

(iv) Costs

An estimate of the costs of acetylene production from ethane was made by the I.G. in connection with the proposed Heydebreck plant.

The capital cost for a plant to produce 1 ton/hour of acetylene, together with 10,000 M<sup>3</sup>/hour of synthesis gas was calculated to be 2 million RM, made up as follows:-

Acetylene Generators (5 units)	700,000 RM
Compressors for acetylene concentration	600,000 RM
Acetylene scrubbing plant	400,000 RM
Secondary treatment of synthesis gas with oxygen	300,000 RM

The estimated operating costs are shown below:-

Ethane	3070 M <sup>3</sup> /hr. @ 0.71 pfg/1000 WE	307.00 RM/hr.
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Acetylene Synthesis costs

Oxygen	3130 M <sup>3</sup> /hr. @ 2.2 Pfg/M <sup>3</sup>	68.20 RM/hr.
Fuel Gas	1.67 x 10 <sup>6</sup> WE @ 0.45 Pfg/1000 WE	7.55
Electric Power	120 KWH @ 0.014 RM	1.68
Cooling Water	160 M <sup>3</sup> @ 0.02 RM/M <sup>3</sup>	3.20
Wages	5 Man hours @ 2.40 RM	12.00
	including 50% oncost.	
Repairs	) 18% on capital value	14.50 RM/hr.
Amortization		
Taxes		
TOTAL		414.13

Acetylene Concentration

Electric Power	1900 KWH @ 1.4 Pfg/KWH	26.60
Cooling & Wash Water	300 M <sup>3</sup> /hr. @ 2.0 Pfg/M <sup>3</sup>	6.00
Lube Oil	1 kg/hour @ 50 Pfg/kg.	0.50
Wages etc.	3 Man/hours @ 2.40 RM	7.20
	including 50% oncost.	
Repairs	) 18% on capital value	20.70
Amortization		
Taxes etc.		
TOTAL		61.00

Secondary Treatment of Synthesis Gas.

Oxygen	349 M <sup>3</sup> /hr. @ 2.2 PfG/M <sup>3</sup>	7.70
Cooling Water	30 M <sup>3</sup> /hr. @ 0.02 RM/M <sup>3</sup>	0.60
Wages	2 Man/hours @ 2.40 RM including 50% oncost.	
Repairs	)	
Amortization	) 18% on capital value	<u>6.20</u>
Taxes etc.	)	
TOTAL		19.30
Grand Total		494.43
Credits	9750 M <sup>3</sup> /hr. Synthesis gas at 2.7 PfG/M <sup>3</sup> <sup>x</sup>	264.00
Cost of 0.975 Tonnes Acetylene		230.43
Cost RM/Tonne Acetylene		236.00

<sup>x</sup> Oppau cost at end of 1939.

The above data should be sufficient for the process to be cost-  
ed under British or American conditions.

(v) Fundamental Data for Design of Burner.

The I.G. have clearly carried out a great deal of fundamental research on flame speeds, flame extinction velocities etc. for various gas mixtures. Some of this work is covered by the documents brought back from Germany but a much closer study of these papers, and possibly further contact with the authors, is necessary in order to prepare an intelligible summary of this research.

## III.

AMMONIA SYNTHESIS

A very casual inspection of the plant and interrogation of Dr. Gogel (head of the Oppau high pressure department) revealed no major developments in this field. The maximum capacity of the Oppau plant was 800 T/day nitrogen as ammonia and a considerable part of this was exported as liquid ammonia to Höchst, Wolfen and Bitterfeld.

There is a plant at Oppau for the synthesis of 60 T/day of Urea. It operates at a pressure of 150 atmospheres without a catalyst. Formerly, the plant was lined with Monel metal but, during the war, lead linings have had to be used. The compressor units attached to this plant have been badly damaged by air attack.

A note prepared by Dr. Wurster (Managing director of Oppau and Ludwigshafen) for the Ludwigshafen Military Government, giving the latest

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estimates of the potential production capacity of the Oppau plant for ammonia and fertilizers, is reproduced in Appendix C.

