THE TEXAS COMPANY

REFINING DEPARTMENT
TECHNICAL & RESEARCH DIVISION



REPORT ON

HYDROGENATION OF CARBON MONOXIDE
CORRELATION OF SYNTHESIS DATA

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Laboratory Engr'g. Dev. Group N.Y.Offie

Report No. 1

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TECHNICAL AND RESEARCH DIVISION

ENGINEERING DEVELOPMENT GROUP (NY. OFFICE)

REPORT NO. 1

HYDROGENATION OF CARBON MONOXIDE CORRELATION OF SYNTHESIS DATA

SUMMARY

The results of several runs on the Beacon synthesis units #7 and #8 which were made at various operation conditions with many different catalysts have been compared graphically in considerable detail with similar data supplied by Hydrocarbon Research Inc.

Correlation:

The correlations obtained are summarized on the following Fig. S. From these graphs, if the fresh feed composition and % contraction are known, it is possible to estimate the degree of conversion attained, the yields of CO_2, light hydrocarbon components, liquid hydrocarbons, oxygenated compounds and the degree of unsaturation of the light hydrocarbon fractions.

Measure of Process Efficiency:

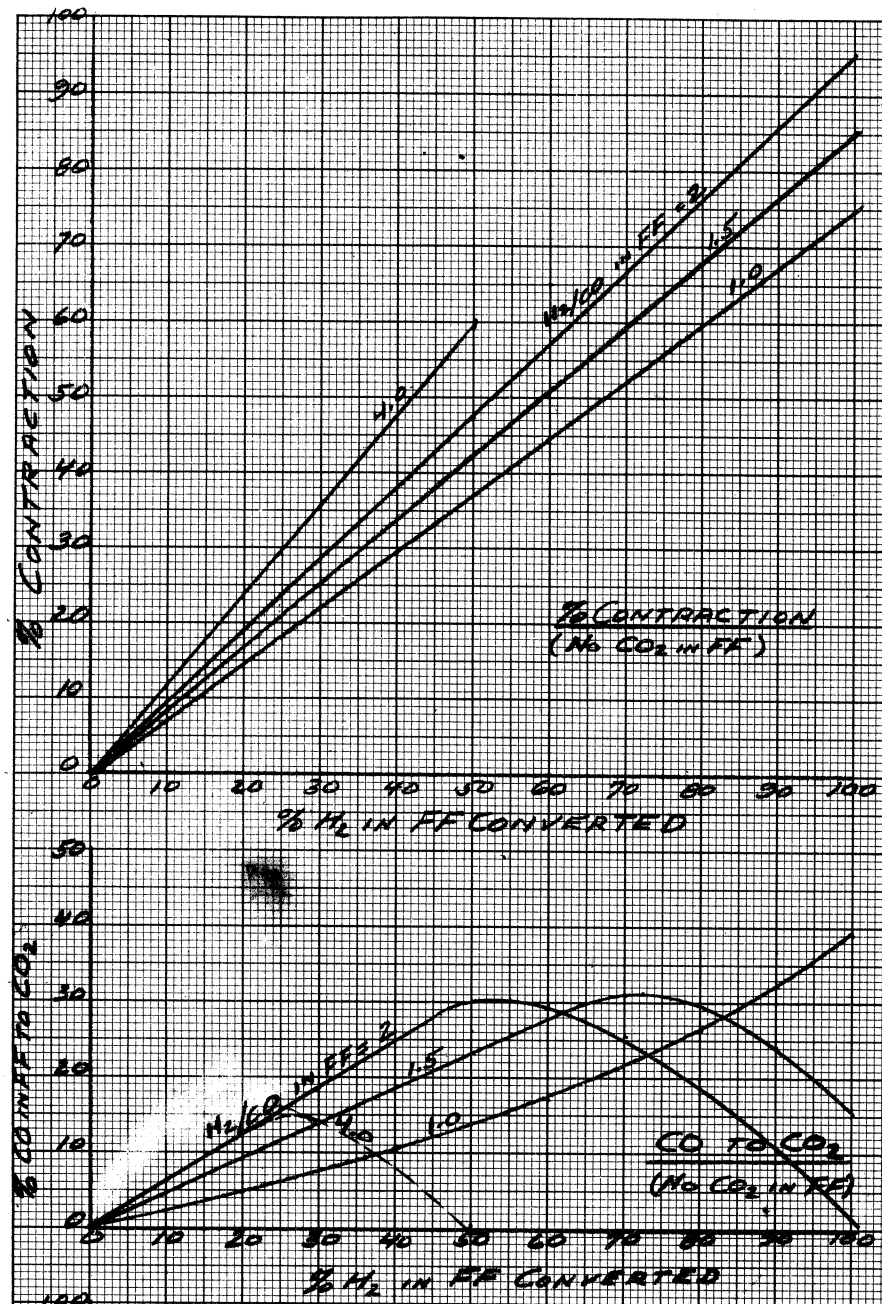
It has been established that CO conversion is a very poor measure of process efficiency. Contraction and disappearance of H_2 in the Fresh Feed are much more significant.

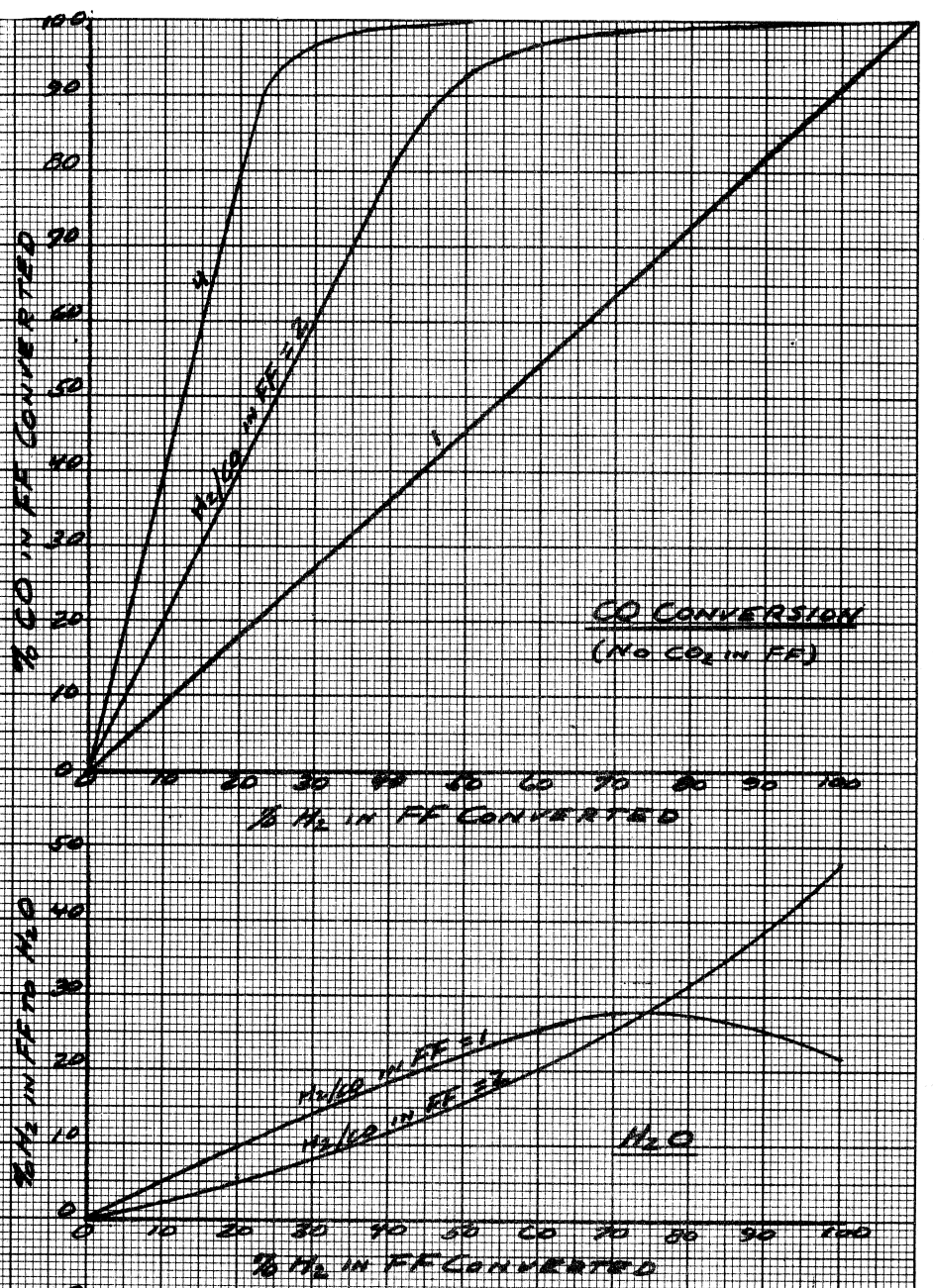
Process Mechanism:

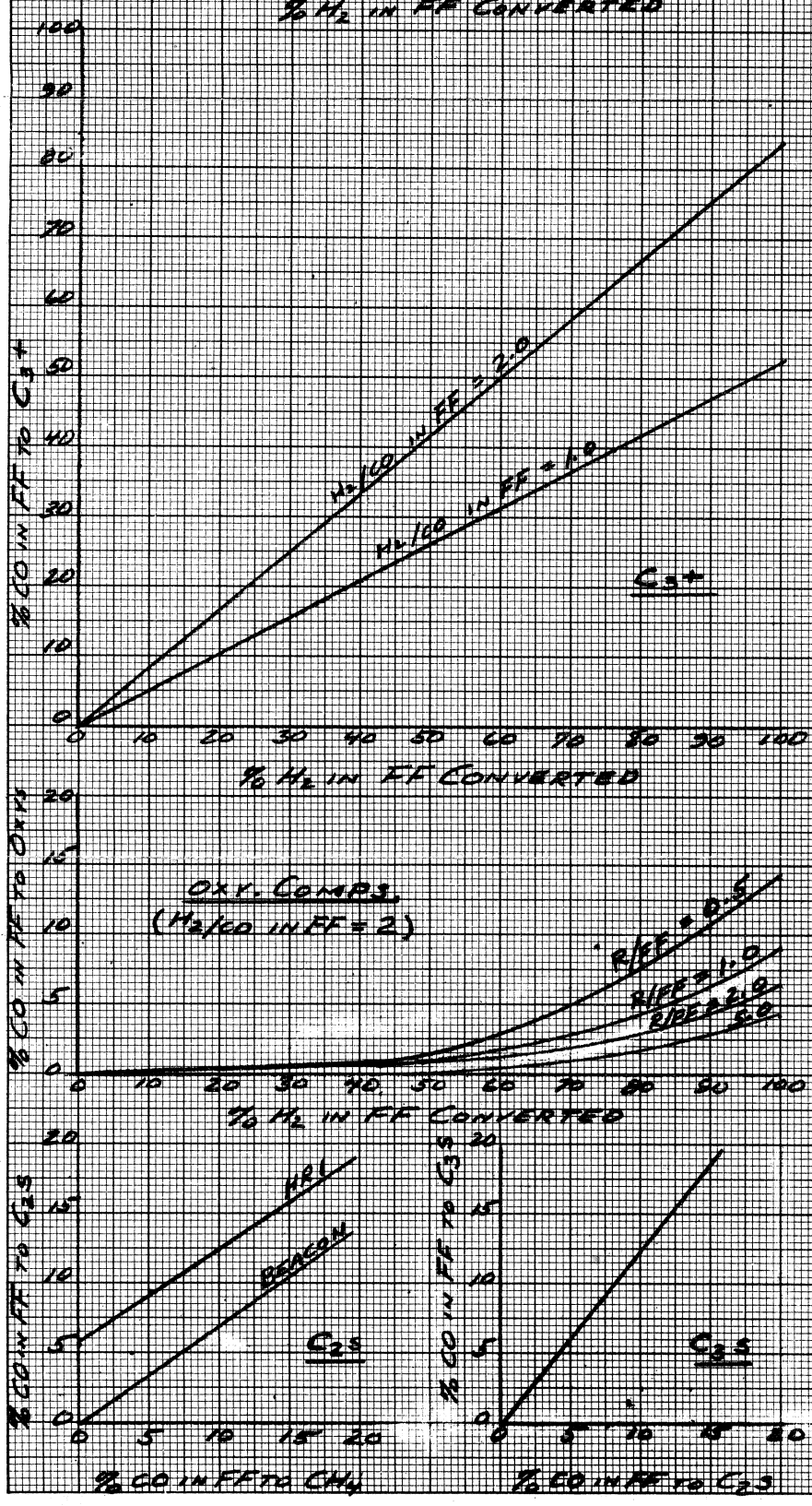
From these correlations it has been deduced that the reactions and mechanism involved in the process are similar to those proposed by Craxford* for fixed bed operation with cobalt catalysts. In the present case however, with a fluidized bed, the catalyst particles whether carbided, oxidized or uncombined are all mixed together so that the reactions proceed more or less simultaneously instead of stepwise as proposed by Craxford.

Notwithstanding this complication, the process appears to be relatively simple and quite inflexible. Although more study and further

* "On the mechanism of the Fischer-Tropsch Reaction", S.R. Craxford - Proc. of Faraday Soc. August, 1946







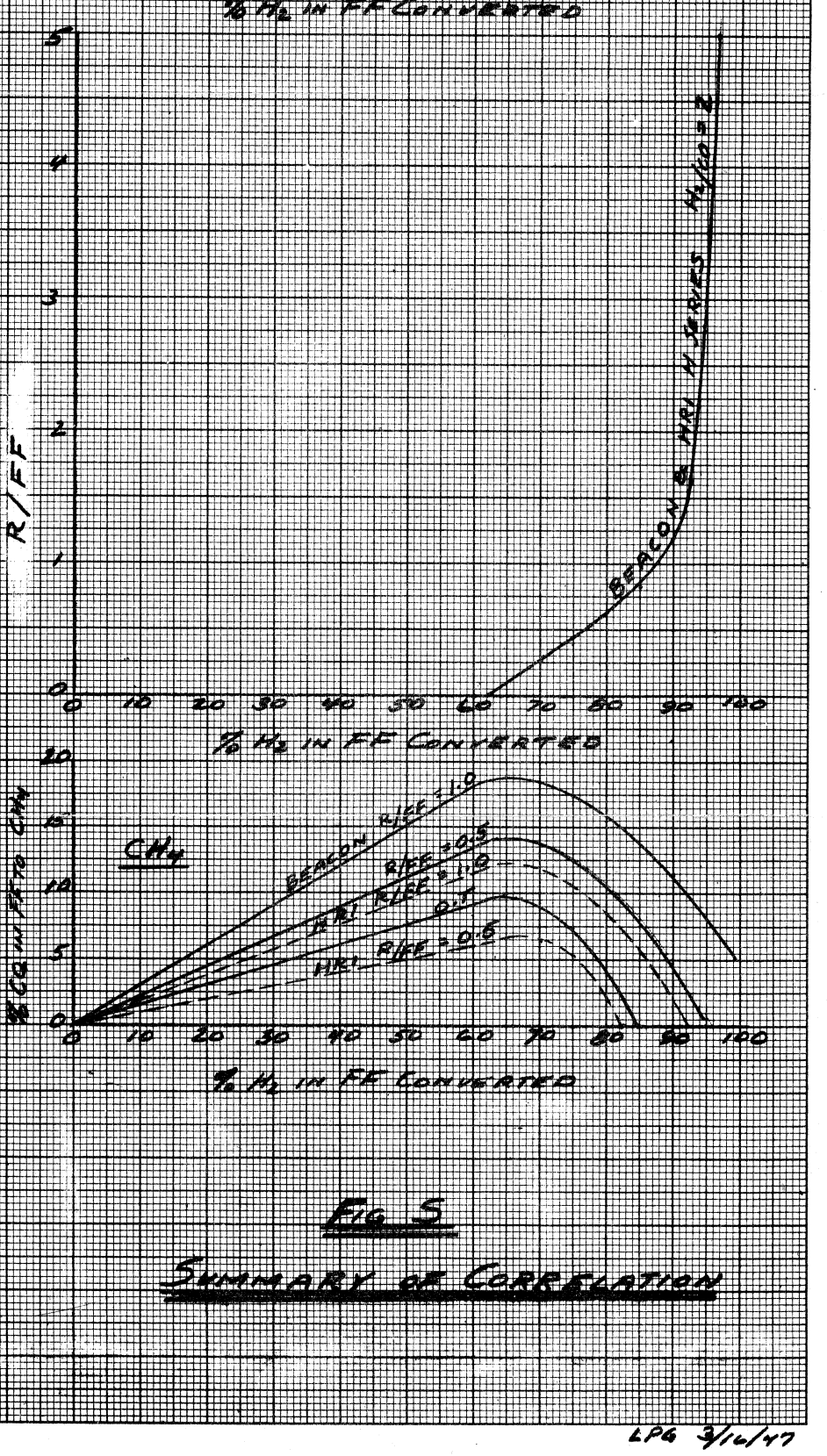


Fig 5

Summary of Correlation

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S-2

quantitative data are required, there are certain deductions which seem well founded at this time and a working hypothesis based on these deductions is proposed.

The process is not one of equilibrium. Instead it involves a series of competing reactions of different rates. Some of the reactions are reversible at these conditions but some are not.

Basic Reactions:

When H_2 and CO are first contacted with a suitable catalyst the two most important reactions are the basic synthesis reaction:

(1) $2H_2 + CO = (=CH_2) + H_2O$

and the water-gas shift to the right:

(2) $H_2O + CO \longrightarrow H_2 + CO_2$

The basic synthesis reaction is about twice as fast as the shift so that, at first, the ratio of consumption of H_2 and CO is about one to one. This is true regardless of the ratio of H_2/CO in the reactor feed.

After these reactions have proceeded far enough to consume most of the CO they both slow down because of the reduced partial pressure of the CO. The shift slows down still further because it is nearer to equilibrium than before as a result of the increase in CO_2 concentration.

Oxygenated Compounds:

At this point the ratio of H_2/CO consumption increases and a third slower reaction begins to manifest itself. This is the reaction or reactions responsible for the production of oxygenated compounds. The exact nature of this reaction has not been established. Furthermore the literature on methanol synthesis is not entirely conclusive. Some authors suggest that the oxygenated compounds are formed through CO_2 thus:

(3) $3H_2 + CO_2 = CH_3OH + H_2O$

while others believe that the all oxygenated compounds are produced through CO and the formaldehyde step thus:

(4) $CO + H_2 = HCHO$

(5) $HCHO + H_2 = CH_3OH$

It seems to be agreed however that the higher alcohols and other oxygenated compounds all stem from methanol through condensation and other similar secondary reactions thus:

(6) $2CH_3OH \rightleftarrows C_2H_5OH + H_2O$

It is also agreed that the oxygenated compound reactions such as the above are completely reversible.

Reversal of Water Gas Shift:

The above primary reactions (three) proceed simultaneously, each at its own relative rate with the continued production of CO_2 and consumption of CO and H_2 until a point is reached where the relative concentration of the reactants dictates that the water-gas shift starts reversing to the left and CO_2 starts to disappear thus:

(2) $H_2O + CO \longleftarrow H_2 + CO_2$

This occurs only if there is enough H_2 left in the system at the time the reversal would normally start. The point where reversal begins does not necessarily coincide with the reaching of the water-gas shift equilibrium. The reversal may start when the ratio $(H_2)(CO_2)/(H2O)(CO)$ is equal to 10 or 60 compared with an equilibrium value of about 22. The point of reversal is dependent not on the concentration of the reactants alone, but on the relative rate of production or consumption of these reactants by the other reactions which are proceeding simultaneously.

Reversal of Oxygenated Compound Reactions:

As the consumption of H_2, CO and CO_2 proceeds still further with the continued production of hydrocarbons and H_2O the concentration of H_2O or oxygenated compounds becomes so great that the oxygenated compound reactions also start to reverse.

Ultimate Product:

Theoretically, the process proceeds as though it were trying to make only $(=CH_2)$ and H_2O. The CO_2 and oxygenated compound production are only the result of reversible side reactions and both of these products would disappear if the reactions could be carried to completion.

Gas Production:

It is believed that the basic synthesis reaction proceeds on the catalyst surface in a manner something like that described by the "carbiding theory" proposed in the literature. That is, unsaturated molecules (multiples of $=CH_2$) continue to grow on the surface until they are detached, probably by hydrogen. According to this theory, unsaturated molecules of

any length may be formed depending to a large extent upon laws of probability and relative concentration at any instant of the active components involved in this mechanism.

It is probable that all the light unsaturated hydrocarbons such as ethylene, propylene and butylene are formed in this manner, as a direct result of primary reactions.

The methane and other light paraffin gases such as ethane, propane and butane on the other hand can be formed in two ways:

A. Directly by primary reactions such as:

(7) $H_2 + (=CH_2) = CH_4$

(8) $3H_2 + CO = CH_4 + H_2O$

(9) $2H_2 + 2CO = CH_4 + CO_2$

(10) $4H_2 + 2CO = C_2H_4 + 2H_2O$

etc.

These primary reactions are slow compared to the basic synthesis reaction and the water-gas shift and occur only under conditions where the CO concentration stays high throughout the reaction time which in turn only happens when the basic and shift reactions are slow.

B. Methane and other light paraffins are formed as a result of secondary hydrogenation-cracking reactions.

According to the carbiding theory the unsaturated primary product molecule may grow to waxlike proportions before being detached from the surface. Such large molecules are slow to desorb and are relatively easy to crack. It is reasonable to believe therefore that a large percentage of the light paraffin gases are produced in this manner. This satisfactorily explains the fact that wax yield is only high when the reaction temperature is low and the methane yield is always relatively high when the reaction temperature is high. This also accounts for the fact that a good cracking catalyst makes a poor synthesis catalyst and vice versa.

Other Secondary Reactions:

There are probably proceeding in varying degrees throughout the reaction zone other secondary reactions involving the products themselves such as polymerization, dehydrogenation, hydrogenation, cracking, etc., which are responsible for the fact that aromatics are found in the liquid

product. This type of reaction may also be responsible partly for the carbon or coke found in catalyst deposit but no consideration has been given to such secondary or trace reactions in this report.

"Catalyst Equilibrium"

The above completes the description of our interpretation of the various steps involved in the entire process.

