the catalyst composition, slurry concentration, catalyst loading and feed H_2/CO

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TABLE VI-4

OPERATING DIFFERENCES IN F-T SLURRY REACTORS

	KOLBEL	DSIR		USBM	IIT
		Period 4	Period 13		
Linear Velocity of Syngas (CM/SEC)	9.5	7.0		2.75	1.5
Catalyst Loading (1 inlet gas/g Fe/h)	3.38	5.7		0.80	~0.6
Catalyst Slurry Concentration (g Fe/Liter)	80	35		300	~160
Gas Hold Up %	~63 (Calculated)	45	15	-	-
H_2/CO Feed Ratio	0.67	Low		1.0	1.33
Catalyst Composition Fe	100	100		100	-
Cu	0.1	1.25		10	-
K_2O	0.05-0.5	1.40		1	

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ratio. These differences obviously make it extremely difficult to critically compare the results of these four investigations. One must assume that Kolbel's work at the large pilot plant level has managed to adjust many of the operating parameters such that high activity and ease of operability were obtained. Whether optimization, even in Kolbel's case, was reached is uncertain as Kolbel claims that compressor output limited his catalyst loading to approximately three liter/gm hr and this could have been doubled. All other parameters being the same this would have increased the space velocity to about 600 which is greater than the ARGE fixed bed process. The high catalyst loading in the DSIR case may have resulted in premature deactivation by over carbonization but if Kolbel's claim is correct this is unlikely. Kolbel claims that the high SO_3 content of the catalyst (a catalyst poison) may be responsible for its low activity.

The very low slurry concentration used by the DSIR may have resulted in insufficient catalyst being available for possible surface adsorption by synthesis gas especially at higher gas holdups of ~45%. This can be seen by the experimental fact that although gas hold up dropped from 45 to 15% from periods four to thirteen the conversion of synthesis gas only dropped 1%.

The difference in feed H_2/CO ratio is also very significant. Kolbel used a low ratio of 0.67 comparable to the raw off gas from a Texaco gasifier. The DSIR did not specify their feed ratio but reported it to be low. The USBM and IIT used quite high feed ratios especially in comparison to the usage ratio.

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The effect of catalyst composition in respect to different levels of promotion and preparation has already been discussed and may well be the key to the differences in performance experienced by the four groups of experimenters.

6.4.4 Reactor Operability

During the course of the experimental runs using the slurry F-T reactors, some operational difficulties were experienced by some groups.

Operation of the Rheinpreussen-Koppers plant apparently proceeded without mishaps worthy of documentation during the 38-day run. Liquid slurry level was maintained by either filtering off some of the high boiling liquid through a pressure filter or by adding quantities of high boiling synthesis products. No details of decline in catalyst activity are given and no problems concerning the fluid dynamic behavior are mentioned.

The experience of the DSIR was different. Fairly rapid initial decline of the catalyst occurred, which may have been due to catalyst overloading or SO_3 poisoning. Then throughout the next 400 hours of the run there was a gradual decline in conversion from 50% to 45%. Eventually the viscosity increase in the slurry, due to free carbon formation, caused the experiment to be terminated. At this point, conversion of synthesis gas had dropped to 35%. Speculation as to the cause of this behavior concluded that an unsuitable catalyst was the prime cause. Why the DSIR did not use a catalyst of more similar composition to Kolbel's is not certain, but is believed to be the result of proprietary limitations.

The USBM experienced operational difficulties in maintaining slurry circulation through the recycle line, but besides these mechanical problems the catalyst experienced a slow continual de-activation due to surface carbon buildup under the prevailing conditions. After 1200 hours on stream total yield of C_3^+ dropped from 105 g/m^3 to 90 g/m^3, but during this period a reactivation using hydrogen at 275°C and one atmosphere pressure was attempted.[31] Apparently catalyst deactivation was confined to carbon buildup on the catalyst surface and no free carbon was produced in the slurry. As a result the slurry did not increase in viscosity as occurred in the DSIR case.

Some initial difficulties of catalyst settling in the slurry recycle line were experienced at the IIT. This was rectified and apparently other unspecified operational problems necessitated the use of a 10-foot reactor. Their overall conclusion with respect to reactor operability was that reactor performance was highly satis-factory in regard to slurry agitation, temperature control and product removal.