## IV.

METHANOL AND HIGHER ALCOHOLS SYNTHESIS

Two methanol units were normally on line at Oppau. Each had a single 800 mm x 12 M converter with a capacity of 70 T/day of methanol. Reaction pressure was 230 atmospheres, reaction temperature 360°C and the catalyst a mixture of zinc and chromium oxides.

Eight similar units were normally in operation for synthesis of higher alcohols. Pressure and reaction temperature is the same as for methanol but the throughput is lower and the catalyst is alkalinized. The average catalyst life is three months. Each unit produced 40-50 T/day crude product of the following average weight composition:-

Methanol	55%
Dimethyl Ether	1.5 - 2.0%
Olefins (C <sub>2</sub> - C <sub>7</sub> )	0.7%
n-Propyl Alcohol	1-1.3%
Iso Butyl Alcohol	11-13%
Higher Alcohols	6-7%
Ketones	0.6-0.7%
Water	20.3-24.2%

The crude product is separated into two layers, the upper layer going to a stabilizer operating at 3 atms. pressure. In this stabilizer the overhead material consists of dimethylether and a part of the olefins. The bottoms pass to column II, operating at atmospheric pressure, where methanol is taken overhead. The bottoms from this column are blended with benzene in the ratio of 2 to 1 and pass to column III where water, benzene and normal propyl alcohol are taken overhead; isobutyl, some n-propyl alcohol and some of the higher alcohols are taken off as a side stream, while the remainder of the higher alcohols and ketones is removed as bottoms. The sidestream from column III is fed to column IV where normal propyl alcohol is removed overhead, and the bottoms are fed to column V which separates isobutyl alcohol from higher alcohols. The isobutyl alcohol coming overhead in column V has a purity of 97-98%.

The overhead from the azeotropic distillation carried out in column III, using benzene, is separated into two layers, and the upper layer, consisting of benzene and normal propyl alcohol, is redistilled in column VI to give benzene (for recycle) as the overhead fraction, and normal propyl alcohol which is sent to storage. Another auxiliary column separates higher ketones which are removed as a sidestream in column II.

An interesting point in the isobutanol synthesis is the fact that all the methanol produced in the process is returned as recycle to the reaction system. The main reason given for this is that the methanol from this process is difficult to refine up to market specifications.

The higher alcohols produced in the isobutanol synthesis have been hydrogenated to the corresponding hydrocarbons which are used as aviation fuel components. The higher ketones, consisting primarily of di-isopropylketone, have been used as solvents and have also been hydrogenated to hydrocarbons.

V. HYDROGENATION & RELATED PROCESSES

(A) Production of Synthetic Fuels at Ludwigshafen/Oppau.

Production of synthetic fuels at Ludwigshafen/Oppau has been limited to the emergency use of the high pressure Research Department pilot plants consisting of 6 - 500 mm. diam. and 4 - 800 mm. dia. hydrogenation converters. The chief production use to which this equipment was put was the improvement of gasoline quality by dehydrogenation (See D.H.D. process)

The feed material was partly imported from Wesseling and partly derived from Bruxhal crude petroleum during the course of its refining to give lubricating oil at Oppau. The maximum output of "D.H.D. gasoline" was at the rate of 25,000 tons/year. It was planned to extend D.H.D. activities, and a plant on the Oppau site for production of roughly 100,000 tons/year had been practically completed. At the time of the Allied occupation this plant was being dismantled and removed for re-erection, probably at Bittefeld.

Distillation connected with the emergency production of D.H.D. gasoline in the research equipment was carried out in new stills built on the Oppau site adjacent to the new D.H.D. plant.

There was also a small production of finished liquid fuel products from the operation of the pilot plant converters principally on tar and petroleum oil residues. This was probably incidental to research work on these raw materials. The total hydrogen delivered to the hydrogenation Research Department was not more than 1,500 - 2,000 M<sup>3</sup> per hour and it is therefore unlikely that the production of finished products could have exceeded 5,000 tons per year.

(B) General Review of German War-Time Operations and Developments.