Unfortunately the reactions do not proceed through these various steps without interruption. The catalyst is apparently a definite intermediate for the primary reactions and it seems to remain active only so long as the oxidizing tendency of the surrounding medium does not equal some function of the carbiding and reducing tendency of the same medium. When these two are equal, or perhaps when one exceeds the other by too much, all primary reactions cease. What relationship of the components in the reactor are responsible for this "catalyst equilibrium" has not been established. It may occur during any of the phases of the process described above, depending upon the initial composition of the feed to the reactor. It may be affected by the amount of undesorbed product on the catalyst but it appears quite likely that the relative concentration of oxidizing, reducing and carbiding components at that instant is the most important factor.

The fact remains, that once this "catalyst equilibrium" condition is reached, further disappearance of H_2 or CO can only be accomplished by upsetting that equilibrium by recycling or by otherwise changing the composition of the reactor feed.

Effect of Operating Variables:

The degree of conversion that can be attained before "catalyst equilibrium" is reached may be influenced by many factors but the most important appears to be composition of reactor feed. This in turn, determines product distribution so it can be seen that both conversion and product distribution can be controlled to a large extent by simply controlling feed composition, that is, fresh feed quality and recycle ratio.

The type and activity of catalyst obviously has a profound effect. Space velocity, temperature and pressure are important particularly with respect to the secondary reactions.

When with a given bed of catalyst, conditions are such that primary reactions are fast and "catalyst equilibrium" is reached and the primary reactions stop early in the bed, then there is more time in the remainder of the bed for secondary reactions to occur. If the basic synthesis reaction and the gas-shift are slow so that "catalyst equilibrium" is not reached until late in the bed or not reached at all, then a higher average concentration of CO is available a longer period of time for the slower reactions and product distribution is affected correspondingly.

A discussion of the effect of some of the variables is included in the report. It is pointed out that when considering the effect of recycle ratio it should be remembered that the effect of recycling will be different with a fresh feed that would have reached "catalyst equilibrium" when running once through than it will be when conditions are such that equilibrium would not be reached in once through operations.

Conclusion:

The study of the effect of operating variables and the full significance and application of this hypothesis is by no means complete and further time and thought on the subject are well warranted. It was felt advisable to present results to date however so that others might benefit from the developments made so far.

F O R E W O R D

Because of the large number of graphs involved in this report, they have all been arranged in the order discussed and have been bound together. It is suggested that they be removed from the report for ease in reference as the report is read.

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I. INTRODUCTION

Many theories have been offered to explain the mechanism and effect of operating variables on the Fischer-Tropsch synthesis of H_2 and CO to hydrocarbons. In the literature however, such theories have been based exclusively on data obtained with fixed catalyst beds and principally with cobalt catalyst.

Several runs have now been made with a fluidized catalyst bed using iron catalysts in the stirred reactor unit #7 and the baffled reactor unit #8 at The Texas Company, Beacon Laboratory. It was interesting to see how these results compared with those obtained by others. To accomplish this comparison, the data were plotted up on a large number of graphs hoping that an analysis of these graphs might empirically lead to correlations which would enable the prediction of yields and product distributions as well as throw some light on the nature of the reactions.

The potentialities of this approach have not been exhausted and there is still much left to be accomplished. However, because of the interest in this development at this time it appeared advisable to report the results to date so that others may make use of the many graphs developed in similar studies. As more data are obtained, it may be necessary to modify and extend some of the relationships presented here but it is believed that continued study along the lines set forth will prove quite profitable.

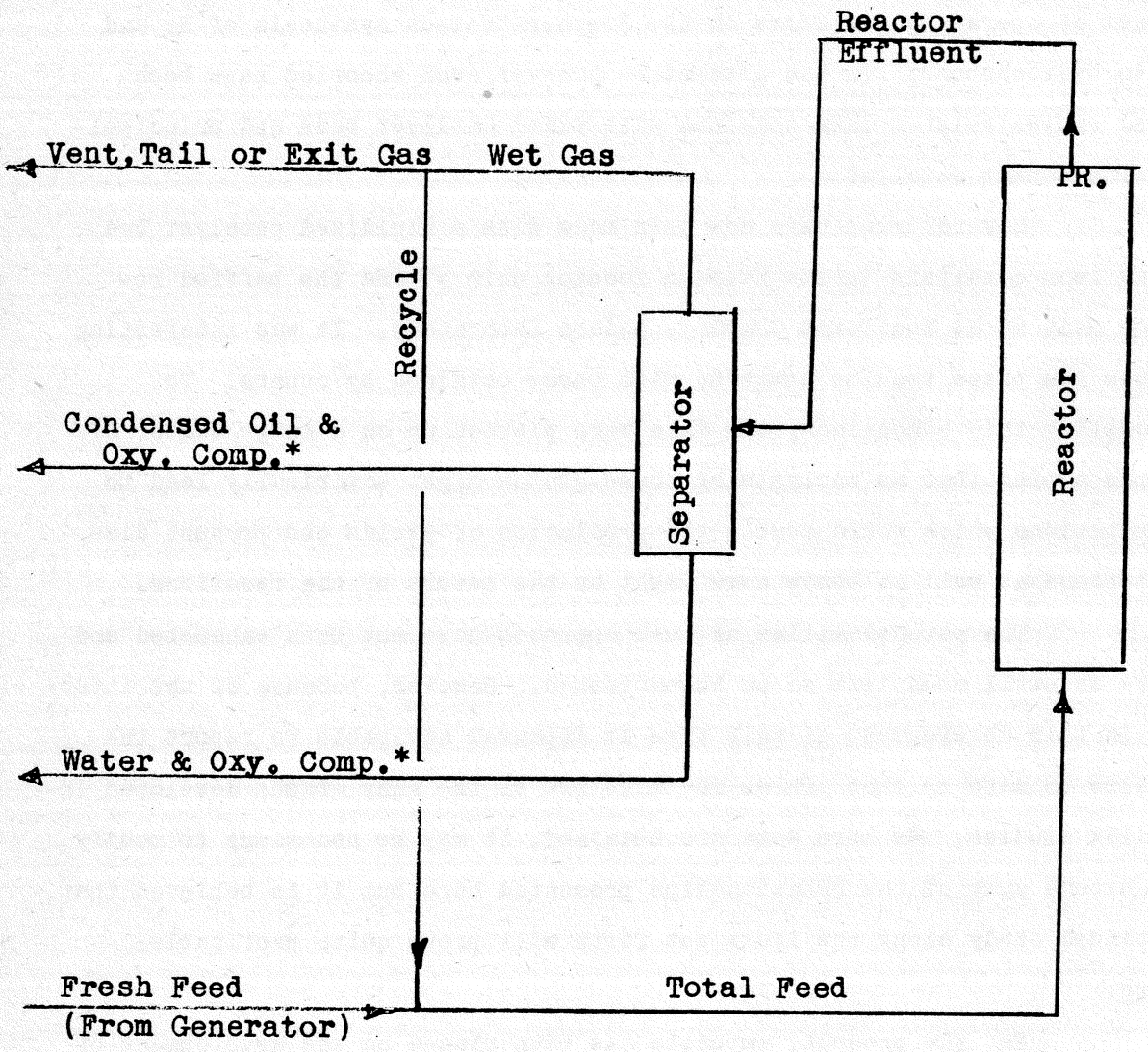
Scope:

For the present, emphasis has been placed on the development of correlations based on Fresh Feed composition and those other operating variables which are subject to direct control.

Attention has been confined to factors affecting yields and distribution of products. No data are presented on quality of products.

II. PROCESS FLOW

In order to clarify the use of terms and the names of each stream used in this report the following simplified flow diagram of the process is presented.



*Oxygenated Compounds divided between these two streams.

III. PROCESS VARIABLES

A rigorous analysis of the data discloses that the degree of conversion, that is, the disappearance of H_2 and CO, may be affected by each one of the following factors:

1. Temperature
2. Gravelocity or Space Velocity
3. Recycle Ratio (Recycle rate/FF rate)
4. Catalyst Type and Composition
5. Catalyst Reduction
6. Fresh Feed Composition
   a) H_2/CO Ratio
   b) CO_2 Content
   c) CH_4 Content
   d) H_2O Content
7. Pressure
8. Reactor Design - Disposition of Cooling Surface, Linear Velocity, Catalyst Bed Depth, Etc.

Items 3 and 6, recycle ratio and fresh feed composition, can be combined into "Total Feed Composition" but for the purpose of practical application of correlations it is better to keep them separate since they can both be controlled independently. It will be clear of course, that the nature of the recycled material will be influenced by degree of conversion, separator conditions and any selective extraction of components from the wet gas before it is recycled. Such extractions or changes in temperature and pressure of the separator may have a profound effect on degree of conversion, product distribution, quality of product and catalyst life. In all the runs with which we are concerned here however, the wet gas was separated from the liquid at about atmospheric temperatures and a portion of the total wet gas stream was recycled without change in composition.

IV. PRODUCT COMPONENTS

The product from the system may be divided as follows:

Unconverted	H_2
Unconverted	CO CO_2 H_2O
Paraffin Gases:	CH_4 C_2H_6 C_3H_8 C_4H_{10} etc.
Olefin Gases	C_2H_4 C_3H_6 C_4H_8 etc.
Hydrocarbon Liquid (C_5+)	Gaso Diesel Cut Waxy BTMS
Oxygenated Compounds	
Solids (Incl. Cat. Deposit)	Free Carbon Coke Wax

V. DATA USED

A. Beacon Data: (H_2/CO in FF = 2.0)

At the time this report was written there were available thirty-two runs or periods (complete with mass spectrometer analyses) made on the Beacon fluid units #7 and #8. These runs were all made with 2/1 H_2/CO ratio in Fresh Feed at 650°F. and 200# except one which was made at 600°F. They may be grouped as follows:

A. CM&S Reduced Catalyst
   1. Once through @ 650°F., Runs 7007, 23, 35A & 35B
   2. Recycling @ 0.5 R/FF & 600°F., Run 7005
   3. Recycling @ 1.0 R/FF & 650°F., Runs 7024, 27 & 8001

B. CM&S Reduced Catalyst with CO_2 added to FF.
   Series 14, 15, 18 & 22 (All once through)

C. CM&S Unreduced Catalyst
   Series 31 (R/FF = 1.0)

D. Other Catalysts:
   Cl. Powder (once through) Series 17
   Limonite K_2O (1.0 R/FF) Run 28
   Limonite KF (1.2 R/FF) Series 32
   Beacon Synthetic Ammonia Type Catalysts
   (1.2 R/FF) Runs 8002, 3 & 4

B. HRI Data (H_2/CO in FF = 1.8 to 2.7)

There were also available to us from the HRI Olean Pilot Unit the following runs complete with mass specs. on the streams:

15 Periods obtained on the H unit.
5 Periods of the 14 series.
5 Periods of the 15 series.

These data were all recalculated for the purpose of this report.

In addition, there were available from HRI summaries, data from the following periods on which mass spec. data were not reported to us and which were therefore plotted direct from the summaries.

6 H Series periods.
27 14 Series periods.

To plot these latter data it was necessary to calculate the % H_2 in FF converted. This was done as follows:

$$\frac{100 \times \%CO \text{ Converted} \times H_2/CO \text{ Consumed}}{100 \times H_2/CO \text{ in FF}} = \% \ H_2 \text{ in FF Converted}$$

C. Stanolind Data (H_2/CO in FF = 2.3 to 5.0)

The data on the Synthol Process developed on the Tulsa pilot unit and included in the Stanolind Oil & Gas Co. reports P46-1A (7-19-46) and

F46-13 (6-20-46) were used in an effort to establish the effect of high H_2/CO ratios and high CO_2 contents in the Fresh Feed.

These data were recalculated and were not too reliable. They are subject also to misinterpretation on our part.

D. Data From Other Laboratories (H_2/CO in FF = 1.0 to 2.0)

In order to permit a study of the effect of low H_2/CO in the Fresh Feed, Hydrocarbon Research Inc. provided us with data from two other laboratories.

From the first laboratory (Lab. A) there were 7 runs which were recalculated into 32 periods and from the second laboratory (Lab. B) there were 4 runs which were recalculated into 20 periods.

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The following tables are summaries of the recalculated data (Table I) and the HRI summary of their data (Table IA).

TABLE I
SUMMARY OF DATA
IN ALL CASES YIELDS ARE EXPRESSED AS % COMPONENT IN FF

Lab.	Run No.	$\frac{R}{FF}$	$\frac{H_2}{CO}$ (FF)	$\frac{CO_2}{CO}$ (FF)	$\frac{CH_4}{CO}$ (FF)	% Contr.*	H_2 Conv.	CO Conv.	CO to CO_2	CO to CH_4	CO to C_2s	CO to C_3s	CO to C_3	CO to Alc.	% Unsat. in C_2	% Unsat. in C_3	% Unsat. in C_4	Tot. CH_4 % CO in FF	Tot. CO_2 % CO in FF	H_2 to H_2O Meas.	Lgt. of Period Hrs.	Catalyst	Temp. oF.	Press.	V/HR/W	V/HR/V	$\frac{(H_2)(CO_2)}{(H_2O)(CO)}$ Reactor Effluent
Beacon Stirred Reactor Unit #7	7005 A-H	0.5	1.86	None	None	49.5	53.3	94.6	29.2	12.1	7.9	10.00	45.41		52.63	81.25		12.08	29.17	24.1	96	Fr.CM & S Red.	600	200	35	-	-
	7007 A-B	0	1.87	None	None	59.4	63.9	98.5	28.0	11.1	6.8	7.38	52.73		62.73	87.50	88.89	11.1	28.0	21.5	34	"	650	200	42	-	31.4
	7023	0	1.86	None	None	59.26	63.1	96.8	27.8	8.6	5.8	7.67	54.63		77.78	87.50	83.33	8.6	27.8	21.61	60	"	650	200	40	-	14.8
	7024	1.0	1.86	None	None	76.62	87.24	98.95	16.19	13.87	9.42	12.57	59.47		60.00	88.89	80.00	13.87	16.19	35.0	16	"	650	200	50	-	27.2
	7027 A-F	1.0	1.86	None	None	79.1	87.7	99.3	13.9	11.4	7.7	11.16	66.26		38.33	79.31	77.14	11.42	13.92	42.8	74	"	650	200	20	-	35.8
	7014	0	1.86	29.02	None	(55.3) 50.29	57.27	94.83	27.30	7.22	6.26	7.49	54.05		75.14	87.68	94.23	7.22	56.32	20.51	18	CM&S Trail Red.	650	200	40	-	22.6
	7015 A	0	1.87	69.03	None	(64.9) 52.44	64.94	93.91	14.39	6.09	5.42	8.13	68.01		81.05	81.05	83.22	6.09	33.42	27.77	24	"	650	200	38.1	-	17.3
	7015 B	0	1.87	64.20	None	(62.7) 51.26	63.17	93.84	17.03	6.33	6.16	7.70	64.32		83.33	86.67	91.67	6.33	81.23	26.22	24	"	650	200	38.1	-	18.5
	7018 A	0	1.86	125.09	None	(59.3) 41.38	60.54	91.29	17.51	7.96	6.76	7.94	59.06		71.43	91.27	100.00	7.96	142.60	27.99	15 1/2	"	650	200	40	-	23.0
	7018 B	0	1.86	125.11	None	(63.6) 44.36	64.26	95.87	10.69	10.07	9.58	11.65	65.53		66.67	94.30	100.00	10.07	135.80	32.00	13 1/4	"	650	200	40	-	36.8
	7022 A	0	1.86	78.81	None	(62.6) 49.05	66.65	93.86	22.55	7.45	5.98	9.44	57.88		75.44	88.33	89.74	7.45	101.36	33.04	12	"	650	200	20.7	-	16.7
	7022 B	0	1.86	79.85	None	(62.0) 48.50	65.79	93.97	20.67	5.82	5.35	15.27	62.13		78.43	92.78	89.23	5.82	100.52	22.30	12	"	650	200	20.7	-	26.8
	7022 C		1.86	80.24	None	(61.1) 47.82	61.79	94.08	19.18	6.29	5.77	6.92	62.84		80.00	100.00	83.27	6.29	99.42	32.75	12	"	650	200	20.7	-	19.6
	7022 D		1.86	81.24	None	(60.1) 46.83	59.00	93.35	16.67	5.47	5.47	8.84	65.74		78.43	72.73	90.00	5.47	97.91	29.10	11 3/4	"	650	200	20.7	-	20.8
	7017 A	0	1.87	None	None	12.45	14.85	28.51	11.54	3.02	4.02	7.46	9.93		50.00	90.43	100.00	3.02	11.54	1.36	24	C.I.Powder	650	200	49	-	10.1
	7017 B	0	1.87	None	None	16.87	18.77	36.87	13.58	5.25	4.28	3.53	13.76		32.97	40.00	75.00	5.25	13.58	3.12	27	"	650	200	49	-	5.6
	7028	1.0	1.99	None	None	43.53	54.64	94.64	34.28	25.34	16.19	8.52	18.83		27.27	29.63	50.00	25.34	34.28	14.19	6 1/2	Limonite K_2O	650	200	18.9	-	56.6
	7031 B	1.0	2.0	None	None	55.0	59.2	85.9	28.7	4.7	5.1	4.13	47.42		72.73	100.00	80.00	4.71	28.70	19.51	6	CM&S UNRED.	650	200	20	-	13.7
	7031 C	1.0	2.0	None	None	70.3	69.3	89.1	14.5	1.3	0.9	1.38	72.44		50.00	75.00	100.00	1.26	14.47	31.82	6		650	200	20	-	5.6
	7031 E	1.0	2.0	None	None	66.0	68.8	93.6	13.9	6.2	6.7	7.58	61.19		65.52	81.82	90.91	6.20	19.52	32.22	6		650	200	20	-	11.6
	7031 F	1.0	2.0	None	None	63.2	66.3	93.6	18.7	7.4	6.9	8.27	58.43		63.33	79.17	84.62	7.35	20.90	27.79	6		650	200	20	-	14.8
	7031 G	1.0	2.0	None	None	60.8	63.1	90.9	21.9	7.4	3.9	4.13	57.75		58.82	83.33	83.33	7.35	21.93	25.43	6		650	200	20	-	12.5
	7031 H	1.0	1.99	None	None	61.6	65.0	93.5	21.3	7.6	7.6	7.57	57.03		63.64	86.36	89.47	7.57	21.29	25.42	12		650	200	20	-	16.1
	7031 I	1.0	1.99	None	None	58.0	62.1	90.3	22.9	7.7	8.3	9.12	51.46		63.89	86.79	88.57	7.69	22.89	22.52	12		650	200	20	-	13.4
	7032 A	1.2	1.99	None	None	57.6	72.9	89.2	23.1	30.3	11.5	7.28	24.32		4.90	16.28	22.22	30.25	23.14	20.41		Limonite KF	650	200	20.1	-	10.9
	7032 B	1.2	1.99	None	None	59.3	-	-	23.3	-	-								23.25	19.48	12	"	650	200	20.1	-	
	7035 A	0	1.99	None	None	57.8	60.5	98.2	28.1	8.6	6.5	8.23	55.09		73.68	91.67	88.57	8.57	28.06	22.12	12	CM&S Red.	650	200	19.8	-	27.8
	7035 B	0	1.99	None	None	56.9	61.2	98.6	28.9	9.9	8.0	10.11	51.72		71.43	88.14	82.00	9.94	28.91	21.69	12	"	650	200	18.5	-	36.9
Beacon Unit #8	8001	1	1.99	None	None	79.76	89.01	98.98	12.99	12.28	10.36	12.79	63.35		29.41	78.57	81.82	12.28	12.99	39.8	82	CM&S	650	200	59	-	20.8
	8002	1.2	1.99	None	None	64.51	82.49	96.55	23.96	32.59	12.59	9.44	27.41		4.84	19.35	46.15	32.59	23.96	24.4	29	Beacon Fe Al_2O_3 & K_2O	650	200	59	-	22.1
	8003	1.2	1.99	None	None	81.59	87.84	99.39	10.36	9.24	9.54	11.27	70.25		65.96	83.78	93.75	9.24	10.36	43.4	59	"	650	200	59	-	35.8
	8004	1.1	1.99	None	None	74.54	88.85	98.78	15.63	23.15	12.99	13.71	47.01		7.81	35.56	68.18	23.15	15.63	35.3	64.5	"	650	200	59	-	21.5

Figures in ( ) are adjusted for CO_2 in FF.