6.5 Product Distribution

Table VI-5 shows the product selectivity obtained from different reactor systems. Three slurry reactor system results are compared to the distribution obtained at SASOL[4] and to the distribution cited by MRDC[1] for a SASOL-type operation.

TABLE VI-5

PRODUCT DISTRIBUTIONS FROM F-T REACTOR SYSTEMS

PRODUCT (Wt % Total C_1^+)	RHEINPREUSSEN KOPPERS (KOLBEL)	D.S.I.R. ENGLAND		USBM	SASOL I [4]		MOBIL [1]
		PERIOD 4	PERIOD 13		ARGE	SYNTHOL	
CH_4	3.2	6.3	10.4	12	2.1	10.6	11.9
C_2H_6		1.1	2.7		1.9	4.3	6.7
C_2H_4	3.6	4.1	6.1	23 (C_3-C_5)	0.1	4.3	4.2
C_3	22.6	5.1	6.3		4.5	14.9	15.3
C_4	5.1	2.9	4.9	~27	4.6	11.7	10.6
C_5–180°C	53.6*	11.6	23.6		18.6	42.5	34.2
180–220	4.0	40.4	44.1	10	14.5	7.4	7.1
220–320	6.0						5.3
>320	1.9	28.5	2.0	28	53.7	4.3	4.6

*Schulz-Flory Maximum (C_5–C_{11}) = 48% (35)

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The results of the Kolbel supervised work at Rheinpreussen show the highest selectivity to gasoline and a low selectivity to methane comparable to that achieved by the ARGE reactor. The SYNTHOL reactor shows the next highest selectivity to gasoline but over 10 wt % methane production. The Mobil baseline case is very close to the SYNTHOL case although the gasoline selectivity is lower for Mobil. The Kolbel yield of C_5-180°C fraction is the optimum allowable from Shultz-Flory probability considerations.

The significant change in product distribution for periods four and thirteen in the DSIR work could be a combination of the temperature differential and the effects of an aging catalyst. If it is temperature that caused the considerable shift from high boiling products ($\Delta T=15^{\circ}C$), then this implies that product distribution is extremely sensitive to temperature changes in the reactor.

6.5.1 Chemical Class Analysis of F-T Products

The USBM produced 27 wt % product boiling in the gasoline boiling range. However, 44 wt % of the light oil product contained oxygenates. This high yield of oxygen containing compounds may have been due to the high concentration of copper promotor, but this product is not a very desirable gasoline feedstock. Kolbel estimated that weight percent of oxygenates in his liquid product to be around 1%.

Table VI-6 shows the percentage of compound type in F-T products from SASOL[5] and two slurry reactor operations. The SYNTHOL reactor

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TABLE VI-6

CHEMICAL CLASS ANALYSIS OF F-T PRODUCTS

	ARGE		SYNTHOL		DSIR	KOLBEL	
	C_5-C_{12}	$C_{13}-C_{18}$	C_5-C_{10}	$C_{11}-C_{14}$	C_5-C_{10}	C_5-C_{10}	$C_{11}-C_{13}$
PARAFFINS	53	65	13	15	13	--	--
OLEFINS	40	28	70	60	76	70	48
AROMATICS	0	0	5	15	1	--	--
ALCOHOLS	6	6	6	5	}10	}~1	--
CARBONYLS	1	1	6	5			--
n-PARAFFINS	95	93	55	60			

GASOLINE* PRODUCTION WT% C_3^+

KOLBEL	SYNTHOL	MOBIL	USBM
62	56	54	~36

Kolbel gasoline IOR = 73

* Gasoline = $(C_5-210^\circ C)$ fraction.

IOR = Intermediate Octane Rating

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produces a very similar chemical class distribution to the slurry reactor especially in the high olefin content of the C_5-C_{10} fraction. Both SYNTHOL and the DSIR produced more oxygenates than the Kolbel experiment. Gasoline production presented as the weight % of C_3^+ is higher in Kolbel's case but closely followed by the fast fluid bed reactors. The intermediate octane rating of the raw gasoline produced from the Kolbel reactor was 73.[26]

6.6 Process Potentials and Implications

It is impossible, in view of the conflicting evidence provided by the operating experiences of the four groups of workers involved in F-T slurry reactors, to unequivocally predict slurry reactor performance in F-T synthesis. However from the pilot plant data provided by Kolbel and substantiated to a large extent by work at the IIT and the University of Tokyo it is possible to identify certain implications pertaining to the process potential.