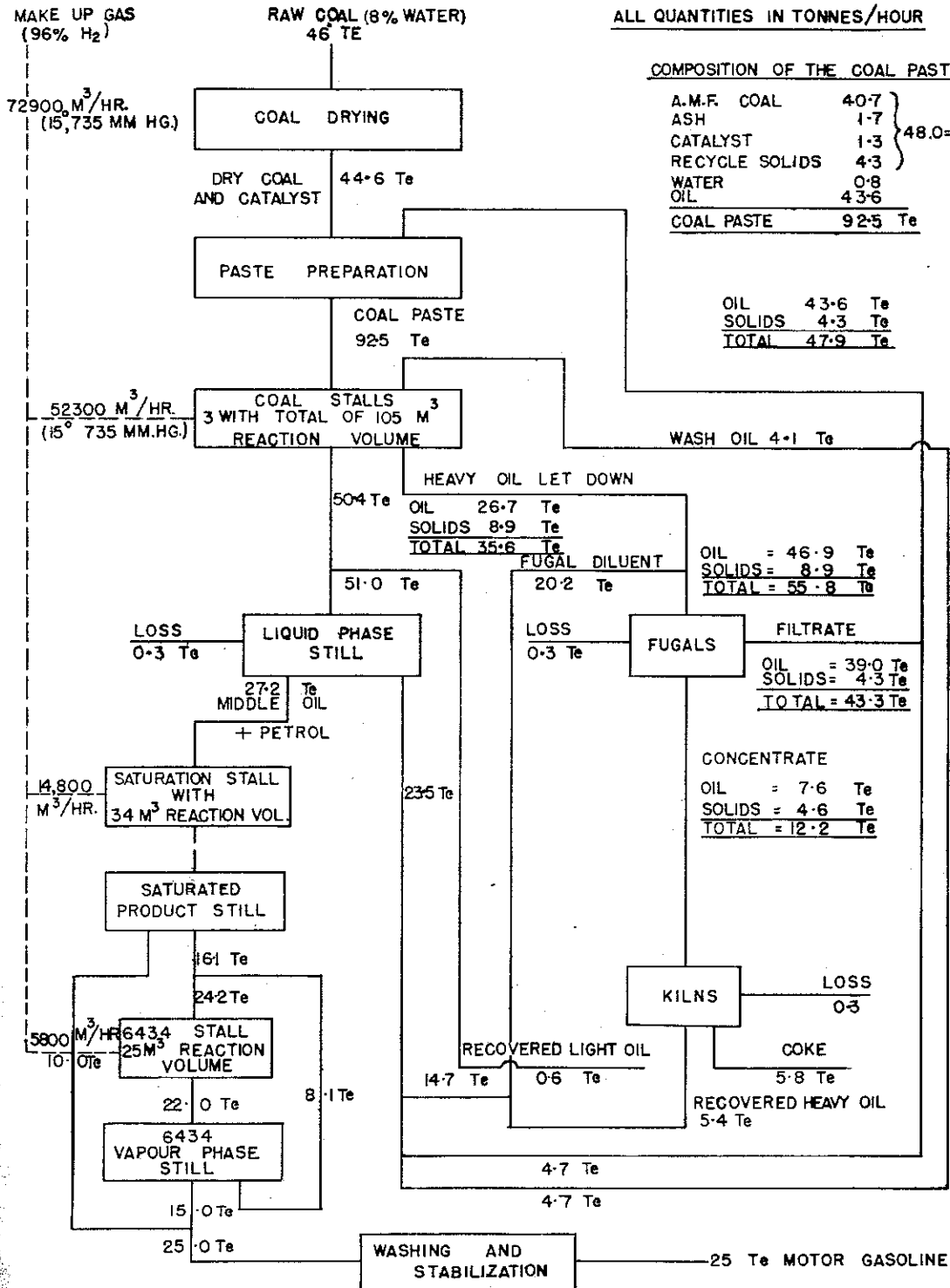
Although there was no large-scale hydrogenation at Ludwigshafen/Oppau, the Research and Technical Department directed by Dr. Pier was known to have played a great part in the planning of the new hydrogenation projects in Germany. All the more important members of the staff of this Department, including Dr. Pier himself, were located in Heidelberg on 1.4.45 and interrogation revealed the following general picture of German war-time hydrogenation development :

a) Bituminous Coal Hydrogenation

The plant at Scholven, put into operation in 1936, employs a pressure of 300 ats. for the coal liquefaction stage. Acid catalyst conditions are employed, i.e. tin oxalate catalyst (.06% on coal) is added to the feed paste and ammonium chloride (.7-1% on the coal) is injected to the first converter. Corrosion is avoided by the injection of sodium carbonate at the end of the last converter.