TABLE I
SUMMARY OF DATA
IN ALL CASES YIELDS ARE EXPRESSED AS % COMPONENTS IN FF

Lab.	Run No.	R	$\frac{H_2}{CO}$ (FF)	$\frac{CO_2}{CO}$ (FF)	$\frac{CH_4}{CO}$ (FF)	% Contr.	H_2 Conv.	CO Conv.	CO to CO_2	CO to CH_4	CO to C_2S	CO to C_3S	CO to C_3 (inc.) (alc.) (bal.)	CO to Alc. (Reported)	% Unsat. in C_2	% Unsat. in C_3	% Unsat. in C_4	Tot.CH_4 % CO in FF	Tot.CO_2 % CO in FF	H_2 to H_2O (Measured)	Lgt. of Period (Hrs.)	Catalyst	Temp. o F.	Press.	v/hr/w	v/hr/v	% Contr. Corrected for CO_2 and CH_4
HRI-H'	2	4.99	2.31	0	7.1	86.0	93.8	99.8	2.2	12.1	9.3	11.3	76.2	3.5	17.2	67.5	68.4	19.6	2.2	42.1	56	Spent CM & S	625	190	44	720	89.0
	3	6.42	2.47	0	11.5	85.6	95.5	99.9	1.8	13.6	10.9	12.4	73.6	3.7	12.2	54.9	55.5	25.5	1.8	43.1	17	"	631	210	(12)	710	89.7
	5A	6.67	2.48	1.1	11.6	86.1	96.6	99.6	-0.6	11.6	13.3	15.4	75.4	4.2	4.6	26.5	42.5	23.2	0.5	39.9	125	"	610	225	(15)	630	88.9
	5B	4.59	1.97	0.6	6.1	88.5	98.3	99.8	9.0	4.5	8.6	12.3	77.6	5.7	12.4	58.2	79.9	10.6	9.6	40.8	72	"	607	235	(18)	700	90.1
	6	4.95	2.54	27.8	15.5	88.5	97.9	99.4	-13.9	- 4.8	8.4	16.6	109.7	9.5	23.7	63.9	78.8	10.7	13.9	46.4		"	618	205	-	660	97.4
	10A	0.95	2.27	1.0	5.4	80.0	87.4	99.7	7.9	8.0	11.0	15.3	72.9	5.3	28.0	56.0	76.5	13.4	8.9	37.3	60	"	608	218	(44)	575	81.4
	11	0.43	2.21	0.7	8.0	67.7	73.6	99.4	19.5	5.5	9.5	13.3	64.9	5.5	36.4	78.0	75.0	13.5	20.2	23.1	74	"	598	219	(51)	690	69.9
	12	0.46	2.20	0	8.6	58.6	62.4	97.4	25.3	3.9	11.0	13.2	57.3	7.4	32.5	78.1	71.4	12.5	25.3	19.2	72	"	592	223	(51)	710	60.6
	14	0.36	1.96	0	6.1	48.6	54.0	89.7	32.6	5.2	9.1	10.8	42.8	2.9	37.9	60.9	63.6	11.3	32.6	9.8	48	"	632	222	(176)	930	50
	24A	2.45	1.94	10.3	6.9	86.5	94.5	99.1	4.6	0.9	4.6	7.4	89.0	6.3	55.6	93.1	97.1	7.8	14.9	46.7	16	"	643	232	(30)	1730	92.1
	24B	1.58	1.92	11.4	9.1	83.0	90.7	98.8	8.1	-2.5	4.5	7.1	88.6	6.3	61.9	90.9	95.2	6.6	19.5	47.6	16	"	650	230	(35)	1780	88.8
	25A	1.07	1.92	13.2	4.9	82.6	91.1	99.2	6.1	1.1	5.4	7.7	86.6	6.1	68.0	95.7	95.2	6.0	19.3	44.8	52	"	648	232	(56)	1050	88.4
	25B	0.79	1.95	12.7	7.3	77.5	85.2	99.4	11.2	-0.7	5.3	11.1	83.7	5.5	70.3	92.3	95.7	6.6	23.9	40.4	36	"	644	215	(56)	890	83.2
	25C	1.05	1.94	13.0	7.6	78.6	87.6	99.6	10.4	0.3	6.2	10.9	82.8	5.9	71.7	96.3	95.8	7.9	23.4	43.3	88	"	646	215	(53)	900	84.6
	17	1.8	2.06	0.3	7.9	85.5	90.8	98.4	7.4	-0.2	6.2	8.1	85.0	5.5	61.8	93.2	88.0	7.7	7.7	40.5			635	230	57.4	989	82.1
HRI-14'	1	1.61	2.08	18.3	9.1	56.3	66.3	88.5	18.9	7.7	4.7	7.1	57.1	3.5	62.5	77.5	91.7	16.8	37.2	27.0	70	Spent Sterlington	608	214	(68)	2540	61
	2	1.21	1.91	16.4	4.4	71.9	83.2	94.6	12.0	5.5	6.7	10.1	70.3	5.7	68.4	97.4	95.6	9.9	28.4	42.5	12	"	641	212		1175	
	3	0.72	1.93	15.8	4.8	61.5	72.1	95.3	21.6	7.7	7.8	12.1	58.2	2.9	59.4	97.0	94.1	12.4	37.4	27.8	40	"	660	213		1100	
	4	2.90	1.95	16.3	6.1	80.6	93.4	96.5	6.7	2.9	7.8	12.9	79.1	5.8	58.7	95.7	92.5	9.0	23.0	44.0	72	Fresh CM&S	647	215	(15)	660	87.1
	5	3.90	1.96	17.0	5.8	42.0	58.3	67.7	18.6	15.1	8.9	10.0	25.2	0.7	12.5	50.0	88.9	20.8	35.6	20.6	48	"	648	216		1120	
HRI-15'	2	2.58	2.0	19.5	12.0	80.8	94.5	96.3	3.0	0.4	7.0	12.5	86.0		47.3	91.0	91.5	12.4	22.5			Spent Trail	646	220	12		
	3	2.44	1.95	18.0	10.4	81.0	94.9	96.7	4.5	0.9	7.0	13.4	81.0		47.4	93.5	80.8	11.3	22.5			Spent Trail	660	200	40		
	4	2.48	1.95	17.8	9.4	80.0	94.2	96.8	7.0	2.4	7.6	13.7	75.9		44.8	92.9	89.7	11.8	24.7			"	658	200	48		
	5	2.59	1.97	17.7	10.8	79.5	94.0	95.6	6.8	1.6	7.8	13.8	75.0		44.8	91.9	84.8	12.3	24.4			"	658	200	12		
	7	2.58	1.96	18.5	9.4	77.5	92.8	94.9	7.4	4.0	8.2	14.5	75.3		38.7	87.8	86.5	13.4	26.0			"	658	200			

' Runs with MS analyses Recalculated from data in HRI summaries.

TABLE I
SUMMARY OF DATA

Lab.	Run No.	R/FF	H_2/CO (FF)	CO_2/CO (FF)	CH_4/CO (FF)	% Contr.	H_2 Conv.	CO Conv.	CO to CO_2	CO to CH_4	CO to C_2S	CO to C_3S	CO to C_3 (incl. alc.)	CO to Alc.	% Unsat. in C_2	% Unsat. in C_3	% Unsat. in C_4	Tot.CH_4 % CO in FF	Tot.CO_2 % CO in FF	H_2 to H_2O (measured)	Lgt. of Period (hrs.)	H_2 to H_2O Ave.O_2& H_2 Balances	Temp.oF.	Press.	% Contraction Corrected for CO_2 & CH_4	v/hr/v	Vel.
Lab. A	17	2.88	1.06	1.2	4.1	54.3	76.44	84.67	28.77	8.39	7.90	9.49	39.61					12.49	29.97	14.67	116	24.4	622	135	57.3	457	.34
	18A	14.54	1.11	0.7	3.5	56.9	90.46	86.26	31.54	19.12	7.92	7.25	27.68					22.62	32.24	37.14	36	20.6	640	309	59.9	260	.35
	18B	7.99	1.02	0.9	4.5	71.6	90.70	92.85	21.55	9.18	5.10	5.74	57.02					13.68	22.45	56.16	8	28.8	617	309	76.6	220	.16
	19A	6.20	1.07	0.9	9.6	52.7	77.07	69.25	17.25	9.81	6.60	5.72	35.59					19.41	18.15	23.28	96	24.5	577	313	56.9	454	.35
	19B	5.61	1.01	0.4	8.8	47.8	68.52	60.67	15.33	8.02	5.50	5.77	31.82					16.82	15.73	19.43	48	21.2	546	293	51.5	492	.37
	19C	5.93	1.02	1.0	8.6	56.9	84.57	88.88	23.76	7.49	8.60	9.05	49.03					16.09	24.76	19.93	45	24.8	596	294	60.8	463	.37
	19D	2.05	1.05	0.4	8.7	28.7	37.35	34.88	9.59	-3.72	4.02	3.29	24.99					4.98	9.99	10.16	19	14.7	550	135	30.4	468	.35
	20A	4.91	1.00	1.0	5.6	56.7	72.81	81.48	23.92	4.94	6.24	6.60	46.38					10.54	24.92	24.00	60	20.2	576	139	60.4	250	.33
	20B	2.87	1.03	0.9	6.8	41.8	60.22	68.43	25.12	8.56	4.82	5.69	29.93					15.36	26.02	13.84	48	12.0	540	134	44.3	406	.35
	20C	6.32	1.02	1.3	6.8	45.6	65.72	67.03	22.49	8.26	4.84	4.96	31.44					15.06	23.79	28.20	14	16.3	495	132	48.7	209	.32
	22A	11.62	1.00	0.8	7.6	58.3	75.87	75.02	18.82	1.46	4.76	6.89	49.98					9.06	19.62	25.69	72	26.1	552	313	61.8	219	.30
	22B	13.81	1.02	0.5	7.6	58.1	72.06	75.22	18.11	1.46	4.70	5.88	50.95					9.06	18.61	22.06	48	25.0	552	313	61.6	212	.33
	22C	13.34	1.04	1.4	6.7	56.4	75.81	75.77	21.28	4.54	5.86	6.14	44.09					11.24	22.68	21.96	48	23.8	596	313	59.8	231	.37
	22D	13.64	1.03	1.5	6.1	64.7	86.44	83.00	21.84	5.69	6.16	7.28	49.31					11.79	23.34	29.66	36	28.1	609	313	69.7	222	.36
	23A	5.32	1.01	1.2	5.5	64.5	91.67	92.03	31.00	7.77	8.00	9.92	45.26					13.27	32.2	22.60	69	24.3	552	294	68.5	435	.30
	23B	5.12	1.98	6.1	2.6	74.1	93.19	97.70	9.77	19.61	16.02	17.99	52.30					22.21	15.87	34.48	36	26.7	553	294	77.8	449	.30
	23C	5.30	0.99	1.0	3.4	63.4	91.43	92.40	31.48	7.41	7.12	11.67	46.39					10.81	32.48	21.19	45	23.6	553	294	65.6	437	.30
	23D	3.32	1.01	1.3	4.0	62.4	87.38	90.07	31.74	6.39	6.86	8.21	45.08					10.39	33.04	22.63	48	22.7	552	294	65.3	636	.30
	23E	2.84	1.01	1.9	3.4	62.5	88.79	92.94	32.90	9.07	7.72	9.39	43.25					12.47	34.8	19.55	48	21.5	550	294	65.9	702	.30
	23F	1.77	1.01	1.6	5.6	59.7	86.20	93.15	35.28	8.44	7.72	9.63	41.71					14.04	36.88	17.60	72	19.2	551	294	63.0	991	.30
	23G	5.51	1.01	1.0	6.9	64.4	94.10	95.38	34.23	8.28	7.64	10.15	45.23					15.18	35.23	23.29	44	23.7	550	294	67.9	690	.30
	23H	3.56	1.03	0.4	6.1	59.7	90.37	93.80	35.20	11.29	8.96	11.34	38.35					17.39	35.6	17.87	41	19.9	551	221	63.2	438	.30
	23I	1.72	1.01	1.1	6.0	62.4	88.69	95.83	35.64	10.04	7.92	9.96	42.23					16.04	36.74	17.57	36	19.5	552	294	66.7	1014	.30
	23J	2.50	0.99	1.5	6.6	67.0	92.77	97.02	33.66	6.16	7.02	9.76	50.18					12.76	35.16	21.11	52	24.0	550	368	71.5	1002	.30
	23K	2.22	1.01	0.3	4.5	65.2	95.19	97.29	36.00	12.55	9.46	10.71	39.28					17.05	36.30	19.43	60	21.0	600	368	69.2	1004	.30
	23L	6.77	1.01	1.7	7.2	69.6	93.95	92.13	28.27	4.25	5.94	7.55	53.67					11.45	29.97	27.35	65	29.1	501	368	75.5	451	.30
	23M	5.20	1.01	0.1	5.2	66.1	95.17	96.10	34.23	9.91	8.60	11.14	43.36					15.11	34.33	27.18	48	23.3	551	294	69.6	444	.30
	24A	5.20	1.03	0.9	5.6	71.3	91.79	92.69	28.12	3.37	3.78	4.58	57.42					8.97	29.02	27.50	72	29.6	551	275	75.9	443	.30
	24B	1.89	1.49	13.5	3.6	74.7	92.78	98.24	18.09	7.10	7.54	10.78	65.51					10.70	31.59	36.74	72	36.4	600	275	82.8	996	.30
	24C	1.00	1.48	2.9	2.0	72.0	89.19	98.46	24.30	11.04	8.78	11.06	54.34					13.04	27.20	29.99	60	31.0	600	200	74.2	995	.30
	24D	6.80	1.49	1.4	2.8	81.7	97.23	98.29	18.88	8.03	7.36	7.60	64.02					9.43	21.60	37.66	60	38.4	550	350	85.8	451	.30
	24E	2.30	1.50	1.0	3.4	75.5	93.40	97.59	22.34	11.63	9.04	11.28	54.58					12.63	25.74	34.64	48	33.7	551	390	79.2	1135	.30

TABLE I
SUMMARY OF DATA

Lab.	Run No.	R/FF	H_2/CO (FF)	CO_2/CO (FF)	CH_4/CO (FF)	% Contr.	H2 Conv.	CO Conv.	CO to CO_2	CO to CH_4	CO to C_2S	CO to C_3S	CO to C_3 (including alc. (C bal.)	CO to Alc. (reported)	% Unsat. in C_2	% Unsat. in C_3	% Unsat. in C_4	Tot.CH_4 % CO in FF	Tot.CO_2 % CO in FF	H_2 to H_2O (measured)	Lgt. of period (hrs.)	Catalyst	Temp. oF.	Press.	v/hr/w	% Contr. Corrected for CO_2 & CH_4	Vel.
Lab.B	5A	0.92	1.52	42.9	5.2	21.0	34.39	36.11	6.63	6.23	1.79	2.41	21.46					11.43	49.53		17		627	264	5.5	25.5	.48
	5B	0.87	1.62	42.0	4.7	57.7	69.51	75.48	- 3.45	7.45	5.16	4.40	66.32					12.15	38.55		13		621	273	6.0	69.8	.44
	6B	2.19	1.19	40.9	3.7	45.9	72.57	87.82	33.94	9.16	8.36	10.58	36.36		20.62	55.26	58.91	12.86	74.84	26.5	65		576	278	1.8	56.8	.42
	6C	2.13	1.18	37.9	3.4	45.0	78.34	91.00	42.55	11.85	10.86	13.14	25.74					15.25	80.45	24.7	48		600	290	1.8	55.0	.42
	6D	1.31	1.18	36.9	3.1	44.6	75.34	89.58	38.78	14.54	9.60	11.02	26.66			7.13	10.72	17.64	75.68	17.9	71		601	343	3.2	54.1	.47
	6E	1.34	1.17	34.9	2.7	37.9	63.51	81.01	34.92	8.20	8.76	10.68	29.13		2.91	11.47	18.09	10.90	69.82	16.0	65		582	345	3.0	45.6	.45
	6F	1.74	1.23	47.0	8.5	53.7	81.36	90.48	20.60	9.92	9.42	10.26	50.54					18.42	67.60	15.8	49		601	279	2.3	68.6	.49
	6GA	1.51	1.25	53.8	12.2	47.5	71.46	82.87	16.96	9.14	6.66	9.35	50.11					21.34	70.76	21.7	21		598	283	4.2	64.8	.51
	6GB	1.87	1.24	55.5	16.8	45.9	73.54	83.84	22.85	6.82	7.78	10.30	46.39					23.62	78.35	18.1	37		590	285	3.4	62.3	.46
	6H	1.90	1.22	55.4	15.6	58.4	82.00	86.36	3.88	1.09	6.38	8.02	75.01					16.69	59.28	7.0	9		555	265	3.2	78.5	.34
	11A	2.02	2.14	26.6	3.5	75.1	83.6	94.1	- 0.3	5.7	4.7	6.75	80.0	4.0				9.2	26.3	31.7	13	Fresh Ammonia Syn.Cat.	637	240	31.5	83.6	1.3
	11B	1.96	2.07	25.7	4.4	73.1	83.8	92.74	2.17	7.19	6.44	7.72	74.14	2.9	46.61	78.60	74.17	11.59	27.87	38.2	48	"	657	235	44.9	81.6	1.4
	11E	2.98	2.08	28.70	7.36	81.65	91.5	95.5	-7.45	4.13								11.49	21.25	45.1	144	"	675	400		93.4	
	11FA	2.38	2.11	29.55	6.52	73.13	87.70	93.53	0.02	11.24	8.41	11.66	22.29					17.76	29.57		106	"	660	399	88.7	83.4	0.8
	11FB	3.02	2.06	27.56	7.77	73.40	89.86	94.27	4.01	11.12	9.59	13.53	25.56	2.9				18.89	31.57		13	"	660	400	82.9	84.8	0.7
	11FC	3.58	2.04	27.93	5.52	63.12	81.81	87.41	8.95	17.75	9.66	12.21	24.80	2.5				23.27	36.88		13	"	612	391	79.4	71.6	0.7
	11FD	4.58	2.02	27.40	6.51	52.53	65.46	76.43	10.32	12.52	6.83	12.19	22.76	2.0				19.03	37.72		13	"	564	396	77.7	59.6	0.7
	12B	2.16	2.13	31.28	9.44	85.97	95.2	98.6	-14.6	4.9				4.5				14.34	16.68		7	"	664	400	55.0	99.6	0.9
	12DA	2.17	2.00	26.12	4.80	69.10	83.0	94.5	6.38	14.4				2.1				19.20	32.50		12	"	647	399	69.0	79.1	0.9
	12DB	1.96	2.10	25.24	5.87		72.1	87.9	15.7	19.0				1.8				24.87	40.94		12	"	647	399	84.0		0.9

TABLE I
SUMMARY OF DATA
STANOLIND

Lab.	Run No.	R/FF	H_2/CO (FF)	CO_2/CO (FF)	CH_4/CO (FF)	% Contr.	H_2 Conv.	CO Conv.	CO to CO_2	CO to CH_4	CO to C_2s	CO to C_3s	CO to C_3 (Including Alc. C (Bal.)	CO to Alc. (Reported)	% Unsat. in C_2	% Unsat. in C_3	% Unsat. in C_4	Tot. CH_4 % CO in FF	Tot. CO_2 % CO in FF	H_2 to H_2O (Measured)	Lgt. of Period (Hrs.)	Catalyst	Temp. oF.	Press.	v/hr/w	v/hr/v	Vel.
						(24.6)																				
Stanolind	298(1)	0.46	4.39	55.3	72.1	18.3	32.54	79.1	9.83	-0.11				7.90				72.0	65.13	11.9	56		633.14	208.57		
Tulsa	320(2)	1.82	2.31	37.2	12.1	(75.3)	75.08	89.7	0.68	8.55				9.00				20.7	37.9	36.1	40		624.2	252.4		
						59.4																				
	325(3)	1.83	2.32	41.1	13.7	(66.9)	69.47	91.2	16.61	7.25				9.11				21.0	57.7	35.1	32		632.75	250.50		
						51.7																				
	19 (4)	2.61	4.93	46.6	14.2	97.1	88.72	95.7	-48.66	-1.94				8.70				12.3	- 2.06	37.9	40		586.80	84.76		
	29 (5)	2.62	5.01	48.3	32.0	Error	81.28	97.8	-44.47	16.39				8.35				48.39	3.83	41.4	32		584.3	153.3		
						100																				
	12 (6)	2.99	4.13	48.8	18.3	Error	103.35	103.2	-51.53	6.37				9.29				24.67	- 2.73	39.1	48		587.8	84.3		
						100																				
	38 (7)	1.35	4.54	39.5	30.3	75.4	76.42	97.1	-24.69	19.60				8.29				49.90	14.81		64		581.3	163.6		
	64 (8)	0.85	4.46	37.16	33.03	53.6	56.43	89.7	- 6.76	25.22				7.65				58.25	30.40		72		585.8	163.1		
	91 (9)	1.12	3.68	43.72	42.79	52.6	66.16	86.9	- 6.69	31.10				7.45				73.89	37.03		48		596.5	163.7		
	104 (10)	0.85	4.40	47.16	52.08	50.9	54.00	89.4	- 5.41	-11.05				7.91				41.03	41.75		32		599.3	164.0		
	109 (11)	0.81	4.19	46.92	47.54	50.4	54.74	86.9	-12.02	3.23				7.38				50.77	34.90		40		599.0	164.0		
	127 (12)	0.99	3.36	52.79	41.80	54.2	59.74	88.6	-11.59	0.44				7.39				42.24	41.20		32		599	164.4		
	177 (13)	0.36	4.11	50.84	55.39	31.0	35.83	77.7	3.13	- 3.15				6.87				52.24	53.97		32		606.50	163.00		
	181 (14)	0.64	4.10	49.63	45.80	(42.3)	35.76	76.4	0.44	6.25				6.54				52.05	50.07		72		601.3	163.2		
						39.1																				
	136 (15)	0.44	4.05			36.5	45.4	91.1	-10.9	4.7																
	46 (16)	1.38	4.37	36.46	34.2	67.2	77.0	96.0	-14.36	43.88				8.26				78.08	22.10		32		580.3	164.0		
	55 (17)	1.00	4.31	34.89	36.07	57.8	66.81	95.1	- 5.01	45.62				8.11				81.69	29.88		72		585.7	163.7		

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	H-13	H-14	H-11	H-12	H-10A	H-18	H-17	H-10B	H-2	H-5B	H-6	H-3	H-5A	H-1
POINT NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
HOURS														
Start	347	360	208	299	74	4	54	138	35	244	325	58	112	5
End	355	408	282	347	134	12	86	184	55	320	365	74	244	14
Period	8	48	74	48	60	8	32	46	20	76	40	16	132	9
REACTOR DATA														
Number and Size of Cooling Tubes					55, 7/8"		K-3 16 BWG tubes, 18'5" long							
Ft^2 Cooling Surface/Ft^3 Bed Volume							21.2							
Free Cross-Section in Reaction Zone, Ft^2							0.735							
Hydraulic Radius in Reaction Zone, Ft.							0.0455							
REACTION CONDITIONS														
Catalyst Number	90	90	90	90	90	96	101[1] Spent Trail	90	92	92	92	92	92	71
Catalyst Type														
Maximum Reaction Temperature, °F.	621	632	598	592	608	625	635	602	625	607	618	630	610	620
Pressure, psig.	227	222	219	223	218	220	230	220	190	235	205	210	225	190
Space Velocity, SCFH FF/lb. Fe	56	176	51	51	44	38	84	26	44	18	---	12	15	7
Linear Velocity, Ft/Sec	.53	.68	0.62	.61	0.63	1.25	1.37	0.54	1.64	1.03	1.23	1.75	1.49	1.86
Recycle/Fresh Feed	0.3	0.5	0.7	0.7	1.2	1.3	1.9	2.8	5.4	5.6	5.7	6.7	7.2	10.1
Catalyst Density, Lbs./Ft^3														
Initial	22	12	22	22	22	35	21.6	20	---	38.5	---	52	47	---
Final	22	7.4	22	21	20	42	15.4	19	23.2	36	---	53.9	38.5	---
Total C in Catalyst, % on Fe														
Initial	---	---	27	---	24	7.5	23	---	---	---	---	---	---	---
Final	32	---	25	---	---	10.9	32	---	---	---	24	---	---	9.2
REACTION DATA														
Contraction, % on Fresh Feed	58	49	68	59	80	75	80	86	87	88	88	87	86	78
CO Reacted, % on Fresh Feed	99	90	99	97	100	99	99	99	100	100	99	100	100	98
CO Converted, % on Total Feed	98	82	98	93	97	95	94	88	89	89	65	92	82	49
% CO Converted to														
CO_2	28	37	20	26	8	17	11	1	2	9	12	2	0	3
C_2^-	8	16	15	16	20	8	10	20	24	15	10	24	26	15
C_3^+	57	44	59	50	67	70	74	73	70	73	97	70	72	79
Alcohols	7	3	6	8	5	5	5	6	4	3	5	4	2	3
Carbon	---	---	---	---	1.1	0.35	---	---	---	---	---	---	---	---
H_2 in FF Converted, %	67.5	54.0	72.0	61.6	86.9	83.4	84.8	94.5	95.6	100	95.1	95.8	95.9	87.0
% Contraction (Adj'd. for CO_2 in Feed)	60	50	69.9	60.6	81.4	76.7	82.1	89.6	89.0	90.1	97.4	89.7	88.9	83.6