If the Kolbel pilot plant data can be duplicated then the likely positive benefits from using a slurry phase F-T reactor are:

- good selectivity to gasoline boiling range hydrocarbons. The product distribution to gasoline could be better than that obtained by the SYNTHOL reactor and would be at or close to the theoretical Shultz-Flory maximum

- much lower production of methane than obtained in the SYNTHOL reactor. This is due primarily to the heat transfer characteristics of the Kolbel system and the lower operating temperatures. This has positive benefits when optimizing on all liquids output from a plant (see Section 7.0).

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- high single pass conversion would probably mean that recycle would be unnecessary. SYNTHOL requires a lower conversion per pass to handle heat transfer requirements

- capability to accept a synthesis gas feed with a low H_2/CO ratio eliminating the need for external water gas shift. Not using an external shift has the potential to achieve a higher overall thermal efficiency

- probable need for considerably less catalyst charge than the SYNTHOL reactor (approximately 55 tons/ reactor as compared to ~120 tons/reactor for SYNTHOL). Also there should be no problems arising from catalyst attrition as micron size particles are quite acceptable for Kolbel. A lower size limit may, however, be dictated by the need to filter off the catalyst when withdrawing excess slack wax.

- implicit in the design of the reactor is the ability to remove heat of reaction more efficiently than in a fast fluid bed gas/solid reactor.

- average hydrocarbon yield per Nm^3 of fresh feed inlet gas is approximately the same as for the SYNTHOL reactor. (SYNTHOL $0.165 kg/Nm^3$ fresh feed gas, Kolbel $0.160 kg/Nm^3$ gas.)

The most significant disadvantages of the slurry reactor, apart

from its non-commercial status, appear to be:

- Space velocities and space-time yields are low, even lower than the ARGE fixed bed and considerably lower than SYNTHOL. Thus larger reactors or more reactors are required to handle the same throughput.

- The effective lifetime of the slurry catalyst is un- known under synthesis conditions. From Kolbel's data the effective catalyst life is in the order of 34 days (compare 49 days for the SYNTHOL catalyst). In addition, no data on ease of regeneration are available.

- The residence time of product species may be difficult to control because of backmixing in the slurry, however from the Rheinpreussen pilot plant data no detrimental effect on gasoline selectivity was observed.

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- Problems may result in removing liquids and filtering off fine catalyst particles from the slurry if high boiling liquids accumulate rapidly in the slurry reactor. In this respect it is probably easier to operate a two phase system (SYNTHOL) rather than a three phase system.

- In full-scale units large cross-sectional area reactors have uniform gas distribution problems. Kolbel states that "The hydrostatic equilibrium is disturbed, the residence time of the gas becomes non-uniform, and this results in a rolling motion of the liquid with vigorous back mixing." Bulk liquid rolling movement can be prevented by means of internal baffles or honeycombs that effectively divide the bulk of the slurry into separate compartments. (For a superficial gas velocity of 10 cm/sec the reactor diameter necessary to receive a gas throughput of 150,000 Nm^3/h is at least 15 feet.)

7.0   ADVANCED GASIFIER - SYNTHESIS COMBINATION PROCESS EVALUATION

7.1   Process Evaluation for Combination of a BGC Lurgi Gasifier
with a Kolbel Synthesis Unit

Coal utilization patterns are different when using advanced
gasifiers. In the Sasol-U.S. case 4,976 tons/SD of coal were sent
to the boiler plant for steam raising. The BGC-Lurgi has a greatly
reduced steam requirement thus more coal can be gasified. In
addition, because of the very small shift requirement for the Kolbel
reactor, additional coal can be gasified rather than be used for
shift steam. It should be cautioned that the BGC Lurgi still requires
sized coal and unless a certain quantity of fines can be injected
and gasified along with the sized coal, the coal utilization patterns
based on steam requirement may have to be compromised. The coal
sent for gasification in this case is 2,100,000 lbs/hr (25,200 t/SD).
The remaining coal (2592 t/SD) is sent to the boiler. In addition
to this coal, tars, oils and phenols produced in the gasifier are
used for plant steam production. Thus a total of 27.8 M t/SD of
coal is fed to the plant as is also used in Sasol-U.S. case.