The number of coal stalls at Scholven has been increased to 6 during the war and the capacity of the plant brought up to 200,000 tons/year of finished product, mainly aviation base gasoline.

MAKE UP (96% H<sub>2</sub>)  
72900 M<sup>3</sup>/t (15,735)  
52300 (15° 72)  
4,800 M<sup>3</sup>/HR  
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FLOWSHEET FOR BITUMINOUS COAL HYDROGENATION (RUHR COAL) TO 200,000 T<sub>e</sub>/YR MOTOR GASOLINE. FIGURE XII

Because of the difficulty in obtaining tin oxalate, other tin compounds, and occasionally lead salts, have been substituted. The latter were found to give higher yields of "unconverted" coal. Apart from minor changes of this type, there has been no modification of the process and no marked improvement in efficiency during the war. The yield of aviation gasoline obtained is just over 50% on the a.m.f. coal.

The new bituminous coal hydrogenation plants, namely, Gelsenberg, Stettin, and Blechhammer, employ a pressure of 700 ats. in the liquid phase stalls. Alkaline catalyst conditions are employed. 1.2 - 1.7% of iron sulphate (including water of crystallization) is added to the coal before drying. 1.5 - 2.5% of Bayermasse (an iron rich residue from aluminium manufacture) is then added and finally, at the pasting stage, .3% of sodium sulphide is introduced. The above quantities are % by weight on the dried coal treated. It should be noted that acid reaction conditions cannot be used at 700 ats. because the iron/HCl/H<sub>2</sub>S equilibrium is such that corrosion occurs in the converter and hot catchpot. At 300 ats, corrosion does not occur above about 350°C and addition of alkali before the products are cooled in the inter-changers is sufficient to avoid corrosion trouble.

The use of the higher pressure permits the use of a higher average reaction temperature, 480°C as compared with about 460°C for the 300 ats process. As a result of the increased temperature and pressure, the throughput of coal for a given reaction volume is some 60% greater in these new plants than at Scholven. On the other hand, standard 700 ats converters have only 75% of the reaction volume of those operating at 300 ats so that the throughput of coal per converter is only some 20% higher at the higher pressure.

From the standpoint of yield, the main advantage of 700 ats. operation is a reduction in the amount of "unconverted" coal residue. This is usually 3-4% on the ash-and-moisture-free coal at 700 ats compared with 7-8% for 300 ats operation. This has the secondary effect that, since less solid material has to be purged from the system, the loss of oil in the sludge recovery section is lower. Under 700 ats operating condition the asphalt destruction is also improved. This leads to much easier handling of the intermediate products and also to an improved efficiency of oil recovery in the carbonisation of the final sludge residue. 700 ats operation gives no reduction of hydrocarbon gas make in the coal liquefaction stage. This is presumably because the alkaline catalyst conditions are, other things being equal, less favourable from a standpoint of gas production than tin and chlorine.

The overall improvement in gasoline & middle oil production from bituminous coal when using 700 ats is roughly 4-5% on the a.m.f. coal, equivalent to 7-8% improvement on the 300 ats results.

Fig. XII and Table I summarise the results which Dr. Pier and his colleagues consider could be achieved under steady operating conditions when hydrogenating a Ruhr coal of 83% carbon content (ash-and-moisture-free basis) to motor gasoline (max. FBP 200°C, minimum octane number 65) The 700 ats alkaline catalyst process is assumed for the coal liquefaction stage, vapour phase treatment of the resulting middle oil

being carried out at 300 ats. This flowsheet data should be compared with the achieved results at Gelsenberg and with any basic flowsheets obtained at Scholven for 300 ats. acid catalyst operation.

b) Brown Coal Hydrogenation.