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	H-13	H-14	H-11	H-12	H-10A	H-18	H-17	H-10B	H-2	H-5B	H-6	H-3	H-5A	H-1
POINT NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
GAS COMPOSITIONS														
Fresh Feed, % as														
H_2	66.3	64.1	66.5	66.4	67.4	63.8	65.5	66.0	68.0	64.5	63.4	67.5	68.5	67.2
CO	29.8	32.8	30.1	30.3	29.8	33.4	31.5	28.9	29.5	32.3	24.7	28.4	27.5	25.3
CO_2	--	--	0.2	--	0.3	--	0.1	2.1	--	0.1	6.6	0.1	0.3	--
CH_4	3.3	2.0	2.4	2.6	1.6	2.2	2.5	1.8	2.2	2.3	3.0	2.9	3.0	6.7
Recycle Gas, % as														
H_2	60.1	57.5	54.5	60.3	42.6	48.4	45.8	25.7	24.8	10.0	14.1	20.5	17.1	40.3
CO	0.9	6.7	0.6	1.9	0.6	1.2	0.9	1.4	0.7	0.7	2.4	0.3	0.8	2.5
CO_2	19.3	21.1	19.0	18.6	13.6	22.9	17.3	16.5	4.4	24.3	29.7	3.7	2.1	3.0
C_2^-	10.0	10.3	17.0	13.2	28.9	15.4	21.7	39.3	55.5	45.7	34.3	58.5	60.2	36.3
C_3^+	6.9	4.4	7.8	5.9	14.1	10.8	13.5	17.0	14.6	19.3	19.5	15.7	19.8	11.1
Reactor Feed, % as														
H_2	65.2	61.7	61.5	63.9	53.9	55.2	52.6	36.1	31.6	18.4	21.4	26.8	23.4	42.8
CO	23.2	24.1	17.9	18.6	13.9	15.2	11.5	8.6	5.2	5.5	5.6	4.0	4.1	.6
CO_2	4.5	7.1	8.0	7.7	7.6	13.0	11.4	12.7	3.7	20.6	26.2	3.2	1.9	2.7
C_2^-	4.9	4.8	8.4	7.0	16.5	9.7	15.1	29.5	47.2	39.1	29.7	52.0	53.1	33.7
C_3^+	1.6	1.5	3.2	2.4	7.7	6.1	8.9	12.5	12.3	16.4	16.5	13.7	17.5	10.1
H_2/CO RATIO														
In Fresh Feed	2.2	2.0	2.2	2.2	2.3	1.9	2.1	2.3	2.3	2.0	2.6	2.4	2.5	2.7
In Reactor Feed	2.8	2.6	3.4	3.4	3.9	3.6	4.6	4.3	6.1	3.4	3.7	6.8	5.7	9.3
At Reactor Outlet	67	8.6	91	32	71	40	51	18	36	14	6	68	21	16
Consumed	1.5	1.2	1.6	1.4	2.0	1.6	1.8	2.2	2.2	2.0	2.5	2.3	2.4	2.4
H_2/CO + CO_2 in Reactor Feed	2.35	1.98	2.38	2.43	2.50	1.96	2.3	1.70	3.55	0.71	0.67	3.73	3.90	5.86
C_3^+/C_2^- in Product	7.1	2.8	3.9	3.1	3.4	8.8	7.4	3.7	2.9	4.9	9.7	2.9	2.8	5.3
HEAT LIBERATED, BTU/HR.														
Total, x 10^{-3}	368	412	323	340	348	537	592	195	252	223	210	254	221	159
Per Lb. of Iron	2470	7100	2120	2280	2440	2020	4630	1470	2600	1050	---	721	877	356
Per Ft^2 Heat Transfer Surface	1690	1880	1480	1550	1590	2970	2800	890	1330	2100	---	1500	1720	---
Avg. ΔT Bed-Coolant, °F.	37	42	35	28	24	51	53	16	23	33	21	22	25	29
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	44.5	44.7	42.3	55.3	66.2	58.2	52.8	55.6	57.8	63.6	---	68.2	68.8	---

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	14-7	14-8	14-7	14-8	14-8	14-7	14-4	H-30	H-30	14-1
POINT NUMBER	21	22	23	24	25	26	27	28	29	30
HOURS										
Start	153	254	105	206	370	9	35	---	---	20
End	185	314	153	242	394	93	107	---	---	90
Period	32	60	48	36	24	84	72	62	12	70
REACTOR DATA	←			K-5		→	K-4	←	K-3A →	K-4
Number and Size of Cooling Tubes				0			4 1/2"		19.1"	
Ft^2 Cooling Surface/Ft^3 Bed Volume				11.4			20.6		9.9	
Free Cross-Section in Reaction Zone, Ft^2				.126			.111		.78	
Hydraulic Radius in Reaction Zone, Ft.				.100			.0518		.078	
REACTION CONDITIONS										
Catalyst Number	135	135	135	135	135	135	129	119	119	123
Catalyst Type					Fresh Trail (1)					Spent Sterlington
Maximum Reaction Temperature, °F.	650	605	645	615	615	655	645	646	649	610
Pressure, psig.	250	150	250	215	155	250	215	209	209	215
Space Velocity, SCFH FF/Lb. Fe	32	45	30	20	103	17	15	70	40	68
Recycle/Fresh Feed	1.3	1.5	1.5	2.2	2.5	2.8	2.9	1.7	2.2	1.6
Linear Velocity, Ft/Sec	1.09	1.13	1.10	1.01	0.90	1.02	.81	0.88	1.07	1.24
Catalyst Density, Lbs./Ft^3										
Initial	61	31	73	46	0	96	109	20	36	55
Final	50	7	64	38	0	78	34	13	23	52
Total C in Catalyst, % on Fe										
Initial	16.0	28.0	13.0	25.7	30.1	02.0	15.8	13.8	---	---
Final	18.7	33.4	16.0	27.3	33.6	11.0	25.3	26.5	13.8	24
REACTION DATA										
Contraction, % on Fresh Feed	54	31	57	50	43	71	81	76	83	56
CO Reacted, % on Fresh Feed	91	62	92	85	82	91	97	98	99	88
CO Converted, % on Total Feed	73	34	73	51	46	48	64	85	86	63
% CO Converted to										
CO_2	32	38	27	30	32	15	7	11	7	21
C_2-	25	26	28	28	39	16	11	14	10	14
C_3+	42	34	43	40	28	66	76	68	78	61
Alcohols	1	2	2	2	1	3	6	7	5	4
Carbon	.27	.34	.21	.27	.18	.67	.92	.30	---	---
H_2 in FF Converted, %	65.6	43.4	71.5	63.7	57.4	86.1	97	83.3	93.6	87.0
% Contraction (Adj'd for CO_2 in Feed)	56.8	33.6	59.9	53.8	46.7	75	87.1	---	---	61

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	14-7	14-8	14-7	14-8	14-8	14-7	14-4	H-30	H-30	14-1
POINT NUMBER	21	22	23	24	25	26	27	28	29	30
GAS COMPOSITIONS										
Fresh Feed, % as										
H_2	60.5	61.5	61.1	61.9	61.0	61.4	60.9	61.3	61.0	61.6
CO	34.0	30.5	33.5	30.8	30.7	32.8	31.3	31.3	31.5	29.6
CO_2	3.8	5.5	3.8	5.4	5.6	3.9	5.1	4.9	4.9	5.4
CH_4	1.2	2.3	1.1	1.7	2.3	1.3	1.9	2.0	1.8	2.7
Recycle Gas, % as										
H_2	42.2	51.2	41.7	38.8	43.2	34.6	20.8	31.7	23.1	47.4
CO	6.5	16.5	5.9	13.6	9.6	8.9	5.7	2.9	2.2	7.4
CO_2	29.5	18.5	28.4	26.2	23.7	30.1	37.0	34.0	40.9	25.7
C_2^-	15.9	9.0	17.3	14.8	18.0	16.9	20.7	19.8	22.3	13.0
C_3^+	5.4	2.1	4.4	4.5	3.2	7.2	13.4	8.9	10.8	4.0
Reactor Feed, % as										
H_2	50.2	55.4	49.6	49.0	48.4	41.0	31.1	42.8	34.8	52.9
CO	18.5	22.1	17.0	16.1	15.7	16.3	12.2	13.4	11.3	16.0
CO_2	12.3	13.3	18.9	19.7	18.6	23.2	28.7	23.2	29.6	17.9
C_2^-	9.5	6.3	11.0	10.7	13.5	12.8	15.8	13.2	15.8	9.1
C_3^+	3.0	1.3	2.6	3.1	2.3	5.3	9.9	5.6	7.4	2.5
H_2/CO RATIO										
In Fresh Feed	1.8	2.0	1.8	2.0	2.0	1.9	1.9	2.0	1.9	2.1
In Reactor Feed	2.7	2.5	2.8	3.1	3.1	2.5	2.3	3.5	3.1	3.2
At Reactor Outlet	6.5	3.1	7.1	2.9	4.5	3.9	3.7	10.9	10.5	6.4
Consumed	1.3	1.4	1.4	1.5	1.4	1.8	1.9	1.7	1.8	1.6
$H_2/(CO + CO_2)$ in Reactor Feed	1.37	1.56	1.38	1.37	1.41	1.04	0.76	1.17	0.85	1.56
C_3^+/C_2^- in Product	1.7	1.3	1.6	1.4	0.72	4.1	6.9	4.9	7.8	4.4
HEAT LIBERATED, BTU/HR.										
Total, x 10^{-3}	87.3	34.1	82.3	49.3	27.5	55.2	36.0	357	376	60.4
Per Lb. of Iron	1450	1330	1380	860	4000	873	750	3730	3350	2880
Per Ft^2 Heat Transfer Surface	4960	1080	5740	2100	--	5410	1230	3020	3170	4930
Avg. ΔT Bed-Coolant, °F.	95	130	99	107	98	87	0	40	56	-5
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	52.2	8.3	58.0	20.1	--	62.1	--	75.5	56.6	--

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	← 14-10 →								
POINT NUMBER	31	32	33	34	35	36	37	38	39
HOURS									
Start	106	130	58	147	187	12	267	231	295
End	130	140	94	183	219	46	279	255	319
Period	24	10	36	36	32	34	12	24	24
REACTOR DATA	← K-6		Below 9'	Above 9' →					
Number and Size of Cooling Tubes			4 1/2" x HSS	None					
Ft_2 Cooling Surface/Ft^3 Bed Volume			20.6	11.4					
Free Cross-Section in Reaction Zone, Ft^2			0.111	0.126					
Hydraulic Radius in Reaction Zone, Ft.			0.0518	0.100					
REACTION CONDITIONS									
Catalyst Number			151						
Catalyst Type			Spent Trail, Copper and Graphite						
Maximum Reaction Temperature, °F.	643	645	646	606	604	655	569	605	635
Pressure, psig.	258	258	261	259	260	203	258	259	258
Space Velocity, SCFH FF/Lb. Fe	236	242	213	165	157	96	114	117	116
Recycle/Fresh Feed	0.4	0.5	0.6	0.8	1.2	1.7	2.0	2.0	2.0
Linear Velocity, Ft/Sec	1.02	1.02	0.94	1.03	1.02	1.02	1.01	1.01	1.02
Catalyst Density, Lbs./Ft^3									
Initial	104	104	107	109	107	101	105	105	104
Final	103	104	107	109	106	107	106	106	102
Total C in Catalyst, % on Fe									
Initial	28	30	18	30	29	9.2	36	35	38
Final	30	30	25	30	33	18	34	38	40
Bed Height, Ft.	← Less than 9' →								
REACTION DATA									
Contraction, % on Fresh Feed	42	37	30	54	28	65	14	31	31
CO Reacted, % on Fresh Feed	80	77	65	88	55	92	25	61	64
CO Converted, % on Total Feed									
% CO Converted to									
CO_2	33	34	36	24	33	17	21	30	30
C_2^-	24	22	15	23	24	21	18	27	30
C_3^+	41	42	46	51	39	60	55	39	37
Alcohols	2	2	3	2	4	2	6	4	3
Carbon	0.05	--	.15	--	.15	.30	.60	.18	.12
H_2 in FF Converted, %	52.0	42.5	35.8	66.0	27.5	78.1	15.0	36.6	41.6
% Contraction (Adj'd. for CO_2 in Feed)									

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	← 14-10 →								
POINT NUMBER	31	32	33	34	35	36	37	38	39
GAS COMPOSITIONS									
Fresh Feed, % as									
H_2	60.5	60.8	60.5	60.7	60.4	61.1	60.2	60.8	60.3
CO	30.7	30.7	30.4	30.9	31.0	30.8	30.8	31.0	30.7
CO_2	6.3	6.4	6.3	6.0	6.0	5.9	6.3	5.8	6.0
CH_4	2.1	1.9	2.6	2.1	1.7	2.0	2.4	1.7	2.4
Recycle Gas, % as									
H_2	50.1	53.2	42.0	56.5	57.0	37.7	58.8	54.3	51.5
CO	10.5	11.0	8.3	15.4	18.3	6.2	26.9	17.3	16.1
CO_2	24.7	23.0	28.0	18.9	15.5	31.3	9.2	16.5	17.3
C_2-	11.3	9.3	15.6	6.2	6.7	18.5	3.7	8.3	9.8
C_3+	3.3	3.5	4.6	1.9	2.1	5.7	1.1	2.2	2.6
Reactor Feed, % as									
H_2	57.6	58.3	53.7	58.8	58.6	46.4	59.1	56.5	54.3
CO	25.0	24.1	22.1	24.0	24.1	15.3	28.2	21.9	20.8
CO_2	11.6	11.9	14.5	11.7	11.2	21.9	8.2	12.9	13.5
C_2-	4.7	4.4	7.5	3.9	4.4	12.4	3.3	6.1	7.3
C_3+	0.9	1.2	1.8	0.8	1.1	3.6	0.7	1.5	1.7
H_2/CO RATIO									
In Fresh Feed	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
In Reactor Feed	2.3	2.4	2.3	2.6	2.4	2.9	2.1	2.6	2.6
At Reactor Outlet	4.8	4.8	5.1	3.7	3.1	6.1	2.2	3.1	3.1
Consumed	1.3	1.1	1.1	1.5	1.0	1.7	1.2	1.2	1.3
$H_2/(CO + CO_2)$ in Reactor Feed	1.58	1.62	1.47	1.65	1.66	1.25	1.63	1.62	1.59
C_3+/C_2- in Product	1.7	1.9	3.1	2.2	1.6	2.9	3.1	1.4	1.2
HEAT LIBERATED, BTU/HR.									
Total, x 10^{-3}	90.4	85.5	79.1	57.9	41.6	51.9	20.3	33.3	36.2
Per Lb. of Iron	8200	7760	8800	3760	3480	4320	1840	3030	3290
Per Ft^2 Heat Transfer Surface	6410	6060	5690	4100	2950	3730	1440	2360	2530
Avg. ΔT Bed-Coolant, °F.	66	68	65	59	54	30	19	45	60
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	97.1	89.1	87.5	69.5	54.6	124	75.6	52.4	42.2

CORRELATING DATA HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	← 14-6 →					← H-25 →			← H-24 →	
POINT NUMBER	41 A	42 B	43 C	44 D	45 E	46 B	47 C	48 A	49 B	50 A
HOURS										
Start	360	428	231	384	400	101	141	45	23	7
End	372	436	348	396	420	137	229	97	39	23
Period	12	8	117	12	20	36	88	52	16	16
REACTOR DATA	← K-4 →					← K-3A →				
Number and Size of Cooling Tubes	0					19-1" XH				
Ft^2 Cooling Surface/Ft^3 Bed Volume	11.4					9.9				
Free Cross-Section in Reaction Zone, Ft^2	.1263					.78				
Hydraulic Radius in Reaction Zone, Ft.	0.100					0.0780				
REACTION CONDITIONS										
Catalyst Number	103									
Catalyst Type	Spent Trail, Ground C & W Original									
Maximum Reaction Temperature, °F.	664	658	645	663	660	644	646	648	650	643
Pressure, psig.	130	200	240	200	200	215	215	232	230	232
Space Velocity, SCFH FF/Lb. Fe	44	57	38	39	32	56	53	56	35	30
Recycle/Fresh Feed	0.3	0.8	0.9	1.3	2.6	0.8	1.0	1.1	1.4	2.3
Linear Velocity, Ft/Sec	0.84	0.94	0.63	0.98	1.04	0.91	1.04	1.05	1.16	1.40
Catalyst Density, $Lbs./Ft^3$										
Initial	23	25	40	26	23	43	35	58	72	73
Final	27	25	29	25	23	39	27	42	66	70
Total C in Catalyst, % on Fe										
Initial	44.5	50.3	36.0	51.4	50.3	38	40.4	24	17.3	---
Final	50.5	55.5	48.0	51.0	49.0	39.6	45.4	38	---	17.3
REACTION DATA										
Contraction, % on Fresh Feed	43	38	64	62	72	78	79	83	83	87
CO Reacted, % on Fresh Feed	91	78	97	92	91	99	98	99	99	99
CO Converted, % on Total Feed	87	89	72	90	85	---	50	94	94	89
% CO Converted to										
CO_2	33	21	18	18	11	13	11	7	9	6
C_2^-	15	18	14	13	17	7	8	7	3	6
C_3^+	47	54	61	61	64	74	75	80	82	82
Alcohols	5	7	7	8	8	6	6	6	6	6
Carbon	.11	1.5	.17	.12	.09	.10	.11	.36	1.4	1.6
H_2 in FF Converted, %	50	54.6	77.6	73.6	86.6	88.5	92.7	93.6	93.6	99
%Contraction (Adj'd. for CO_2 in Feed)	46.6	49.5	69.7	67.5	78.0	83.2	84.6	88.4	88.8	91.2

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	← 14-6 →					← H-25 →			← H-24 →	
POINT NUMBER	41 A	42 B	43 C	44 D	45 E	46 B	47 C	48 A	49 B	50 A
GAS COMPOSITIONS										
Fresh Feed, % as										
H_2	61.6	51.1	60.9	61.6	61.8	61.4	61.1	61.2	61.0	61.8
CO	30.7	25.2	30.8	30.3	30.0	31.5	31.5	31.8	31.7	31.9
CO_2	6.0	21.2	6.0	6.0	5.8	4.0	4.1	4.2	3.6	3.3
CH_4	1.7	1.9	2.2	2.1	1.9	2.3	2.4	1.9	2.9	2.2
Recycle Gas, % as										
H_2	53.3	52.0	40.6	42.5	29.7	35.6	31.2	31.5	33.2	25.1
CO	4.8	12.1	2.9	6.4	9.4	2.0	2.7	1.5	2.3	2.2
CO_2	27.0	19.4	32.2	29.2	31.0	34.8	35.0	35.4	36.2	35.3
C_{2-}	7.8	9.3	13.6	11.1	18.3	16.2	17.9	17.9	16.6	23.7
C_{3+}	4.1	4.2	7.5	6.8	9.1	7.5	9.2	9.7	7.7	9.7
Reactor Feed, % as										
H_2	59.7	--	51.3	50.8	38.7	50.0	46.2	44.6	44.8	36.2
CO	24.7		17.6	16.8	15.1	18.4	17.1	16.0	14.6	11.2
CO_2	10.8		18.4	19.1	24.0	17.7	19.6	20.5	22.7	25.6
C_{2-}	3.1		7.6	7.2	13.7	8.5	10.2	10.3	10.9	17.2
C_{3+}	0.9		3.6	3.8	6.6	3.3	4.6	5.1	4.5	6.8
H_2/CO RATIO										
In Fresh Feed	2.0	2.0	2.0	2.0	2.1	1.9	1.9	1.9	1.9	1.9
In Reactor Feed	2.4	2.5	2.9	3.0	2.6	2.7	2.7	2.8	3.2	3.3
At Reactor Outlet	11.1	--	14	6.6	3.2	18	12	21	15	11
Consumed	1.1	1.4	1.6	1.6	2.0	1.7	1.8	1.8	1.8	1.9
$H_2/(CO + CO_2)$ in Reactor Feed	1.68		1.42	1.41	0.99	1.38	1.26	1.22	1.20	0.98
C_{3+}/C_{2-} in Product	3.1	3.0	4.4	4.7	3.8	10.6	9.4	11.4	27.0	13.7
HEAT LIBERATED, BTU/HR.										
Total, x 10^{-3}	49.5	45.0	60.3	58.6	32.0	565	572	572	544	503
Per Lb. of Iron	1650	1700	--	--	1630	1870	2890	1790	1900	1720
Per Ft^2 Heat Transfer Surface	1820	1900	2700	2250	1660	2830	2870	3360	5170	5101
Avg. ΔT Bed-Coolant, °F.	35	10	33	29	9	84	92	92	100	98
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	52.0	190	81.8	77.6	184	33.7	31.2	36.5	51.7	52.0