Table VII-1 shows the products from gasification of this quan-
tity of coal in the BGC-slagging Lurgi gasifier. All units are in
lb mole/hour. This gasifier output is compared to the output from
the Sasol-U.S. case using the dry bottom Lurgi. The lb moles of
gas shown are for clean shifted gas ready for input into the
respective F-T synthesis reactors. In the BGC case the H_2/CO ratio
is adjusted to 0.67 for feed to the Kolbel unit while for the Sasol-
U.S. case the ratio is 2.54 for use in the Synthol reactor. In practice

TABLE VII-1

GASIFICATION PRODUCTS

	BGC LURGI (for Kolbel)	SASOL – US
CO (lb moles/hr)	57,650	18,500
H$_2$ (lb moles/hr)	38,510	46,985
CH$_4$ (lb moles/hr)	7,490	12,460
C$_2$H$_4$ (lb moles/hr)	26	21
C$_2$H$_6$ (lb moles/hr)	341	277
Gasifier Naphtha (lb moles/hr)	178	160
TOTAL (lb moles/hr)	104,195	78,403

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the raw gasifier ratio of 0.5 could probably be used with no shift but since Kolbel data are for an input gas of ~0.67 H_2/CO ratio.[25] for comparability this ratio is used as input to the Kolbel reactor throughout this report.

The considerably higher total lb moles/hr from the BGC unit is attributed to the use of 10% more coal in the BGC gasifier and also to the fact that the synthesis gas from the Sasol-U.S. case has already been shifted and has rejected a considerable quantity of CO_2.

Table VII-2 shows the products from the Kolbel synthesis unit obtained from the BGC gasifier output tabulated in VII-1. For comparison the output from the Synthol reactor in the Sasol-U.S. case is also tabulated. Also shown on this table are the primary gasifier products from the two Lurgi systems demonstrating the much higher methane make in the dry-bottom system. Details of how the Kolbel raw product distribution was obtained are given in Appendix B.

The energy loss through the Kolbel F-T unit in relation to total heat of combustion of synthesis gas to heat of combustion of synthesis derived products is 2751 MM Btu/hr (see Appendix B) giving an overall efficiency for the process of 76.6% (Theoretical 78.1). This compares to 80% for the F-T Synthol unit in the Sasol-U.S. case (Theoretical 81.0). The Kolbel unit must necessarily be less efficient because it must, in addition to undergoing the highly exothermic F-T reactions, also undergo the exothermic water gas shift reaction internally.

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TABLE VII-2

PRODUCTS FROM F-T SYNTHESIS UNITS

	BGC + KOLBEL	SASOL-US
Methane + Ethane (lbs/hr)	13,643	45,103
C_2H_4	15,079	10,087
C_3	96,458	36,847
C_4	21,781	25,468
40 – 180°C	228,577	82,477
180 – 200°C	16,993	17,179
220 – 320°C	25,610	12,865
>320°C	7,899	11,217
Alcohols	7,181	23,744
TOTAL (lbs/hr)	433,221	264,987
Primary Gasifier Products		
CH_4	120,139	199,858
C_2H_4	729	589
C_2H_6	10,270	8,329

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The raw F-T derived gasoline product emerging from the Kolbel
synthesis units does not meet consumer product specifications and
must be upgraded. The raw primary gasoline fraction (25-190°C) from
the Kolbel synthesis has a Reid vapor pressure of 0.55 atmospheres
and an intermediate octane rating of 73.[25] It should be noted that
values of 55 are given for the octane rating of the raw F-T gasoline
produced at SASOL.[3] The diesel fuel fraction (190-310°C), however,
had a solidification point of -13° and an ignition value of over 70
(cetane number).

Table VII-2 illustrates the considerable difference in the
product distribution obtained from Kolbel and the Synthol reactors.
The light gases, methane, ethane and ethylene account for only 6 wt%
of the total products in the Kolbel case whereas they account for
over 21% in Synthol. This difference has obvious implications when
considering an all-liquid output plant as, in the Kolbel case, far
less reforming of C_1 and C_2 hydrocarbons will be required, result-
ing in a higher overall efficiency. The high selectivity of C_3
hydrocarbons obtained from Kolbel also has a beneficial impact on
the gasoline yield. Eighty percent of these C_3's are olefinic and
can be processed via catalytic polymerization to form gasoline
boiling range hydrocarbons. This source of polygasoline plus very
positive benefit for a synthetic fuels plant whose objective is
optimization of gasoline.