The Leuna plant was forced to turn over to brown coal tar hydrogenation as a result of air raid damage in 1944, but prior to this the main raw material at this factory continued to be brown coal. The capacity of the plant had been considerably increased to more than 1,000,000 tons of dried brown coal per year. Bayermasse was used as catalyst. The Leuna plant suffered from the disadvantage that the pressure was low (230-250 ats). There have been no major modifications of the process since the war.

Rhine brown coal is hydrogenated at Wesseling to give about 200,000 tons/year of finished product. This particular brown coal is "older" than the middle German coals, and the coal liquefaction stage is operated at 700 ats.

c) Brown Coal Tar Hydrogenation, T.T.H. and M.T.H. Processes.

The three Brabag plants, Bohlen, Magdeburg and Zeitz, have continued to operate on brown coal tar and one of the newer plants, the Hermann Göring Factory at Brux, also operates on this raw material. The output of finished products from the three Brabag plants has been of the order of 250,000 tons a year each, while the Brux plant has a capacity of 400,000 tons/year. At Bohlen, Magdeburg and Brux the process was in all major respects identical to that operated before the war, with the exception that iron on active coke had replaced molybdenum on coke as liquid phase catalyst. This was necessary because of the scarcity of molybdenum.

The above brown coal tar plants produced motor and aviation gasoline and also a certain amount of diesel oil. Latterly, they produced considerable quantities of jet fuel. (See Jet Fuel).

The brabag plant at Zeitz operated under entirely different conditions using a process developed by the Ludwigshafen Research Department. This, the T.T.H. process, consists of single pass treatment of crude brown coal tar over an active hydrogenation catalyst under low temperature conditions. The refined tar, product, is fractionated to give low quality petrol, a moderately good diesel oil, a refined wax and lubricating oil. The main features of the process are shown in Fig. XIII. In order to reduce its solids to less than .1%, the tar is first fuggalled and filtered. The fuggalled tar is then preheated with hydrogen (2,500 m<sup>3</sup> hydrogen per ton of oil) and fed to reactors operating at 300 ats and an average temperature of 360°C. The catalyst employed is tungsten sulphide (5058) or a new saturation catalyst (8376) which will be described later under vapour phase hydrogenation. The throughput is 1 kilo per litre of catalyst per hour. Catalyst life is of the order of 6 months. The hydrocarbon gas make is 1-2% of the fresh feed and the hydrogen absorption 500-550 m<sup>3</sup> per ton of tar.