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	14-9					14-11			14-12	
POINT NUMBER	61 A	62 B	63 C	64 D	65 E	66 A	67 B	68 C	69	70
HOURS										
Start	168-204	384	8	288	336	49-93	171	105	21	37
End	444-460	444	132	324	372	127-159	195	117	33	57
Period	52	60	124	36	36	108	24	12	12	20
REACTOR DATA	K-5					K-6				
Number and Size of Cooling Tubes			0			Below 9' 4 1/2" XHSS			Above 9' None	
Ft^2 Cooling Surface/Ft^3 Bed Volume			11.4			20.6			11.4	
Free Cross-Section in Reaction Zone, Ft^2			.126			0.111			0.126	
Hydraulic Radius in Reaction Zone, Ft.			0.100			0.098			0.100	
REACTION CONDITIONS										
Catalyst Number			140				160		165	166
Catalyst Type			Jersey Pyrites				Coarse #140		Zircon	Zircon
Maximum Reaction Temperature, °F.	570	565	585	575	575	603	588	556	638	635
Pressure, psig.	225	250	255	255	250	259	258	259	154	154
Space Velocity, SCFH FF/Lb. Fe	19	18	12	11	9	17	18	17	1950	264
Recycle/Fresh Feed	1.7	2.1	2.3	3.8	5.0	1.8	1.8	1.9	.37	.38
Linear Velocity, Ft/Sec	.98	0.98	0.71	0.85	0.84	0.92	.93	.92	1.21	1.20
Catalyst Density, Lbs./Ft^3										
Initial	38	39	43	36	35	50	46	45	103	100
Final	42	42	38	36	34	43	47	46	103	101
Total C in Catalyst, % on Fe										
Initial	10.5 19.4	17.0	3.1	14.0	15.3	7.6 12.1	13.0	10.3	---	---
Final	11.0 20.0	19.4	9.6	15.1	16.4	9.5 12.1	13.1	11.3	---	96
Bed Height, Ft.						19.6	19.6	19.7		
REACTION DATA										
Contraction, % on Fresh Feed	63	67	75	75	76	77	75	73	.6	-.7
CO Reacted, % on Fresh Feed	97	95	98	97	96	99	98	98	1.3	-1.1
CO Converted, % on Total Feed	83	77	85	64	57	90	86	78	1.0	-0.8
% CO Converted to										
CO_2	23	18	13	12	13	10	14	15	60	---
C_2^-	22	25	19	22	21	15	15	16	40	---
C_3^+	52	54	65	64	64	71	65	64	---	---
Alcohols	3	3	3	2	2	4	6	5	---	---
Carbon	.12	.16	.46	.24	.36	(0.26 (0.0	.02	.50		
H_2 in FF Converted, %	81.6	84.9	88.2	91.8	91.2	89.1	88.1	87.6		
% Contraction (Adj'd. for CO_2 in Feed	68	72.4	81.2	81.5	82.4	83.7	81	78.8		

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	← 14-9 →					← 14-11 →			← 14-12 →	
POINT NUMBER	61	62	63	64	65	66	67	68	69	70
GAS COMPOSITIONS										
Fresh Feed, % as										
H_2	60.7	60.2	60.8	60.5	60.9	60.5	60.8	60.7	61.0	60.6
CO	31.4	31.6	31.0	31.4	30.9	31.0	31.2	31.4	30.7	30.7
CO_2	5.2	5.6	5.5	5.8	5.1	5.8	5.7	5.2	6.0	6.1
CH_4	2.1	1.9	2.1	2.2	2.6	2.2	1.7	2.1	1.6	1.9
Recycle Gas, % as										
H_2	34.0	28.5	22.4	18.4	15.3	21.5	27.8	34.0	61.0	60.6
CO	3.2	3.5	2.1	4.2	4.2	1.7	2.4	3.2	30.5	30.8
CO_2	33.4	34.2	38.5	37.4	37.0	38.7	38.6	33.4	6.3	6.1
C_{2-}	20.9	24.1	24.2	28.6	28.9	23.9	18.8	20.9	1.7	1.6
C_{3+}	6.2	7.9	11.0	11.4	12.9	12.3	10.9	6.2	--	--
Reactor Feed, % as										
H_2	43.9	38.8	34.0	27.2	22.9	35.4	39.7	43.9	38.8	38.4
CO	13.6	12.6	10.8	9.9	8.7	12.2	12.7	13.6	19.4	19.5
CO_2	23.0	25.0	28.5	29.7	31.8	27.0	26.9	23.0	3.9	3.9
C_{2-}	14.0	17.0	17.5	23.0	24.6	16.2	12.7	14.0	1.0	1.1
C_{3+}	3.9	5.4	7.7	9.2	10.7	7.9	7.0	3.9	--*	--*
									36.4	36.6
H_2/CO RATIO										
In Fresh Feed	1.9	1.9	2.0	1.9	2.0	2.0	2.0	1.9	1.99	1.97
In Reactor Feed	3.4	3.0	2.9	2.7	2.8	3.0	3.1	3.3	2.00	1.97
At Reactor Outlet	11	8	11	4.4	3.6	13	12	11	2.00	1.97
Consumed	1.6	1.7	1.8	1.8	1.9	1.8	1.8	1.7	--	--
$H_2/(CO + CO_2)$ in Reactor Feed	1.20	1.03	0.87	0.69	0.57	0.91	1.00	1.20	1.67	1.64
C_{3+}/C_{2-} in Product	2.4	2.2	3.4	2.9	3.0	4.7	4.3	4.0	--	--
HEAT LIBERATED, BTU/HR.										
Total, x 10^{-3}	64.4	70.3	52.2	43.1	34.1	68.5	69.6	68.6	--	--
Per Lb. of Iron	939	926	645	600	494	926	954	893	--	--
Per Ft^2 Heat Transfer Surface	2140	2400	1800	1390	1080	1910	1940	1910	--	--
Avg. ΔT Bed-Coolant, °F.	78	58	83	26	7	33	45	34	4	10
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	27.4	41.4	21.7	53.5	154	57.8	43.1	56.2	--	--

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	15-2	← 15-3 →			15-4	15-4	15-5	15-5	15-5	15-5
POINT NUMBER	71	72	73	74	75	76	77	78	79	80
HOURS										
Start	250	371	407	439	484	506	3	23	51	69
End	418	403	427	455	494	530	19	39	63	75
Period	168	32	20	16	10	24	16	16	12	6
REACTOR DATA	← K-4 →									
Number and Size of Cooling Tubes					4 1/2"					
Ft^2 Cooling Surface/Ft^3 Bed Volume					20.6					
Free Cross-Section in Reaction Zone, Ft^2					0.111					
Hydraulic Radius in Reaction Zone, Ft.					0.0518					
REACTION CONDITIONS										
Catalyst Number	103	90 →			90	90	← 123 →			
Catalyst Type	Spent Trail →						← Spent Sterlington →			
Maximum Reaction Temperature, °F.	645	659	664	664	655	658	658	657	657	662
Pressure, psig.	220	210	200	200	212	240	200	200	200	240
Space Velocity, SCFH FF/Lb. Fe	23	22	40	47	47	49	---	9.1	12	12
Recycle/Fresh Feed	2.71	3.21	1.83	2.06	1.69	1.62	1.55	1.13	0.62	0.67
Linear Velocity, Ft/Sec	1.19	1.40	1.51	1.66	1.34	1.21	1.35	1.45	1.51	1.31
Catalyst Density, Lbs./Ft^3										
Initial	36	36	30	27	27	24	96	131	152	152
Final	23	31	29	26	26	27	117	143	152	152
Total C in Catalyst, % on Fe										
Initial	40	33	40	38	--	52.5	--	10	11.6	12.5
Final	64	40	36	--	48.8	50.8	--	11	12.3	12.8
REACTION DATA										
Contraction, % on Fresh Feed	79	73	61	48	67	70	92.1	71	60.0	60
CO Reacted, % on Fresh Feed	96	92	82	89	94	88	98	98	92	91
CO Converted, % on Feed	63	48	61	63	95	97	99	98	89	89
% CO Converted to										
CO_2	6.7	13.3	20.4	17.2	14.8	14.6	2.3	12.9	18.8	20.6
C_2-	10.3	17.0	25.8	32.1	23.7	16.9	22.8	12.8	17.5	12.2
C_3+	77.7	67.5	51.6	47.5	57.5	63.5	70.7	69.2	59.5	62.3
Alcohols	5.3	2.2	2.2	3.2	4.0	5.0	4.2	5.1	4.2	4.9
Carbon	.67	1.1	-.58	--	--	-0.17	--	.71	.54	.18

CORRELATING DATA FOR HYDROCOL, SERIES 14 and SERIES 15 RUNS

TABLE IA

HRI SUMMARY

RUN NUMBER	15-2	← 15-3 →			15-4	15-4	15-5	15-5	15-5	15-5
POINT NUMBER	71	72	73	74	75	76	77	78	79	80
GAS COMPOSITIONS										
Fresh Feed, % as										
H_2	60.3	60.5	60.1	60.5	60.6	60.5	60.9	60.8	61.1	61.0
CO	30.8	30.7	30.2	30.7	30.6	30.8	31.2	31.2	31.5	30.4
CO_2	5.6	5.6	5.8	5.8	6.0	5.7	5.7	5.7	5.8	5.8
CH_4	3.0	3.0	3.7	2.8	2.7	2.6	1.7	1.6	1.0	2.2
Recycle Gas, % as										
H_2	18.4	17.8	32.8	49.3	29.2	25.8	25.1	39.2	45.5	45.8
CO	6.0	9.4	7.9	6.3	5.5	11.7	4.0	2.5	6.5	6.9
CO_2	36.4	33.4	29.1	20.4	31.1	32.0	34.5	33.4	28.0	28.8
C_2^-	23.4	24.9	23.1	19.0	23.2	18.9	25.2	16.4	12.4	11.6
C_3^+	12.6	10.6	6.1	4.0	7.0	8.3	10.3	7.2	5.1	3.9
Reactor Feed, % as										
H_2	29.7	27.9	42.4	53.0	40.8	39.0	39.2	49.3	55.0	54.7
CO	12.7	14.5	15.8	14.3	14.9	19.0	14.6	15.9	21.8	21.0
CO_2	28.1	26.7	20.9	15.6	21.8	22.0	23.2	20.5	14.4	15.1
C_2^-	17.9	19.7	16.2	13.7	15.6	12.7	16.0	9.5	5.4	6.0
C_3^+	9.2	8.1	3.9	2.7	4.4	5.1	6.3	3.8	2.0	1.6
H_2/CO RATIO										
In Fresh Feed	1.96	1.97	1.99	1.97	1.98	1.97	1.95	1.95	1.94	2.01
In Reactor Feed	2.33	1.92	2.68	3.71	2.74	2.74	2.68	3.10	2.52	2.60
At Reactor Outlet	3.03	1.89	4.15	7.83	5.32	2.20	6.28	15.7	7.00	6.64
Consumed	1.91	1.98	1.74	1.27	1.77	1.93	1.85	1.65	1.48	1.55
$H_2/(CO + CO_2)$ in Reactor Feed	0.73	0.69	1.16	1.77	1.11	0.95	1.04	1.35	1.52	1.52
C_3^+/C_2^- in Product	7.54	3.97	1.99	1.48	2.43	3.76	3.10	5.40	3.40	5.10
HEAT LIBERATED, BTU/HR.										
Total, x 10^{-3}	48.2	46.6	63.6	53.9	70.0	73.4	77.9	90.1	113	111
Per Lb. of Iron	1270	1170	1860	1830	2360	2470	--	450	540	530
Per Ft^2 Heat Transfer Surface	1176	1140	1551	1315	1710	1790	1900	2200	2760	2710
Avg. ΔT Bed-Coolant, °F.	16	21	31	34	34	37	48	47	41	48
Avg. Overall Heat Transfer Coefficient, BTU/Hr. - Ft^2 - °F.	73.5	54.3	50.0	38.7	50.3	48.4	39.6	46.8	67.3	56.5

Accuracy of Data

The accuracy of many of these data was not too good. The atomic balances and the overall material balances were poor. Therefore, when judging the cause of deviations from the correlations it must be remembered that much of the deviation may be due to experimental error rather than to the specific effect of some variable. In many instances the graphs presented cannot be considered correlations. They must be viewed simply as a graphical comparison of the data.

On the other hand, it must be remembered that many of the relationships developed in this report can actually be used to check the accuracy of certain measurements and, since all the same measurements are not involved in each relationship, a point may be off on one plot but in line on another.

Range of Variables Covered:

The range of operating variables used by the various laboratories is shown on the following Table II.

TABLE II

RANGE OF VARIABLES COVERED BY DATA

Lab.	Unit	H_2/CO	CO_2/CO	CH_4/CO	R/FF	% Contr.	Temp.°F.	Press.	V/Hr/W	V/Hr/V	Lin.Vel.fps
Beacon	#7	1.86-2.00	0-125	None	0-1.2	12-79	600-650	200	18-50		
Beacon	#8	199	None	None	1.0-1.2	64-81	650	200	59		
HRI	H	1.92-2.54	0-27	4.9-15.5	0.4-6.7	48-88	592-650	190-235	12-176	575-1780	
HRI	14	1.78-2.08	11-84	3.3-9.1	0.3-5.0	6-81	556-664	130-261	9-1950		0.63-1.24
HRI	15	1.94-2.01	18.2-19.6	3.2-12.3	0.6-3.2	48-92	645-664	200-240	9-49		1.19-1.61
A	-	0.99-1.98	0.1-13.5	2.0-9.6	1.0-14.5	28-81	495-640	132-390		209-1135	0.16-.37
B Runs 5 & 6	-	1.17-1.62	34.9-55.4	2.7-16.8	0.87-2.19	21.58	555-627	264-345	1.8-6		0.34-.51
B Runs 11 & 12		2.00-2.14	25.2-31.3	3.5-9.4	1.96-4.58	52-85	564-675	235-400	31-88		0.7-1.4
Stanolind		3.36-4.54	36.5-52.8	30.3-55.4	0.36-1.38	31-75	580-606	163-164.4			

VI. APPARATUS USED

A description of the reactors used by the various laboratories is included in the following Table III.

TABLE III

Reactors Used

Beacon Unit #7 (Stirred)

Reactor 1-5/8" I.D. Reaction Space 20" Lg.
Stirrer shaft 5/8" O.D. Jacket Cooled

Beacon Unit #8 (Fixed baffles)

Reactor 3/4" I.D. by 9 ft. lg.

HRI H Unit:

Reactor 11.5" I.D. x 18-1/2' lg. See HRI Summary Table IA for Dow therm cooling surface and other data. Expanded section above reactor 24" long. Filters used for catalyst separation.

HRI 14 Unit:

Reactor 4.5" I.D. x 18' lg. See HRI Summary Table IA for Dowtherm cooling surface and other data.

HRI 15 Unit:

Reactor same as 14 Unit except catalyst circulated through standpipe outside reactor. See HRI Summary for Dowtherm cooling surface.

Laboratory A:

Reactor - 9 ft. lgt. of 2" std. pipe expanded to a settling zone consisting of a 30" lgt. of 6" std. pipe. Dowtherm jacket cooled.

Laboratory B:

Reactor - 10" diam. by 40 ft. lg. overall top 10 ft. expanded to about 16" diam. Dowtherm jacket cooled with cyclones inside expanded area.

Stanolind Pilot Unit:

8" Reactor - jacket dowtherm cooling.

VII. CORRELATIONS

A. Conversions and Distribution of Product

Until further data are obtained for the specific purpose, it is impossible to establish accurately the independent effect of many of the operating variables listed above. As a matter of fact, the magnitude of the effect of some of the factors, within the range studied, may be so small as to be well within the accuracy of the data used.

It is recognized that a more careful study of the individual points might disclose effects that went unnoticed. However, the time available, dictated that only the major effects could be studied at this time.

It has been found that for good catalysts there are certain broad relationships between degree of conversion and product distribution which appear to be independent of the conditions used to attain that degree of conversion. These broad relationships will be presented first.

Measure of degree of Conversion:

It has been found that CO disappearance is a poor index of the process efficiency. The CO disappears very rapidly in all cases even though the % H_2 disappearance is low. When catalyst activity is improved or better operating conditions are used, however, the H_2 disappearance will increase while the CO disappearance, already high, may change very little.

Better measures of degree of conversion are:

1. % Contraction (readily available on the unit)
2. H_2 Disappearance (% of H_2 in FF converted)
3. Water yield
4. Other liquid yield
5. Beyond 60% contraction with a given catalyst the CO_2 content in the product is an indication of conversion. This decreases as conversion increases.

For purpose of this correlation it has been found desirable to use H_2 disappearance expressed as % H_2 in the Fresh Feed as the measure of degree of conversion. This is called "H_2 Conversion" throughout the report.

% Contraction vs. H_2 Conversion:

The % Contraction, expressed as Fresh Feed minus Exit Gas divided by Fresh Feed, correlates reasonably well against H_2 Conversion as shown by Figs. I, IA, IB, IC & ID.

Figure IA is a plot of all the HRI data with the % Contraction calculated directly, that is, without correcting for the CO_2 or CH_4 in the Fresh Feed. (FF in SCFH - Exit Gas in SCFH divided by FF in SCFH). The H Series data correlate extremely well but the 14 Series data all show a broad scattering and a lower contraction for a given H_2 Conversion.

Since the CO_2 and CH_4 content of the Fresh Feed was somewhat higher in these H Series runs than in the others, it was felt that a better correlation could be obtained if the % Contraction were recalculated basis a pure H_2 + CO feed, that is, considering the CO_2 and CH_4 in FF inert and by removing this amount of CO_2 and CH_4 from both the fresh feed and exit gas. This was permissable because there was no evidence of CO_2 or CH_4 disappearance except in Run H-6.

The adjusted % Contractions are plotted against H_2 Conversion on Fig. IB. The deviation is less than that in Fig. IA but again there is a real difference between the 14 Series data (direct from summaries) and the H Series data. Whether this is due to the difference in method of calculation or to differences in operating variables will be considered later. Assuming the data accurate, it does indicate that in the 14 Series more of the H_2 went to gas than in the H Series.

This plot shows graphically and readily, which runs gave high conversions and which were poor. The reasons for the differences in degree of conversion will be considered later.

Fig. IC is a similar plot of % Contraction basis H_2 + CO in Fresh Feed vs. H_2 Conversion for the data supplied us by HRI which were obtained with low H_2/CO in fresh feed. In general, these data correlate well and make possible a family of curves with H_2/CO in the fresh feed as the parameter.

The solid lines of Fig. IC are reproduced on Fig. ID which is a plot of the Stanolind data, most of which were obtained with an H_2/CO

ratio in the fresh feed of 4.0 or more.

In these runs the Fresh Feed contained considerable CO_2 and CH_4 (CO_2/CO in FF = 35 to 55) and except in periods 1, 2, 3 and 14 much of the CO_2 and some of the CH_4 apparently disappeared along with some of the surplus H_2. The theoretical relationship between H_2 Conversion and % Contraction with and without CO_2 reacting is shown below.

H_2/CO in FF	CO_2/CO in FF		% Contraction H_2 Conv.	Theor.*	Actual
1	0	$3H_2 + 3CO \longrightarrow 2CH_2 + CO_2 + H_2O$	100	83.3	75.0
		$3H_2 + 3CO \longrightarrow 1.5CH_2 + 1.5\ H_2O + 1.5CO$	100	75.0	
2	0	$2H_2 + CO \longrightarrow CH_2 + H_2O$	100	100.0	95.0
4	0	$4H_2 + CO \longrightarrow CH_2 + H_2O + 2H_2$	50	60 60 (Adj.)	-
4	0.5**	$4H_2 + CO + 0.5CO_2 \longrightarrow CH_2 + H_2O + 2H_2 + 0.5CO_2$	50	54.5	
4	0.5	$4H_2 + CO + 0.5CO_2 \longrightarrow 1.5CH_2 + 2H_2O + 0.5H_2$	87.5	90	

The dotted lines on Fig. ID are those representing the above theoretical relationships with and without CO_2 reacting. It will be evident that in these runs the % Contraction was in general not as high as would be expected if all CO_2 were to disappear. This may indicate that CO_2 disappearance is not as rapid as CO or that more gaseous product is made when there is a surplus of H_2 in the Fresh Feed. On the other hand the deviations may be due largely to experimental error or an error in our interpretation of the Stanolind data.

Fig. I shows the Beacon data compared with the correlation of Figs. IB and IC. In this case the fresh feed contained no CO_2 or CH_4 except in the series 14, 15, 18 and 22 but these were adjusted to CO_2 free basis because no net disappearance of CO_2 occurred. (The runs with CO_2 added were all once through).

The following will be noted from Fig. I.

1. The once through runs with CM&S reduced catalyst (7, 23, 35A and 35B) are a good check on each other and the once through results are only 63% H_2 Conversion and 58% Contraction.

2. H_2 Conversion is increased to 88% and contraction to 78% by

*Assuming all CH_2 is liquid.
**No CO_2 reacted.

recycling with a R/FF of 1.0 (Runs 24, 27 & 8001). The contraction here however was less than experienced by HRI.

3. Lowering the temperature to 600°F. (Run 7005) more than offsets the beneficial effect of recycling at 0.5 R/FF.

4. CM&S unreduced catalyst at 1.0 R/FF results in an H_2 Conv. and % Contraction little better than those obtained without recycling with the same catalyst reduced.

5. Adding CO_2 to the feed increase H_2 Conversion and % Contraction slightly.

6. C.I. Powder is not a suitable catalyst.

7. Limonite with KF is better than Limonite with K_2O but both are very poor when compared to the CM&S reduced catalyst used at the same R/FF in Runs 24 and 27.

These two catalysts apparently convert H_2 faster than the others indicating a tendency to produce more CH_4, more H_2O and a more saturated hydrocarbon fraction.

8. The correlation of Fig. I, that is the line for $H_2/CO = 2.0$, is satisfactory for the purpose of currently estimating the H_2 conversion from the % contraction which can be determined easily on the unit as the run progresses.

9. Of all the runs included here only five, Runs 7024, 7027, 8001, 8003 and 8004 attained a degree of conversion comparable to those obtained in several runs at Olean.

10. The three runs on unit #8 with special catalysts will be discussed separately under "Effect of Catalysts".

H_2 Conversion vs. CO Conversion

Fig. IIA is a plot of % H_2 in FF Converted vs. % CO in FF Converted for all the HRI data which it will be remembered were obtained with the fresh feed having an $H_2/CO = 2$.

It will be noted that in general the 14 Series data show a lower CO Conversion for a given H_2 Conversion than the H Series. This may be due partly to the fact that the CO_2 content of the Fresh Feed was higher (6%) in the 14 Series than in the H Series (0.2%).

On the other hand the difference may be due to apparatus design and partly to catalyst used. The latter definitely influences the relative rate of CO and H_2 disappearance as we shall see later from the Beacon data.

On this plot there are shown as dotted lines, the relationship between H_2 Conversion and CO Conversion if the following equations occurred.