The details of the refining scheme used to upgrade the raw
Kolbel synthesis products is the same as the U.S.-SASOL case and

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has already been discussed in Section 4 of this report. The difference
in the product distribution from Kolbel as compared with the U.S.-SASOL
Synthol case necessitated that the upgrading of the individual com-
ponents be considered in detail in order to take advantage of the
favorable raw product distribution from the Kolbel reactor. The
details of the Kolbel product refining are contained in Appendix B.

The refining analysis is not strictly rigorous as hydrogen and
steam requirements for the refinery are not identified. In addition,
many of the light gas streams that are either recovered or used
internally as fuel gases are not fully identified. However, the
uncertainties in these secondary streams were resolved by assuming
the overall refinery efficiency to be identical to the 94.4% achieved
in the Sasol-U.S. base case (see Figure 7-1). This may, in fact, be
conservative as the fraction of the Kolbel product already in the
gasoline range is higher than that of the base case.

Table VII-3 shows the final product slate obtained from the
refining of the raw Kolbel products. For the mixed output case the
finished products consist of SNG, gasoline, C_3 LPG, diesel, fuel oil
and alcohols. The small amount of butane produced is blended in with
the gasoline fraction. Table VII-3 also shows the products obtained
from coupling the BGC Lurgi with a F-T Synthol synthesis reactor and the
Sasol-U.S. dry-bottom-Synthol base case for comparison. The Kolbel-BGC
system produces a finished product slate containing less SNG and a far
greater quantity of gasoline. The Kolbel system produces 39% more

TABLE VII-3

PRODUCTS AFTER DOWNSTREAM PROCESSING
(Mixed Product Case)

	BGC (Kolbel)	BGC (F-T)	SASOL (US)
SNG (MM SCF/SD)	94.2	147.9	173.3
Gasoline (B/SD)	30,766	19,137	13,580
C_3 LPG (B/SD)	3,084	1,604	1,107
C_4 LPG (B/SD)	-	212	146
Diesel (B/SD)	3,821	3,343	2,307
Fuel Oil (B/SD)	398	901	622
Alcohol (B/SD)	618	2,650	1,829
Total Liquids (B/SD)	38,687	27,847	19,591
FOE* (B/SD)	47,636	47,418	44,950
Efficiency, percent **	60.4	60.1	57.0
B Liquid Fuels/Ton Dry Coal	1.93	1.37	0.98
B Liquid Fuels C_4^+/Ton Dry Coal	1.78	1.31	0.92

* Fuel Oil Equivalent = $\Sigma HHV/6.0 \times 10^6$

** Product HHV/Coal HHV $\times$ 100

liquid products than the BGC-Synthol system and 97% more liquids than the Sasol-U.S. dry-bottom Synthol system. The (HHV) efficiencies based on total coal input to plant are similar for the BGC Synthol and Kolbel coupled systems and are three efficiency points higher than the base case. Total liquids expressed as barrels per ton of dry coal for BGC-Kolbel are double that of the Sasol-U.S. case. It should be emphasized that the figure of 1.78 barrels of liquid products/ton dry coal represents barrels of finished consumer grade products and not barrels of a synthetic crude oil that has to be further refined.