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FIG. XIII

FLOW DIAGRAM

T.T.H. PROCESS

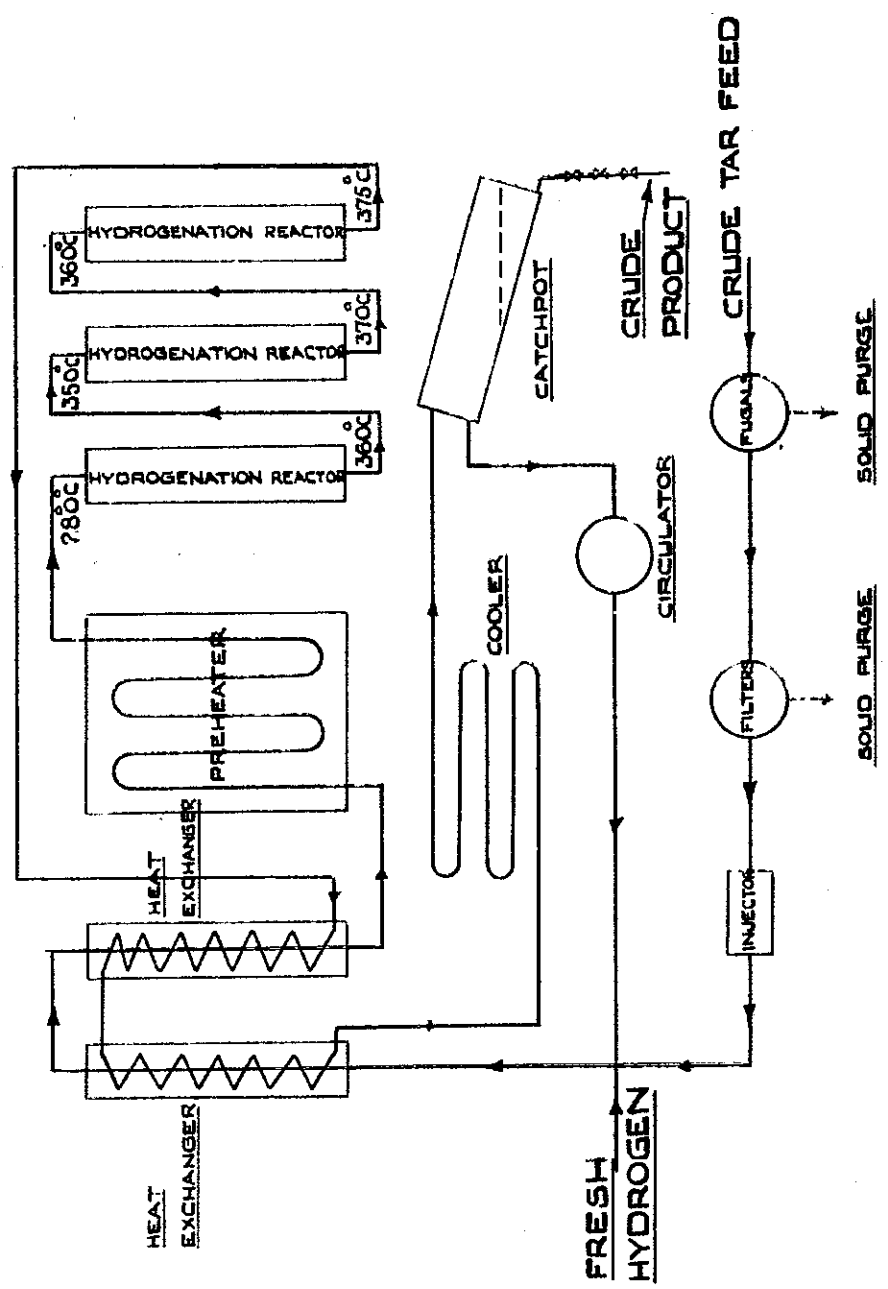




TABLE I

Hydrocarbon Gas Production when making Motor  
Gasoline from Different Raw Materials

200,000 t/year = 25 t/hour Motor Spirit

<u>Raw Material</u>		<u>Bituminous Coal</u>	<u>Bituminous Coal High Temperature Tar</u>	<u>Natural Oil Residuum</u>
<u>Liquid Phase</u>				
Methane	t/hr	2.3	1.3	0.96
Ethane	"	2.0	1.2	0.63
Propane	"	2.6	1.5	1.16
n-Butane	"	1.3	0.76	0.95
i-Butane	"	0.16	0.09	0.02
<u>Total</u>	t/hr	<u>8.36</u>	<u>4.85</u>	<u>3.72</u>
<u>Saturation</u>				
Methane	t/hr	0.13	0.13	0.08
Ethane	"	0.10	0.10	0.06
Propane	"	0.27	0.27	0.17
n-Butane	"	0.16	0.16	0.10
i-Butane	"	0.16	0.16	0.10
<u>Total</u>	t/hr	<u>0.82</u>	<u>0.82</u>	<u>0.51</u>
<u>Splitting</u>				
Methane	t/hr	0.028	0.037	0.035
Ethane	"	0.014	0.018	0.016
Propane	"	0.28	0.37	0.35
n-Butane	"	0.24	0.32	0.30
i-Butane	"	0.71	0.94	0.90
<u>Total</u>	t/hr	<u>1.272</u>	<u>1.685</u>	<u>1.601</u>
<u>Overall</u>				
Methane	t/hr	2.46	1.47	1.08
Ethane	"	2.11	1.32	0.71
Propane	"	3.15	2.14	1.68
n-Butane	"	1.70	1.24	1.35
i-Butane	"	1.03	1.19	1.02
<u>Total</u>	t/hr	<u>10.45</u>	<u>7.36</u>	<u>5.84</u>