1) $H_2 + 2CO \longrightarrow CH_2 + CO_2$

2) $2H_2 + 2CO \longrightarrow CH_4 + CO_2$

3) $2H_2 + CO \longrightarrow CH_2 + H_2O$

4) $3H_2 + CO \longrightarrow CH_4 + H_2O$

The data indicate that at first, the H_2 and CO disappear in the ratio of 1/1 and equation (2) most nearly represents what actually occurs at the beginning when the ratio of H_2/CO in the fresh feed is 2/1.

Fig. II shows all the Beacon data (also H_2/CO in FF = 2.0) compared with the H Series line of Fig. IIA. The data with the CM&S reduced catalyst are an excellent check on the HRI H Series data.

It will be noted also that adding CO_2 to the feed definitely lowers the CO Conversion for a given H_2 Conversion. There is no consistent relationship between the magnitude of this effect and the amount of CO_2 added. It appears that a small amount of CO_2 (10% of Fresh Feed) has essentially as much an effect as a large amount of CO_2 (30% of Fresh Feed).

This bears out the previous suggestion that the 14 Series data shown on Fig. IIA may be low partly because the CO_2 content of the Fresh Feed was about 6%.

From this plot it will be noted that:

1. As previous mentioned, CO Conversion alone is not a good measure of catalyst activity or of the effect of operating variables. CO Conversion is always relatively high and not materially effected by temperature or recycle rate. Whereas both of these have a profound effect on H_2 Conversion and % Contraction.

Even with mild conditions or a mild catalyst, the CO practically all disappears, but much of it goes to CO_2. More drastic conditions increase CO Conversion a little but their principal effect is to reduce the CO_2 initially formed with further disappearance of H_2. Therefore, H_2 Conversion or % Contraction is a better indication of degree of conversion.

2. Adding CO_2 to the feed reduces CO Conversion but does not materially affect H_2 Conversion.

3. Recycling 1/1 with unreduced catalyst results in an H_2 conversion little better than that obtained once through with reduced catalyst and the CO conversion is a little less. There is no consistent indication that the catalyst would eventually have conditioned itself to give the same results as obtained with the reduced catalyst in Runs 24 and 27.

4. The results with both limonite catalysts were very poor but there is some indication that the additives have some selective qualities. The KF gives a lower CO disappearance and higher H_2 disappearance than the K_2O.

Fig. IIB is a plot of the H_2 Conversion vs. CO Conversion of all the data from the laboratories A & B. Most of the data from Laboratory A were obtained with a Fresh Feed having an H_2/CO ratio of 1 and a CO_2 content of less than 1%. These particular data are denoted by open squares and it will be noted that, although the scattering is fairly great, they correlate reasonably well on a straight 45° line indicating that in this case H_2 disappears just as fast as CO as would be expected with an equation such as equation (2) above, viz; $H_2 + CO \longrightarrow 1/2\ CH_4 + 1/2\ CO_2$.

Some of the data from Laboratory B were obtained with a fresh feed having an H_2/CO ratio of 2 but the CO_2 content in these runs was 7.5 to 8.5% (CO_2/CO = 25 to 30) and the CO Conversion was considerably less than those in the HRI and Beacon 2/1 runs, the line for which is shown on Fig. IIB for comparison.

The runs from Laboratory A with 1.5 H_2/CO ratio in the Fresh Feed fall about where expected. In these the CO_2 content of the feed was low. Many of those of Laboratory B however, where the CO_2 content varied from 13 to 19% (CO_2/CO = 35 to 55%) show low CO Conversions. The line for H_2/CO = 1.5 and CO_2 in FF = 0 is approximate only.

Fig. IIC shows the H_2 Conversion vs. CO Conversion of the Stanolind data. The solid line on this figure is that for H_2/CO in FF = 2 reproduced from Fig. IIB and the dotted line is that calculated for 4/1 ratio assuming that at the beginning, CO and H_2 disappeared on a 1/1 basis the same as they

apparently do when the fresh feed H_2/CO is 1/1 or 2/1.

The Stanolind fresh feed always contained 7 to 10% CO_2 (CO_2/CO = 35 to 55%) and considerable CH_4. The H_2/CO ratio was 4 or more in all except three runs. In two of these it was 2.3 as noted. These two runs fall more or less where expected. In the other runs however, the H_2 disappearance was considerably greater than expected. Some of the surplus H_2 was used up in reaction with the CO_2 to produce Hydrocarbons and H_2O.

Probably for all of these data a better correlation could be obtained if CO + CO_2 Conversion were plotted instead of CO Conversion.

H_2 Conversion vs. CO in FF to CO_2

Fig. IIIA shows H_2 Conversion vs. CO to CO_2 for all the HRI data. The data may be divided into three groups:

A. H_2/CO in FF = 2, % CO_2 in FF = 0
H Runs 5B, 14 and 17

B. H_2/CO in FF = 2, % CO_2 in FF = 4-6
Five of the calculated H Series runs and all the 14 Series runs.

C. H_2/CO in FF = 2.2-2.5, % CO_2 in FF = 0
The remainder of the H Series runs.

These data and those from other laboratories to be submitted below indicate that both H_2/CO ratio in FF and CO_2 content of FF effect CO_2 yield for a given degree of conversion. Therefore three lines have been shown as noted.

It is possible that a more careful analysis of the 14 Series data, which scatter badly, would show the effects of other variables on CO_2 yield but time did not permit such a study at this time.

It will be noted that CO_2 yield definitely goes through a maximum and after the H_2 Conversion exceeds 50 to 55%, it decreases as conversion increases.

Fig. IIIB shows the data of Laboratory B Runs 11 and 12 which were made with a fresh feed having an H_2/CO ratio of 2.0 with a CO_2 content of 7 to 8% (CO_2/CO in FF = 25-30). All but one point fit reasonably well on a single curve drawn through the only point available at Beacon and HRI Run H 6 with approximately the same CO_2 content in the Fresh Feed.

Fig. IIIC is a plot of all the data available with the H_2/CO ratio in the Fresh Feed equal to 1.0 (Lab. A). There is a slight indication that CO_2 yield drops off as CH_4 in FF increases but this effect is probably within the accuracy of the data.

Since the shape of this curve is radically different from those for 2/1 feed there was some doubt about the accuracy of the data.

However, if we assume the relationships previously established to be correct it is possible to calculate the maximum possible yield of CO_2 stoichiometrically as follows:

For $H_2/CO = 1.0$

H_2 Conv.	CO Conv. Fig. IIB	% Contr. Fig. IC	Max. Yield CO_2/CO	Limiting Condition
25	25	17	12.5	O_2 Balance
50	50	37	25.0	O_2 Balance
75	75	57	36.0	Contraction
100	100	75	50.0	Both

For $H_2/CO = 1.5$

H_2 Conv.	CO Conv. Fig. IIB	% Contr. Fig. IC	Max. CO_2/CO	Limiting Condition
25	37.7	20.1	18.5	O_2 Balance
50	75.2	42.2	37.5	O_2 Balance
75	93.3	63.6	46.6	Both
100	100	85.0	37.5	Contraction

For $H_2/CO = 2.0$

H_2 Conv.	CO Conv. Fig. II	% Contr. Fig. IC	Max. CO_2/CO	Limiting Condition
25	50	23.5	25.0	O_2 Balance
50	92.5	47.2	47.0	O_2 Balance
75	99.5	71.2	36.0	Contraction
100	100	95	15.0	Contraction

Fig. IIID shows these calculated maxima curves in solid compared with those predicted by the data in dotted.

Fig. IIIE is a plot of all the data available for a fresh feed having an H_2/CO ratio = 1.2 to 1.5. The data from Laboratory A fall where they should but many of those from Laboratory B show a much lower yield of CO_2 than would be expected perhaps because the CO_2 and CH_4 content of the fresh feed was very high. The data of run 5A are obviously in error and are so designated.

Fig. III compares all the Beacon data with the correlation of H_2 Conversion vs. CO in FF to CO_2. It will be noted that:

1. The runs with reduced CM&S catalyst are a good check on the relationship established from HRI data.

2. Adding CO_2 to the feed materially reduces the amount of new CO_2 formed somewhat in proportion to the CO_2 added. If H_2 Conversion were increased by increasing temperature, recycling or catalyst activity, some net disappearance of the CO_2 added could be effected. This however at the expense of some reduction in CO Conversion as shown in Fig. 2.

There is some indication, in Run 22, that CO_2 formation and H_2 formation decrease with catalyst age.

3. The selective qualities of Limonite catalysts are evident here as well as in Figs. I and II. The K_2O produces much more CO_2 than the KF. This may account for the higher CO Conversion and lower H_2 Conversion with the K_2O.

4. The unreduced CM&S catalyst also has a selective effect which changes somewhat with catalyst age. In general it produces less CO_2 which is consistent with the lower CO Conversion experienced at a given H_2 Conversion. The latter is of course considerably lower than was obtained at the same conditions with reduced catalyst.

On Fig. III there are also plotted the Stanolind data for a fresh feed of high H_2/CO ratio and high CO_2 content (CO_2/CO = 35 to 55). It is evident that the CO_2 disappears very rapidly as H_2 disappearance increases.

H_2 Conversion vs. CO to C_3+

Having established the actual CO_2 yield for a given H_2 or CO Conversion, we can calculate by carbon balance what the maximum possible total yield of Hydrocarbons and oxygenated compounds could be, expressed as % CO in the fresh feed as follows: (Assuming of course, that no CO_2 or CH_4 in the fresh feed was converted).

For H_2/CO in FF = 1:

H_2 Conv.	% CO Unconv. (Fig. II)	% CO to CO_2 (Fig. III)	% CO to HCs & Oxy. Comps.
25	75	6	19
50	50	13.5	36.5
60	40	17.0	43.0
75	25	23.6	51.4
90	10	32.0	58.0
100	0	39.0	61.0

For H_2/CO in FF = 2.0:

H_2 Conv.	% CO Unconv. (Fig. II)	%CO to CO_2 (Fig. III)	% CO to HC_s & Oxy. Comps.
25	50	15.6	34.4
50	7.5	30.2	62.3
60	3.3	29.4	67.3
75	0.5	23.0	76.5
90	0.3	12.2	88.5
100	0	2.5	97.5

The yield of C_3+ for the recalculated HRI data and the Beacon results with CM&S reduced catalyst are compared with the above mathematical results of total HC yield for a 2/1 feed (dotted line) on Fig. IV. If the data can be presumed correct, then the deviation of any point from the dotted line shows the magnitude of the $C_1 + C_2S$ yield. It will be noted that:

1. The reported yield in Run H_6 is much higher than that mathematically possible even when the conversion of some of the CO_2 in the Fresh Feed is accounted for.

2. When the H_2 Conversion is above 85%, contraction over 80%, the yield of C_3+ can vary appreciably even though there is no net disappearance of CO_2. Since the points in question correlated well on the CO_2 yield and CO conversion relationships, it must be concluded that if the data are correct, certain conditions tend to produce more hydrocarbon gas ($C_1 + C_2S$) than others. It appears that the gas production was highest in the Beacon runs (no CO_2 or CH_4 in FF), lower in H Runs 2, 3, 5A and 5B (no CO_2 but some CH_4 in FF) and lowest in H Runs 17, 24 and 25 (considerable CO_2 and some CH_4 in FF). This indicates that adding CO_2 or CH_4 in the FF can reduce gas yields. On the other hand this effect could well be caused by a combination of other factors and no conclusions should be drawn at this point. The solid line shown can be used only for a rough approximation of the C_3+ yield.

Fig. IVA is a plot of C_3+ yield for all the HRI data taken directly from the HRI summaries. The solid line is that reproduced from Fig. IV. The C_3+ yields obtained in the 14 Series runs 7, 8 and 9 were all considerably lower than those obtained in the H Series.

Fig. IVB is a plot of the C_3+ yield for the Laboratory A data (Low H_2/CO ratio feed) compared with the calculated maximum and the line

for the 2/1 feed. Here again the scatter is very great but the deviation in this case is apparently due to error or a combination of several factors because no consistent parameter could be found. The solid line through the data is intended for rough approximation purposes only.

Fig. IVC shows all the Beacon data other than that obtained with CM&S reduced catalyst. It will be evident that:

1. Adding CO_2 to the feed increase C_{3+} yield.

2. The C_{3+} yield with unreduced catalyst at 1/1 recycle ratio was about the same as that obtained with reduced catalyst running once through.

3. The C_{3+} yields with the Limonite and other special catalysts was less than that obtained with CM&S reduced catalyst except perhaps for Beacon catalyst #3 which produced a little higher yield than the CM&S catalyst.

H_2 Conversion vs. CO to $C_1 + C_2S$

Fig. V is a plot of the yield of hydrocarbon gas ($C_1 + C_2S$) for all the HRI recalculated data and the Beacon results obtained with CM&S reduced catalyst.

The dotted line is that calculated by Carbon balance assuming that the previously established relationships including the solid line through the data for C_{3+} yield were correct. It will be evident that the wide deviation from any average line is more or less in line with previous comments.

Fig. VA is a similar plot of the Laboratory A data. (H_2/CO in FF = 1.0).

It will be clear that in order to prevent the calculated lines on either of these plots from going through a reversal at high conversions as shown, it would be necessary to materially taper off the straight lines for C_{3+} yield, reduce the CO_2 yield or increase the % CO converted, none of which are justified by the data. It is indicated therefore that the yield of CH_4 and C_2S may at first increase as H_2 conversion increases and then become less as degree of conversion is further improved.

H_2 Conversion vs. CO to CH_4

The methane yield for the HRI data are plotted on Fig. VIA.

These indicate that methane yield goes through a reversal and increases with recycle ratio.

It appears also from this plot, that adding CH_4 and CO_2 to the fresh feed will reduce the amount of CH_4 made. This is notable in Run 6 where both CH_4 and CO_2 in the fresh feed were high.

Fig. VI is a plot of the methane yield for all the Beacon data, with the lines of Fig. VIA shown dotted. This plot confirms the effect of recycle ratio on methane yield indicated by the HRI data. It also shows that in those Beacon runs which had no CH_4 or CO_2 in the fresh feed, the methane yield was considerably higher than in the HRI runs where the CH_4/CO in the Fresh Feed ranged from 5 to 12 in all cases and the CO_2/CO varied from 0 to 20. The higher yield of CH_4 in the Beacon runs on the other hand, may be due to temperature which in general was 20 to 50° higher in the Beacon runs.

It will be noted from Fig. VI that in the Beacon runs where CO_2 was added deliberately to the Fresh Feed, the methane yield dropped. It will also be noted from this same figure that certain catalysts promote methane yield whereas, the unreduced CM&S catalyst produced less methane for a given H_2 Conversion.

The methane yield is apparently influenced by all of the following factors:

1. H_2/CO ratio in Fresh Feed
2. CO_2 content of Fresh Feed
3. CH_4 content of Fresh Feed
4. Recycle ratio
5. Type of catalyst
6. Temperature

Item #4, recycle ratio, effects the ratio of CH_4/CO_2 in total feed and also the ratio of CH_4/H_2O in total feed. Changes in these ratios may be responsible for the apparent effect of recycle ratio on methane yield.

The only data available where both CO_2 and CH_4 were missing from the fresh feed are those obtained at Beacon. These are plotted together with all the other Beacon data on Fig. VI.

Fig. VIB shows the HRI 2/1 Line for methane yield when the R/FF = 3.0 compared with the Laboratory B 2/1 data obtained at the R/FF ratios ranging from 2.0 to 4.6. The Fresh Feed compositions (approx. averages) of the HRI and Laboratory B data shown are compared below.

	HRI	Laboratory B
H_2/CO in FF	2	2
CO_2/CO in FF	19	28
CH_4/CO in FF	11	8

Some of the Laboratory B data check the HRI Line but in general the methane yield was higher than obtained in the HRI runs perhaps because the CH_4 in the fresh feed was a little less. Since the CO_2 in the FF was greater in the Laboratory B runs, this indicates that CH_4 content of the FF has a more profound effect on CH_4 formation than the CO_2 content.

Fig. VIC is a plot of all the Laboratory A data where the H_2/CO ratio in the fresh feed was 1.0. No sensible correlation has been found for these data but it will be noted that in general the methane yield for a given conversion was as high or higher than in the HRI runs with 2/1 H_2/CO in the feed. Perhaps this is because the recycle ratio was almost always high in the Laboratory A runs. On the other hand, it is indicated that when H_2/CO ratio in the FF is low, factors other than recycle rate may control methane formation.

An inspection of the data where the fresh feed H_2/CO ratio was between 1.0 and 2.0 indicates that within this range methane formation is not a function of H_2/CO ratio in the feed.

With the Stanolind high H_2/CO ratio feeds the methane yield varies all over the lot. (As shown on Fig. IVD) Some being very high for no apparent reason and some being very low. It is believed that these data can be considered unreliable and it cannot be concluded that high H_2/CO ratios in the fresh feed inevitably result in high methane yields.

CH_4 Yield vs. Yield of C_2S

Suspecting that the same factors which effect methane yield might also effect the yield of C_2S, a plot of one vs. the other was made for all the Beacon data in Fig. VII. The relationship is not bad for the CM&S Catalyst but breaks down with catalysts that tend to selectively promote

high methane formation.

A similar plot of the HRI data is shown on Fig. VIIB. In general, the HRI runs produced much more C_2S for a given yield of methane.

Fig. VIIC shows the same relationship for all the Laboratory A and Laboratory B data. If the earlier runs 18, 19 and 20 are discounted there is evidently a relationship for these data which falls between that for Beacon and HRI data. These Laboratory A and B data indicate that the relationship between CH_4 and C_2 yield is independent of H_2/CO ratio in the fresh feed. As this increases from 1 to 2 the CH_4 and C_2 yields both increase.

H_2 Conversion vs. Yield of C_2S

A plot of H_2 Conversion vs. yield of C_2S for the Beacon data is included as Fig. VIID. A similar plot Fig. VIIE is included for the HRI data.

Yield of C_2S vs. Yield of C_3S

Fig. VIII is a plot of the C_2 yield vs. the yield of C_3S for all the data. The accuracy of determination of one or the other or both of these is not too great. Except for the few Beacon runs with special catalysts there is no good explanation for the wide deviation experienced. Run #6 of HRI is apparently in error as to C_3 or C_2 determination. The HRI 15 Series runs may actually have produced a higher ratio of C_3S to C_2S but no reason for this is conjectured. The special catalysts tried at Beacon all have a tendency to produce more C_2S as well as more CH_4 than the others but the production of C_3S was apparently in line with that experienced with other catalysts.

Yield of Methane vs. % Unsats. in C_2S

Fig. IX is a plot of methane yield vs. % unsaturates in C_2 fraction. Apparently the factors which increase methane yield also increase ethane yield since unsaturation of C_2 fraction decreases as methane yield increases.

On this plot points 27 and 1 are out of line probably because the ethane and ethylene were erroneously reversed when the data was reported. The other points out of line are those obtained with cast iron powder catalyst and one of the catalysts made at Beacon. These it seems tend to

selectively saturate the C_2 fraction.

Fig. IXA is a plot of the corresponding factors for the HRI data. The Beacon line of Fig. IX is reproduced for comparison.

Again the relationship appears to hold fairly well except for Runs H5, H6, H25 and part of the 14 Series. Why these particular runs are out of line is not evident.

The % Unsaturation of the C_2 fraction for a given methane yield was considerably lower in the HRI runs than in the Beacon runs. This may be significant but the reason is not obvious. It may be due to consistent error in analyses.

% Unsats. in C_2S vs.% Unsats. in C_3S and % Unsats. in C_4S

Fig. X shows the relationship between unsaturation of C_2 fraction and that of the C_3 fraction for all the runs on which such data was available. Bearing in mind the large possibility of error in the determinations, the relationship is good for all but 4 or 5 pts. In addition, two or three of the points representing runs with special catalysts show a lower % unsaturation for the C_3 fraction than the others.

Figs. XI and XII show similar relationships between the unsaturation of the C_2, C_3 and C_4 fractions.

H_2 Conversion vs. H_2 to H_2O

Fig. XIII shows the relationship between H_2 Conversion vs. % H_2 in FF to H_2O (as measured) for the HRI data, the Beacon data with CM&S reduced catalyst and data from other laboratories on 2/1 feeds.

If we assume that the CO Conversion and the CO_2 yield relationships are correct, then by oxygen balance we can calculate the maximum possible H_2O yield as follows:

For H_2/CO in Feed = 1.0 (400 H_2, 400 CO)

H_2 Conv.	O in CO UnConv.	O in CO_2	O in H_2O	H_2O/H_2 in FF
25	300	48	52	13.0
50	200	108	92	23.0
75	100	189	111	27.7
90	40	256	104	26.0
100	0	312	88	22.0

For H_2/CO in Feed = 1.5 (900 H_2, 600 CO)

H_2 Conv.	O in CO UnConv.	O in CO_2	O in H_2O	H_2O/H_2 in FF
25	375	139.2	85.8	9.5
50	150	313.6	136.4	15.2
60	76	334	190	21.1
75	40	372	188	20.9
90	16.8	290.4	292.8	32.6
100	0	192	408	45.3
For H_2/CO in Feed = 2		(200 H_2, 100 CO)		
25	50	31.2	18.8	9.4
50	7.5	60.4	32.1	16.1
60	3.3	58.8	37.9	19.0
75	0.5	46.0	53.5	26.8
90	0.3	24.4	75.3	37.7
100	0	5.0	95.0	47.5

The latter is shown dotted on Fig. XIII. Since the calculated line includes the oxygen that went to alcohols, it is evident that the reported water yields in many of the runs may be too high.

Similar lines are shown with the Laboratory A data for feeds having H_2/CO ratios of 1 and 1.5 on Fig. XIIIA.

On XIIIB are shown the Beacon data for the runs other than those made with CM&S reduced catalyst.

H_2 Conversion vs. Yield of Oxygenated Compounds

It was hoped that the H_2O correlation might throw some light on the factors influencing the yield of alcohols and other oxygenated compounds. This is not the case however, and the only data on this item available at this time are those reported by HRI. These have been plotted on Fig. XIV which indicates that the yield of oxygenated compounds increases with H_2 Conversion and decreases as recycle ratio is increased.

VII. CORRELATIONS

B. Effect of Operating Variables

Effect of Recycle Ratio:

It is evident from an inspection of the data that the degree of conversion; that is, the % Contraction, H_2 disappearance or CO disappearance, can be materially increased by simply changing the composition of the fresh feed or the recycle ratio, both of which influence the composition of the total feed. This in turn also profoundly effects the distribution of product for a given conversion.