Figure 7-1 schematically represents the system energetics for the BGC-Kolbel mixed product case. The overall efficiency expressed as a ratio of the Btu flux crossing the synthesis input to the Btus leaving is .817. Because this plant configuration produces SNG and liquid fuels, both a F-T synthesis unit and a methanator are unit processes in the synthesis section. The F-T synthesis (Kolbel unit) is 76.3% efficient which compares to a theoretical efficiency for the unit of 78%. The C_1 and C_2 hydrocarbons formed during the synthesis are sent to the methanator unit. The C_1 hydrocarbons are inert while the C_2 hydrocarbons are converted predominently to methane. The methanation of unconverted carbon monoxide to methane is only a minor fraction of the total flow to the unit, hence the overall efficiency of the unit is 99%. The refining and upgrading section contains the liquids upgrading and the SNG train. The overall thermal efficiency of the section is 95.8% with the liquids refinery being 94.4%.
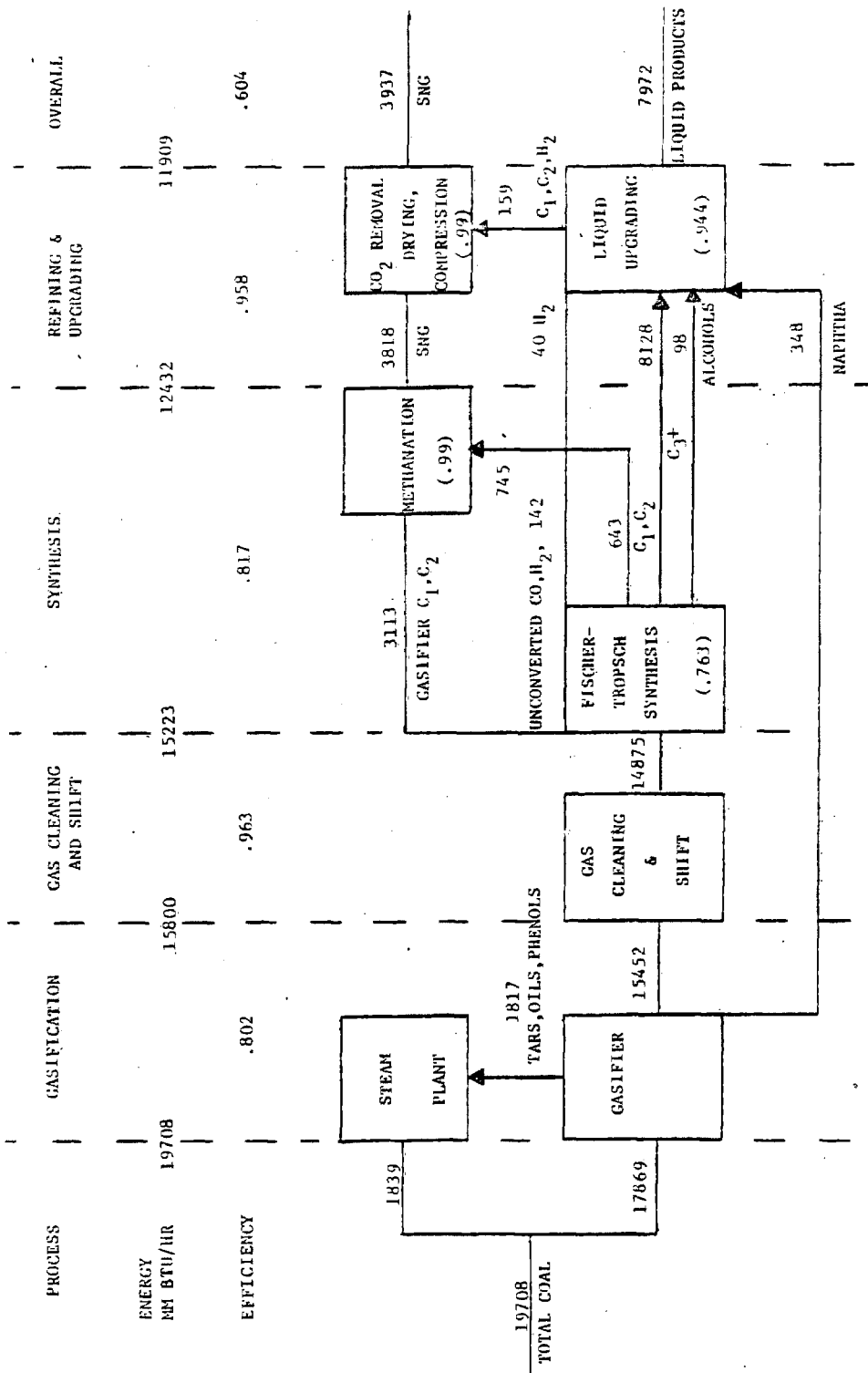
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FIGURE 7-1
SYSTEM ENERGETICS FOR BGC GASIFICATION/
KOLBEL SYNTHESIS (MIXED PRODUCT CASE)