Fig. XV is a plot of H_2 Conversion vs. R/FF for the HRI H Series data and the Beacon data obtained with CM&S Reduced Catalyst. It will be evident that increasing recycle ratio increases conversion. As a matter of fact recycling is essential if the H_2 Conversion is to be increased above 60-65% which is the conversion consistently obtained when operating with 2/1 H_2/CO feed once through.

On the other hand recycling is apparently not the only means to increase conversion. Fig. XVA shows some of the HRI 14 Series data taken directly from their summaries. These data show that under some conditions it is necessary to recycle more than in the H Series runs in order to obtain the same degree of conversion. It should be noted from Fig. IVA that in most of these 14 Series high recycle runs, the yield of C_{3+} for a given conversion was low and the CO Conversion was low (Fig. IIA) indicating perhaps that high recycle ratios have a detrimental effect and that to obtain maximum yields one should operate with conditions and catalysts which will produce a high H_2 Conversion at a recycle ratio of no more than 1 or 1.5.

The reasons why high recycle ratios were necessary in most of the 14 Series runs is not clearly evident because we do not have available to us all details on the type of catalyst that was used. The catalysts may be partly responsible but in some cases notably 14-9 and 14-11 lower temperatures were used than in the H Series runs and this alone may have been enough to cause the deviation.

The 14-10 Series data which were obtained with diluted catalyst did not correlate at all against recycle ratio. They did however correlate

well against temperature, as will be seen later, indicating that in the cases of low catalyst activity, temperature instead of total feed composition becomes the dominating factor.

Fig XVB is a similar plot of H_2 Conversion vs. R/FF of all the Stanolind and Laboratory A and Laboratory B data.

The Stanolind, with H_2/CO in FF varying from 3.4 to 5.1, all correlate very well on a single line which has a shape similar to that of the HRI 2/1 data. The temperature in the Stanolind runs ranged from 580 to 600° and the pressure was about 160#. The low temperature and low pressure may account for the higher recycle ratios required for a given H_2 Conversion. It will be recalled that the Stanolind fresh feed always contained a high CO_2 content and therefore although the H_2/CO ratio was high, the H_2 Conversion was apparently at the same rate as though it was 2/1. In other words, CO_2 in the feed had about the same effect as CO so far as H_2 Conversion is concerned.

The significance of the high recycle ratios used in the Laboratory A and B low H_2/CO runs will be discussed later.

R/FF vs. Total Feed Composition

The effect of recycling on total feed composition for the good HRI and Beacon runs with 2/1 feed is shown on Fig. XVI.

H_2 Conversion vs. Total Feed Composition

Figs. XVII, XVIIA and XVIIB were prepared to obtain some idea of the effect of total feed composition on H_2 Conversion.

Effect of Temperature

Fig. XVIII is a plot of all the HRI and Beacon data that can be used to establish the effect of temperature.

The line labeled HRI 14-10 shows all the data of the series that was made at high space velocity with diluted catalyst. It will be recalled that these data did not plot at all against R/FF ratio. It is indicated that temperature is the dominating factor when catalyst activity is low or space velocity is high.

Run H-14 which was also made at a high space velocity, checks well with this curve.

The Beacon data indicate that even with an active catalyst and low space velocity, temperature has an effect when the recycle ratio is low, about 0.5 to 1.0, but when the recycle rate is increased and conversions are high, the HRI and Beacon data together indicate that the temperature effect is small.

Fig. XVIIIA shows the effect of temperature on H_2 Conversion for the Stanolind high H_2/CO ratio data and the low H_2/CO ratio data of Laboratories A and B. The former show no relation with temperature. The latter indicate that temperature is important both in Runs 11 and 12 with 2/1 ratio fresh feed and in the 1/1 ratio runs. It also indicates that lower pressure tends to reduce conversion.

Effect of Pressure

Inspection of the data indicates that pressure has an effect on degree of conversion. Low pressures give lower conversions. However, the range of pressures covered by the data was relatively small and the obscuring effect of other variables was so great that the magnitude of the pressure effect could not be established.

Effect of Space Velocity

As in the case of pressure, inspection of the data shows that space velocity has a definite effect on conversion, particularly at the low conversion levels; but the effect was so obscured by changes in other variables that its magnitude could not be established.

Effect of Catalyst

These will be considered under "Discussion".

VIII. DISCUSSION

Through intensive study of the relationships presented above and a careful point by point consideration of the data, it might be possible to deduce a consistent, plausible and conclusive theory of mechanism for the reactions involved in this synthesis. This was the intent of the present study but so many variables are involved that considerable further work is required before conclusions can be reached. At this stage of development all that can be done is to present a working hypothesis hoping that this will be confirmed and can be extended as time goes on.

Approach - Fixed Bed Theory

The approach used to interpret these data is similar to that used by Craxford* in interpreting the results obtained over a fixed bed of Cobalt catalyst.

He concluded that under these conditions the oil is formed first through the reaction

$$CO + 2H_2 = H_2O + (=CH_2)$$

followed, when conditions permitted, by the water-gas shift

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

If the space velocity was very small the reaction occurred completely in the bottom part of the bed, where the catalyst was carbided, and the remainder of the bed, where oil synthesis was not taking place, was left relatively free of carbide and therefore available for the water-gas shift. Under these conditions, CO_2 yield (from the shift) was high and in addition, the oil formed at the bottom of the bed was subjected to hydrogenation - cracking as it passed through the rest of the bed thereby producing a large amount of methane.

If the feed rate was increased, more and more of the bed was used for oil synthesis leaving less for the water-gas shift and hydrogenation-cracking until a point was reached where the oil yield was at its maximum and the CO_2 and CH_4 yield very low.

A further increase in feed rate resulted in a drop in oil yield because "the gas is not left in contact with the catalyst long enough for

* "Mechanism of Fishcer-Tropsch reaction", S.R. Craxford
Proceedings of Faraday Society - August, 1946

the synthesis to go to completion". At such high rates the methane and CO_2 yield drop still further.

When catalyst activity drops off with use i.e., as the synthesis reaction becomes slower, the length of catalyst bed required for synthesis becomes greater and greater so that the amount available for the water-gas shift and for hydrogenation-cracking becomes progressively less.

Craxford states that the above confirms the previously proposed theory that "oils are synthesized when the cobalt in the catalyst surface is in the form of carbide, whereas, uncombined cobalt gives methane, allows the water-gas shift reaction to take place and is active for the hydrogenation-cracking of hydrocarbons".

Craxford is not clear concerning the factors which determine the point where oil synthesis stops and the water-gas-shift begins but presumably, according to previous Craxford Publications, it is a function of the relationship between the catalyst carbiding, reducing and oxidizing tendencies of the components in the catalyst surrounding medium at that instant.

Fluid Bed "Working Hypothesis"

The present process deals with a fluidized bed of iron catalyst where the catalyst particles, whether carbided, oxided or uncombined, are constantly agitated.

Therefore, the reaction steps that Craxford speaks of, oil synthesis, water-gas-shift and hydrogenation cracking all go on simultaneously instead of step wise. Furthermore it appears from the present data that methane and other light saturated hydrocarbons may be formed as the result of primary reactions as well as through hydrogenation-cracking.

The following is an overall statement of the "working hypothesis" proposed. Proof of some of the conclusions will be presented later.

In this process, judging from the graphs presented here, the reactions try to produce only unsaturates and water through a basic synthesis reactions such as the following:

1) $2H_2 + CO = (=CH_2) + H_2O$ or

$2n\ H_2 + nCO = C_nH_{2n} + nH_2O$

If the H_2/CO ratio in the feed is less than two then CO_2 becomes an inevitable by-product until at a ratio of one to one the results will be as follows, and at least 33-1/3% of the CO will go to CO_2:

2) $3H_2 + 3CO = (=CH_2) + CO_2 + H_2O$

When the ratio is less than one the H_2O will decrease and CO_2 increase until at 0.5 to one the product will be:

3) $H_2 + 2CO = (=CH_2) + CO_2$

For ratios higher than two, the excess H_2 will appear in the product. For a ratio of four to one the following is the goal:

4) $4H_2 + CO = (=CH_2) + H_2O + 2H_2$

In such cases where there is excess H_2 in the feed, CO_2 can be added to utilize the excess H_2 thus:

5) $7H_2 + 2CO + CO_2 = 3(=CH_2) + 4H_2O$

If only H_2 and CO_2 are charged the ultimate reaction becomes

6) $3H_2 + CO_2 = (=CH_2) + 2H_2O$

These goals might be attained directly if it were not for side and secondary reactions which, in a fluidized bed, proceed simultaneously with the above. The most influential of the side reactions is the water-gas-shift.

7) $H_2O + CO \rightleftharpoons H_2 + CO_2$

This reaction at first proceeds to the right competing with the synthesis reactions for the utilization of the important component, CO.

Phases

The path of the process is divided into two major phases. In the first phase CO_2 is made and in the second phase it is consumed.

As will be proved later, when H_2 and CO are first contacted with an active catalyst there are only two important reactions; the basic synthesis reaction and the water-gas shift proceeding to the right. The basic synthesis reaction is, at the beginning, about twice as fast as the shift reaction so that H_2 and CO are consumed at a ratio of one to one and CO_2 and H_2O are formed thus:

$$4H_2 + 2CO = 2\ (=CH_2) + 2H_2O$$

$$\underline{H_2O + CO \longrightarrow H_2 + CO_2}$$

$$3H_2 + 3CO = 2\ (=CH_2) + H_2O + CO_2$$

This initial ratio of H_2/CO consumption is independent of the H_2/CO ratio in the feed.

The basic synthesis reaction apparently may produce unsaturates of any molecular weight although the boiling range of the product may be markedly affected by factors such as H_2 content or free Fe in the catalyst mixture which according to the carbiding theory of mechanism may control the length of the molecules before they are detached from the catalyst. The factors affecting quality of product are not considered in this report and for the present purpose it is assumed that unsaturates of all molecular weights may be formed simultaneously.

As CO concentration is reduced by the above reactions the rate of both reactions decreases. The rate of the gas shift is reduced still further by the fact that it is approaching equilibrium and the ratio of H_2 to CO consumption increases.

Oxygenated Compounds

As a result of the reduced rate of the above reactions as well as the fact that CO_2 concentration in the reactor has been increased, a third primary but slower reaction begins to manifest itself. This, it is suggested, is that which produces oxygenated compounds.

The oxygenated compound production continues to increase until it reaches a maximum and then starts to decrease as the conversion of H_2 and CO is continued. In this respect, the oxygenated compound reactions act in the same manner as the gas shift.

What reactions are involved in the formation of oxygenated compounds has not been established but the following is interesting in this connection.

In the October 1930 issue of Ind. & Engrg. Chem. there are presented a series of articles related to the so-called methanol synthesis. The one by Frolich et al* contains some conclusions which may apply as well

*"Catalyst for the formation of alcohols from CO and H_2". Frolich & Cryder p. 1051

under the conditions of hydrocarbon synthesis with which we are concerned.

They state that all oxygenated compounds may stem from methanol by the process of stepwise condensation. The methanol being produced through formaldehyde as an intermediate thus:

$$CO + H_2 = HCHO$$
$$HCHO + H_2 = CH_3OH$$
$$2CH_3OH = C_2H_5OH + H_2O$$

It is stated that to produce higher alcohols the water concentration must be reasonably low otherwise the water will saturate the catalyst and condensation cease.

Throughout the papers it is taken for granted that the reaction,

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

is completely reversible.

Smith & Hirst, (p. 1037) suggest that the formation of methanol may not proceed directly from CO at all, but may proceed through the water-gas-shift and the resulting CO_2 stage thus:

$$3H_2 + CO_2 = CH_3OH + H_2O$$

Equilibrium constants for this and other similar equations are presented.

"Catalyst Equilibrium"

When most of the CO has disappeared, usually over 85% the primary reactions mentioned above appear to stop. Some kind of equilibrium has been reached and further disappearance of H_2 and CO can only be accomplished by upsetting that equilibrium through recycling or by adding some reactant to the fresh feed.

Why the reactions should stop cannot be deduced for sure from the data presented here but, it is conjectured that the catalyst acts as an intermediate in all the reactions involved and apparent equilibrium is reached when the partial pressure of the components in the medium surrounding the catalyst is such that the catalyst surface or catalyst composition itself has reached equilibrium with the medium and is therefore no longer effective. This idea is consistent with what Mr. C.W. Watson has been contending all the time.

There is no doubt that such an equilibrium is reached and it is evident that this phenomenon is related to the relative partial pressures of the various components at the time. What that partial pressure relationship is, has not been established. It may be influenced by the amount of product which has not yet desorbed from the catalyst but this is not the only factor involved by any means. The ratio at the moment of those components in the reactor or catalyst surrounding medium which tend to carbide the catalyst to those which tend to oxidize and those which tend to reduce the catalyst are also influential and "catalyst equilibrium" may be reached when the oxidizing tendency is equal to some combination of the reducing plus carbiding tendency.

The degree of conversion of CO and H_2 and the liquid hydrocarbon yield that can be attained before this "catalyst equilibrium" is reached can be influenced by many factors such as space velocity, temperature pressure, catalyst activity and principally feed composition as will be explained below.

Water-Gas-Shift Equilibrium

This is not an equilibrium process but instead it is a series of competing reactions. As a result, the reversal of the gas shift can occur at anytime depending upon the effect of the other reactions on the partial pressure of any one of the components involved in the shift. In other words the shift can start reversing before it has reached its theoretical equilibrium or it can proceed to the right beyond its theoretical equilibrium. When "catalyst equilibrium" is reached and the reactions stop, the water-gas-shift equilibrium ratio may vary anywhere from 10 to 60 thus:

$$\frac{(H_2)\ (CO_2)}{(H_2O)\ (CO)} = 10 \text{ to } 60$$ compared with about 22 at temperatures involved.

Gas Production:

The production of unsaturated gas components such as ethylene, propylene, etc., can, for all practical purposes, be considered to result directly from the basic synthesis reactions thus:

$$2H_2 + CO \longrightarrow (=CH_2) + H_2O$$

The methane, ethane and other light paraffins are apparently produced predominantly through hydrogenation-cracking as suggested by Craxford.

The basic synthesis reaction apparently proceeds on the surface of the catalyst and some of the unsaturated chains apparently grow to heavy wax proportions before being detached. These when once formed are slow to desorb and since they crack quite easily it is reasonable to believe that a large percentage of paraffins are produced as a result of the hydrogenation cracking of these heavier molecules. This would account for the fact that wax is not found in the product at high temperatures whereas the methane production is then high.

Methane and other light paraffins may also be formed directly by primary reactions such as the following:

$H_2 + (=CH_2) = CH_4$ or

$3H_2 + CO = CH_4 + H_2O$ or

$2H_2 + 2CO = CH_4 + CO_2$

These primary reactions normally are slow compared to the basic synthesis reaction and the gas shift and they occur to an appreciable extent only when conditions are such that the basic synthesis and the water-gas-shift are slow or "catalyst equilibrium" is reached slowly thereby leaving the CO concentration high a longer period of reaction time. These reactions apparently stop at the same time the other primary reactions stop, when "catalyst equilibrium" is reached.

Other Reactions

In addition to those mentioned above there are other secondary or trace reactions which may proceed involving the products themselves such as polymerization, aromatization, naphthenization, dehydrogenation, etc. It is known, for example, that the hydrocarbon liquid does contain some aromatics. No consideration will be given to such secondary reactions at this time, but they probably continue even after "catalyst equilibrium" is reached.

Carbon or coke formation reactions will not be considered in this report.

Application of Hypothesis

According to the above hypothesis, when synthesis gas is passed through a given amount of catalyst of given activity at a given space velocity, three things can happen.

1. The "catalyst equilibrium" can be reached and primary reactions cease early in the bed so that only secondary reactions proceed throughout the remainder of the bed. In such cases the proportion of secondary products such as methane, to primary products such as C_{3+} will be high.

2. The reactants use up practically the whole bed before reaching "catalyst equilibrium". In such cases the product distribution can be called normal.

3. The reactants leave the bed before catalyst equilibrium is reached at all.

It is the fact that these three possibilities exist that complicates the entire picture. Before this complexity can be resolved some fundamental data must be obtained on the effect of space velocity with various catalysts and feed compositions.

It is indicated however that with good catalysts the "catalyst equilibrium" is reached and the primary reactions cease only when the concentration of the reactants H_2, CO, CO_2 and H_2O is such that the water-gas-shift is somewhere near to equilibrium. Therefore although the deviation from this rule may be very broad, the degree of approach to the water-gas-shift equilibrium can be used as an index of the approach to "catalyst equilibrium" until some more accurate index is developed. This same index does not apply when a catalyst is poor.

From the above hypothesis it is possible to predict the qualitative effect of various changes in feed composition and other operating variables as follows:

Effect of Catalyst Activity:

A catalyst may be inactive relatively for three reasons:

1. The "catalyst equilibrium" may be reached while the CO and H_2 Conversion are still low.

2. The catalyst may activate the primary reactions so little that equilibrium is not reached before the reactants leave the bed.

3. The catalyst may be effective for some of the reactions involved but not for others.

In the Beacon runs with special catalysts, the C.I. Powder catalyst may have been an example of the second case because, although the CO and H_2 conversion was very low, the distribution of product was not materially out of line with that expected from the correlations.

The unreduced CM&S catalyst was apparently an example of the third case. Here again catalyst equilibrium may not have been reached (water-gas-shift equilibrium ratio was only 5 to 16) and all reactions were slower than with reduced catalyst but the gas shift and primary methane forming reactions were apparently slower compared to the basic synthesis reaction because the methane and CO_2 yields were low while the C_3+ and water yields were high.

The Limonite and the iron synthetic ammonia type catalysts prepared at Beacon may have been examples of case 1 to varying degrees. Here the "catalyst equilibrium" may have been reached early while there was still plenty of CO left for the continuation of the methane reactions or these catalyst may selectively speed up the methane reactions.

Effect of Temperature

Lowering temperature slows up all reactions as well as the cracking reactions so that at low temperature more of the bed will be used before "catalyst equilibrium" is reached. Under such conditions less methane will be made because of the slowness of the primary methane forming reactions and the reduced tendency for hydrogenation-cracking. More wax will be formed because of the latter.

Effect of Space Velocity in Once Through Operations

There are no once through data where space velocity was changed while all other conditions were maintained equal but a comparison of once through data obtained at different space velocities but with slightly different H_2/CO ratios and a comparison of Beacon recycling data indicated that space velocities of 20 to 60 SCFH/# Cat. had no effect. This is consistent with the theory presented above and confirms that reactions stop after "catalyst equilibrium" is reached otherwise a greater H_2 and CO conversion would have been obtained at the lower space velocity. It indicates further that permissable space velocities can be more than 60 before "catalyst equilibrium" is not reached.

The space velocity at which "catalyst equilibrium" will just be reached should be determined since this will establish how much catalyst is required. Any surplus catalyst or any lower space velocity is apparently of no value and may be undesirable from the standpoint of allowing secondary reactions.

With this critical amount of catalyst present, if the space velocity is further increased the CO conversion will be reduced until a point will be reached where no oxygenated compounds will be produced and the ratio of H_2/CO consumed will be one. The yield of oil then will be about 33% of the CO in the Fresh Feed or about 41.2% of the CO converted.

Effect of Adding CO_2 to the Feed in Once Through Operations

From the above theory of the process it would be reasoned that adding CO_2 to the feed would have the following effects.

1. Less CO would be consumed by the shift before "catalyst equilibrium" was reached and the reactions stopped.

2. The average rate of the water gas shift would be reduced because its driving potential, distance from equilibrium, would be less at the start.

3. During the period of reaction, more CO would be available for the faster basic synthesis reaction and more oil would be formed.

4. The "catalyst equilibrium" would be reached sooner in the bed so that less methane would be formed through the primary methane forming reactions before the primary reactions ceased.

5. The critical CO_2 concentration would be reached sooner and more oxygenated compounds would be formed. This would show a higher yield of C_3^+ (by carbon balance) even though the oil yield were not increased.

6. Because of item 5 the H_2 conversion might be the same or somewhat greater than before in spite of a lower CO Conversion.

7. CO_2 yields would be materially reduced proportional to the amount of CO_2 added to the feed.

8. H_2O yield would increase, consistent with the increase in yield of C_3^+ and oxygenated compounds.

A glance at the various plots of Beacon data will show that in general all of these effects occurred. The net CO_2 yield was reduced in direct proportion to the CO_2 added, and with some allowance for inaccuracies in the data, the H_2 Conversion , % Contraction and yield of C_{3+} increased in proportion to CO_2 added. The CO Conversion decreased.

It is indicated that "catalyst equilibrium" was reached in all cases (Sp.Vel. was 20 to 40) and these results show that when CO_2 is added to the feed in once through operations it produces a higher yield of C_{3+} (by carbon balance) and H_2O. Further data are necessary to determine what part of this increase in C_{3+} was oil and what part oxygenated compounds. It appears quite conclusive however that oxygenated compound yield can be increased without reducing oil yield and methane and CO_2 yield can be reduced by adding CO_2 to the feed. This can only be accomplished at the expense of a reduction in CO Conversion and in commercial application it will require a reduction in space velocity. More quantitative data and an economical study will be required to establish whether this is desirable or not.

Effect of Recycling

Compared to the concentration in the reactor effluent when running once through, recycling reduces the concentration of CO_2, H_2O and ($=CH_2$) and increases the concentration of H_2 & CO. As a result, recycling upsets the "catalyst equilibrium" and causes the further conversion of CO and H_2 than that attainable once through.

On the other hand if the recycle ratio is raised too much, a longer period of time is required in the reactor before reaching "catalyst equilibrium" leaving more time for the slower methane reactions to proceed causing a higher ultimate yield of methane. There appears to be no justification for a recycle ratio higher than 1.5 to 2.0.

The methane reactions are apparently irreversible because recycling increases methane concentration in the reactor and yet methane yield is higher at high recycle rates.

Recycling also increases the concentration of components other than CH_4, CO_2, CO and H_2. Among these components is a large percentage of oxygenated compounds and since the oxygenated compound reactions are reversible a high recycle ratio tends to reduce the yield of oxygenated compounds.

It must be remembered that the effect of recycling or of increasing recycle ratio will be different under two different sets of conditions:

A. When conditions are such that "catalyst equilibrium" was reached before the recycle ratio was increased.

B. When the "catalyst equilibrium" was not reached.

In the latter case recycling is detrimental.

Effect of H_2/CO Ratio in Reactor Feed

As pointed out above, the H_2/CO ratio in the reactor feed does not effect the relative rate of the basic synthesis reaction and the water-gas-shift. It has a profound effect however on the time required to reach "catalyst equilibrium" and cessation of primary reactions.

When the ratio in the feed is 2/1 with no CO_2 or CH_4 in the feed "catalyst equilibrium" occurs when the H_2 conversion is about 62.5% and the CO Conversion about 98%. The product distribution then is as shown below under "Once Through Operations".

When the H_2/CO ratio is reduced to one to one the "catalyst equilibrium is evidently reached sooner and more recycling is necessary to effect a high conversion of CO. This may account for the high recycle ratios consistently used in the Laboratory A runs. Of course a high yield of CO_2 is a mathematical consequence of low H_2/CO ratios in the FF.

When the H_2/CO ratio is high, catalyst equilibrium may never be reached at all because the reducing tendency is always high so that high CO Conversions can probably be obtained once through or at low recycle rates with high H_2/CO ratios but only at the expense of a waste in H_2. If CO_2 is added to a high H_2/CO feed to use up the extra H_2 it acts then as just though CO had been added. The wax yield should be lower with high H_2/CO in the feed but the methane yield need not necessarily be higher. It is unfortunate that no data are available on high H_2/CO ratio feeds with no CO_2 in the feed.

Since the CO_2 disappears rapidly when the $H_2/CO + CO_2$ is high a lower oxygenated compound yield is to be expected with this type of feed.

Once Through Operations

With an active reduced CM&S catalyst and a pure $2H_2$ plus 1 CO feed operating once through at 650°F. and 200# the reactions do not stop until the water-gas-shift equilibrium has been reached or soon after, at which time 98% of the CO has disappeared, 62.5% of the H_2 and the contraction is 58 to 59%. The product is about as follows:

% CO in FF Unconverted	2.0
% CO in FF to CO_2	27.5
% CO in FF to CH_4	9.5
% CO in FF to C_2S	6.7
% CO in FF to C_3+	54.3
% CO in FF to Oxy. Comps.	Small
% H_2 in FF Unconverted	37.5
% H_2 to H_2O	21.5
% H_2 to CH_4	9.5
% H_2 to C_2S	4.0
% H_2 to Hydrocarbons	27.5
% Unsats. in C_2S	70.0
% Unsats. in C_3S	90.0
% Unsats. in C_4S	85.0
Ratio H/C in C_3+	2.0
Ratio H_2/CO consumed	1.28

The overall reaction can be written roughly as follows:

$$200\ H_2 + 100\ CO = 75\ H_2 + 2CO + 27.5\ CO_2 + 43\ H_2O + 9.5\ CH_4 + 1\ C_2H_6 + 2.35\ C_2H_4 + 54.3\ CH_2\ (C_3+)$$

The water-gas-shift equilibrium ratio was as follows:

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(75)(27.5)}{(43)\ (2)} = 24$$ compared with the theoretical of 22 at 650°F.

As a matter of interest the overall reaction may be broken down into the following:

$$\begin{array}{rlcrlcrl}
28.5 & H_2 & + 9.5\ CO = & 9.5 & CH_4 & + & 9.5 & H_2O \\
9.4 & H_2 & + 4.7\ CO = & 2.35 & C_2H_4 & + & 4.7 & H_2O \\
5 & H_2 & + 2\ CO = & 1 & C_2H_6 & + & 2 & H_2O \\
108.6 & H_2 & + 54.3\ CO = & 54.3 & CH_2 & + & 54.3 & H_2O \\
\hline
151.5 & H_2 & + 70.5\ CO = & -- & -- & + & 70.5 & H_2O \\
27.5 & H_2O & + 27.5\ CO = & 27.5 & H_2 & + & 27.5 & CO_2
\end{array}$$

It will be noted that twice as much CO went to oil via the basic synthesis reactions as to CO_2 by the water-gas-shift and about half as much went to methane, ethane and propane.

Water Gas Shift Equilibrium - Quantitative Data

If the water-gas-shift were extremely fast compared to the other reactions then at conditions of low CO conversion either the water or the CO_2 formed by the other reactions would be used up by the water-gas-shift as rapidly as formed in its effort to reach equilibrium.

This is not the case. In the Beacon once through runs with the relatively inactive C.I. Powder as the catalyst, the water-gas-shift equilibrium was not reached at all but even so the water and CO_2 yields were substantial. The CO conversion was less than 40% and H_2 conversion less than 20% but the product distribution including C_{3+} yield was very much as would be expected if all reactions involved were slowed up equally, except that there was definitely a higher yield of methane and other light saturated hydrocarbons as pointed out before.

It is pointed out that when starting with a pure H_2 and CO feed with no H_2O or CO_2 initially present, it is clear that some of the other reactions must proceed to make H_2O or CO_2 before the water-gas-shift can begin. Whether the CO_2 or H_2O is formed first is not particularly important but it appears that water is the first by product and the water-gas-shift proceeds to the right.

To check the question as to whether the reaching of the water-gas-shift equilibrium coincides with the point at which all reactions stop we can work backwards along the graphs starting from the point represented by the once through yields reported above, where the H_2 conversion was 62.5%.

Suppose we start with H_2 conversion = 55% then the graphs show the following pertinent yields:

	%	Mols
CO Converted =	95.2	
CO Unconverted =	4.8	4.8
CO to CO_2 =	30.5	30.5
H_2 Unconverted =	45	90
H_2 to H_2O =	17.5	35

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(90)(30.5)}{(35)(4.8)} = 16.3$$

At H_2 conversion = 60% the corresponding figures are

$$\frac{(80)(29.5)}{(40)(3)} = 19.8$$

Obviously it seems safe to assume that the reactions do not stop until the water-gas-shift equilibrium is reached.

Ratio of H_2/CO Consumption - Quantitative Data

The graphs of H_2 Conversion vs. CO Conversion (Group II) indicates that when there is nothing but H_2 and CO in the feed, the H_2 and CO disappear at first in the ratio of one to one regardless of the original concentration of H_2. That is, this appears to happen whether we start with a 2/1 feed, a 1/1 feed or a 4/1 feed. It seems to happen as well whether the catalyst is active or not.

This may be quite significant from the standpoint of mechanism. It will be noted that where the H_2/CO ratio in the feed is more than 1 a break in the curves occurs after a certain amount of CO has disappeared. For a 2/1 feed this break apparently occurs when 80% of the CO and 40% of the H_2 have disappeared.

It was thought that perhaps this is the point at which the water-gas-shift equilibrium is first reached and the point from which continued reaction occurs through reversal of this reaction. This is not confirmed by the CO_2 plots (Group III) which indicate that reversal begins only when 50% of the H_2 has disappeared however, it was possible that these were in error and that the point of reversal should be moved to the left. To scout this possibility, the following analysis was made.

If the ratio of CH_2 and CO_2 production experienced in the above once through runs is used and it is assumed that no methane reaction occurred before this point was reached, then the reactions would be as follows:

$$4H_2 + 2CO = 2CH_2 + 2H_2O$$
$$H_2O + CO = CO_2 + H_2$$
$$3H_2 + 3CO = 2CH_2 + CO_2 + H_2O$$

and for this particular case:

	Feed	Reacted		Unreacted	
	Mols	%	Mols	%	Mols
H_2	200	40	80	60	120
CO	100	80	80	20	20

$$\frac{80}{3} H_2 + \frac{80}{3} CO = 40\ CH_2 + \frac{80}{3} CO_2 + \frac{80}{3} H_2O$$

water-gas-shift ratio $\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(120)(80/3)}{(20)\ (80/3)} = 6$

Obviously the water-gas-shift equilibrium was not reached.

If a third equation is added to form methane and still retain the H_2/CO consumed at one to one; thus:

$$2H_2 + 2CO = CH_4 + CO_2$$

and the methane is assumed to be produced at about 1/6 the rate of production of CH_2 as in the once through runs cited above then we have the following combination.

$$12H_2 + 6CO = 6CH_2 + 6H_2O$$
$$3H_2O + 3CO = 3CO_2 + 3H_2$$
$$2H_2 + 2CO = CH_4 + CO_2$$
$$\overline{11H_2 + 11CO = 6CH_2 + CH_4 + 4CO_2 + 3H_2O}$$

or for 40% H_2 converted and 80% CO converted we have

$$200\ H_2 + 100\ CO = 120\ H_2 + 20\ CO + 43.6\ CH_2 + 7.26\ CH_4 + 29.1\ CO_2 + 21.8\ H_2O$$

and the water-gas-shift ratio although a little higher is still too low as follows:

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(120)(29.1)}{(21.8)(20)} = 8.0$$

The data of the once through runs cited above do not justify a further material increase in the assumed methane yield.

From the graphs themselves at 40% H_2 Conversion the following products are indicated:

% CO Converted = 80%

% CO Unconverted = 20
% CO to CO_2 = 25

% H_2 Unconverted = 60.0
% H_2 to H_2O 11.8

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(120)(25)}{(23.6)(20)} = 6.35 \text{ still too low}$$

From this analysis it was concluded that this break point in the CO Conversion curve (Fig. II) was not caused by the reaching of the water-gas-shift equilibrium at this particular point.

Beginning of Oxygenated Compound Reactions

Instead, from a comparison of the above overall reactions and those written for the once through runs reported above it is indicated that at this break point the concentration of one of the primary products has

become great enough so that some other reaction sets in which causes a much higher ratio of consumption of H_2/CO (2.5 to 1) than before as well as the production of appreciable water. It will be noted from Fig. XIII that to some extent the data indicate a similar break point in the water yield curve.

It is indicated that the component whose effective concentration has been reached at this point is CO_2 because its concentration does not change materially from this point on until the equilibrium is reached and all reactions cease. Note that this concentration of CO_2 amounts to about 18% of the total reactants at this time and the ratio of CO_2/CO is 1.2 to 1.33.

What reaction is promoted by the reaching of this particular CO_2 concentration is not at all clear. It is certain that it involves a relatively high consumption ratio of H_2 and CO and it produces H_2O as the by product. It could easily be the methane reaction such as

$$3H_2 + CO = CH_4 + H_2O$$

or the ethane reaction such as

$$5H_2 + 2CO = C_2H_6 + 2H_2O$$

but these are apparently produced even at low CO_2 concentration and in the C.I. Powder run where the CO_2 concentration was very low the ratio of ethane yield to methane yield was even higher than in the runs of high CO_2 concentration.

It is suggested that perhaps this is the point where the production of oxygenated compounds begins through reactions such as the following:

Alcohols) $\quad 2n\ H_2 + nCO \longrightarrow C_n H_{2n} + 2\ O + n\text{-}1\ H_2O$

Ketones & Aldehydes) $\quad 2n\text{-}1\ H_2 + nCO \longrightarrow C_n H_{2n}\ O \quad + n\text{-}1\ H_2O$

Acids) $\quad 2n\text{-}2\ H_2 + nCO \longrightarrow C_n H_{2n}\ O_2 \quad + n\text{-}2\ H_2O$

Why these reactions should wait until the CO_2 concentration is high before they occur is not clear when the oxygenated compound reactions are written in this manner. Perhaps they should be written with CO_2 as the starting component as follows:

$$3H_2 + CO_2 = CH_3\ OH + H_2O$$

$$2H_2 + CO_2 = HCHO + H_2O$$

$$4H_2 + 2CO_2 = CH_3\ COOH + 2H_2O$$

This theory accounts very well for the increased rate of H_2 disappearance and H_2O production after a certain CO_2 concentration has been reached.

Conclusion

It will be obvious that considerably more work can be done along the lines laid out and there are more variables to be discussed. It was felt advisable to leave these for subsequent reports however, as time will allow, in order not to delay the presentation of the results obtained so far.

Asst. Dr. of Res: duBois Eastman
Report by: L. P. Gaucher

WEK-LCK JR. (2)-CEL-WAM-WMS-KGM-dBE(CAL.)-LPG

LRS 3/12/43

FIG. I A

H_2 CONVERSION VS % CONTRACTION

MRI DATA

(NOT CORRECTED FOR CO_2 AND CH_4 IN FF)

⊙ H SERIES MS ANALYSES AVAILABLE RECALCULATED

● 14 SERIES " " " "

x 15 SERIES " " " "

⊙ H SERIES DIRECT FROM MRI SUMMARIES

• 14 SERIES " " " "

% CONTRACTION $\left(\frac{FF - EXIT\ GAS}{FF}\right)$

H_2 CONVERSION (% H_2 IN FF DISAPPEARED)

FIG. I A

LPC 2/13/42

FIG. 1B

H_2 CONVERSION VS % CONTRACTION

MRI DATA

ADJUSTED FOR CO_2 & CH_4 IN FF

- ⊙ H SERIES M5 RECALC.
- ● 14 SERIES "
- ○ H SERIES DIRECT FROM MRI SUMMARY
- • 14 SERIES " " " "

% CONTRACTION (BASIS N_2+CO IN FF)

H_2 CONVERSION

FIG. 1B

65

LPG 3/16/47

Fig. IC

H_2 Conversion vs % Contraction
Adjusted for CO_2, CH_4 & N_2 in FF

- □ LAB. A — H_2/CO = 1.0
- ■ LAB. A — H_2/CO = 1.5
- ▨ LAB. B — H_2/CO = 1.2 - 1.4 AS NOTED
- ⊗ LAB. B — H_2/CO = 2.0

% Contraction (Basis H_2+CO in FF)

H_2/CO in FF = 2.0

H_2/CO in FF = 1.5

H_2/CO in FF = 1.0

H_2 Conversion

Fig. IC

LPG 3/14/67

FIG. I D

H_2 CONVERSION VS % CONTRACTION

STRANDLAND DATA

H_2/CO = 2.3 & 4.0 +

△ UNADJUSTED FOR CO_2, CH_4 & N_2 IN FF

▲ ADJUSTED " " " " " " "

% CONTRACTION (NOT ADJUSTED EXCEPT AS NOTED)

H_2 CONVERSION

FIG. I D

LPG 2/16/47

FIG. I

H_2 CONVERSION VS CONTRACTION

BEACON DATA

- ⊙ FRESH CM&S REDUCED CAT.
- ⊗ FRESH CM&S REDUCED CAT. CO_2 ADDED TO F.F. % CONTR. ADJUSTED FOR CO_2 IN FF
- ◒ C.I. POWDER
- × LIMONITE K_2O
- □ LIMONITE KF
- ● CM&S UNREDUCED
- △ RUNS ON UNIT #8

		K_2O / 1.5	Al_2O_3 / 7.0
1.	CM&S		
2.	BEACON	0.5	5.0
3.	"	2.2	6.9
4	"	0.6	2.7

NOTE: H_2/CO VARIES FROM 1.8C TO 2.0

% CONTRACTION

H_2 CONVERSION

0 10 20 30 40 50 60 70 80 90 100

H_2/CO = 2.0 Figs. 1B & 1C

H_2/CO = 1.9 Figs. 1B & 1C

H_2/CO = 1.8 Figs. 1B & 1C

FIG. I

LPC. 7/7/47

Fig. II A

H_2 Conversion vs CO Conversion

MRI Data

$H_2/CO = 2$

- ◉ H Series MS Analyses Recalculated from Summaries
- ● 14 Series " " " Recalculated from orig. data
- X 15th Series " " " Recalculated from Summaries
- ◎ H Series Direct from MRI Summaries
- • 14 Series " " " "

H Series (Low CO_2 in FF)

14-15 Series (Higher CO_2 in FF)

For $H_2/CO = 2.0$

CO Conversion (Basis FF)

H_2 Conversion (Basis FF)

Fig. II A

LPG 3/17/47

FIG. II

H_2 CONVERSION VS CO CONVERSION

BERGIUS DATA

H_2/CO IN FF = 2.0

⊙ FRESH CMnS REDUCED CAT.

⊗ SAME CAT. BUT CO_2 ADDED TO FF

● C.I. POWDER

✕ LIMONITE K_2O

□ LIMONITE KF

● CMnS UNREDUCED

△ RUNS ON UNIT #8 (See Fig. I for catalysts)

CO CONVERSION (BASIS CO IN FF)

H_2 CONVERSION (BASIS FF)

FIG. II

LPG 2/13/47

FIG. II-B

H_2 CONVERSION VS. CO CONVERSION

DATA WITH LOW H_2/CO IN FF

- □ LAB. A $H_2/CO = 1.0$
- ■ LAB. A $H_2/CO = 1.5$
- ▣ LAB. B $H_2/CO = 1.2$ TO 1.6 AS NOTED
- ⊗ LAB. B $H_2/CO = 2.0$

$H_2/CO = 2.0$ CONV. FF = 0

$H_2/CO = 1.5$ CONV. FF = 0

$H_2/CO = 1.0$ CONV. FF = 0

CO CONVERSION (BASIS FF)

H_2 CONVERSION (BASIS FF)

FIG. II-B

3/18/47 LAC

FIG IIC

H_2 CONVERSION VS CO CONVERSION

STANOLIND DATA

H_2/CO IN FF = 4 TO 5 EXCEPT AS NOTED

% CO_2 IN FF = 7 TO 10 %

% CH_4 IN FF = 2 TO 10 %

CO CONVERSION

H_2 CONVERSION

$H_2/CO = 4$

THEORETICAL

FIG IIB

FIG IIC

72

LPG 2/19/47

FIG III A

H_2 CONVERSION VS % CO IN FF TO CO_2

HRI DATA

⊙ H SERIES RECALCULATED
● 14 SERIES "
X 15 SERIES "
⊙ H SERIES FROM SUMMARIES
● 14 SERIES " "

$H_2/CO = 2$, % CO_2 IN FF = 0
$H_2/CO = 2$, % CO_2 IN FF = 4 TO 6
$H_2/CO = 2.5$, % CO_2 IN FF = 0

RUN 238
LAB. A
4% CO_2
$CO_2/CO = 15$-20

% CO IN FF TO CO_2

H_2 CONVERSION

FIG III A

LPG 2/21/47

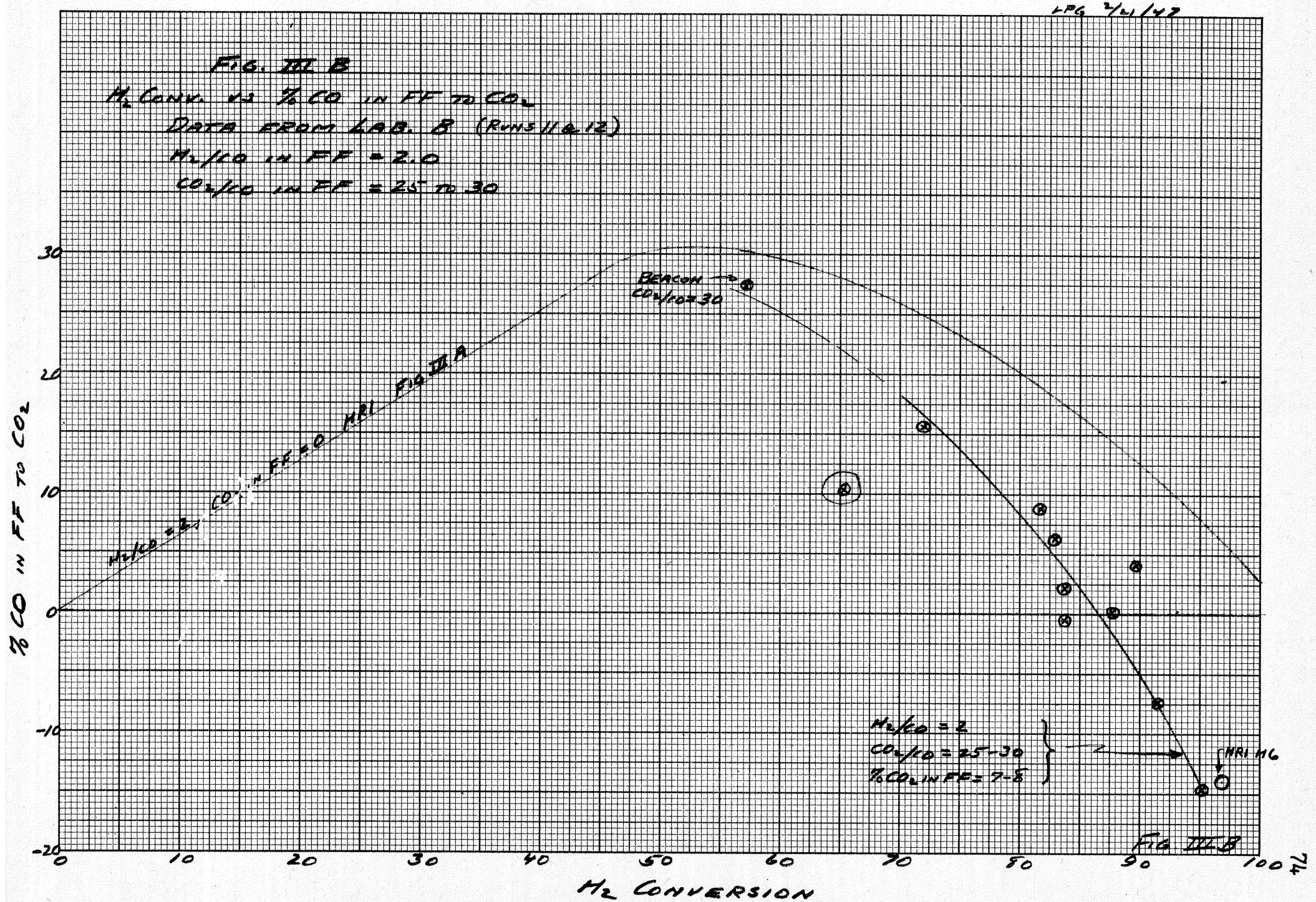
FIG. III B

H_2 Conv. vs % CO in FF to CO_2

Data from Lab. B (Runs 11 & 12)

H_2/CO in FF = 2.0

CO_2/CO in FF = 25 to 30



LPG 2/21/47

Fig III C

H_2 Conv. vs % CO in FF to CO_2

Data from Lab. A

H_2/CO in FF = 1.0

CO_2/CO in FF = 0.4 to 1.7

CH_4/CO in FF = 3.5 to 9.6 (as noted)

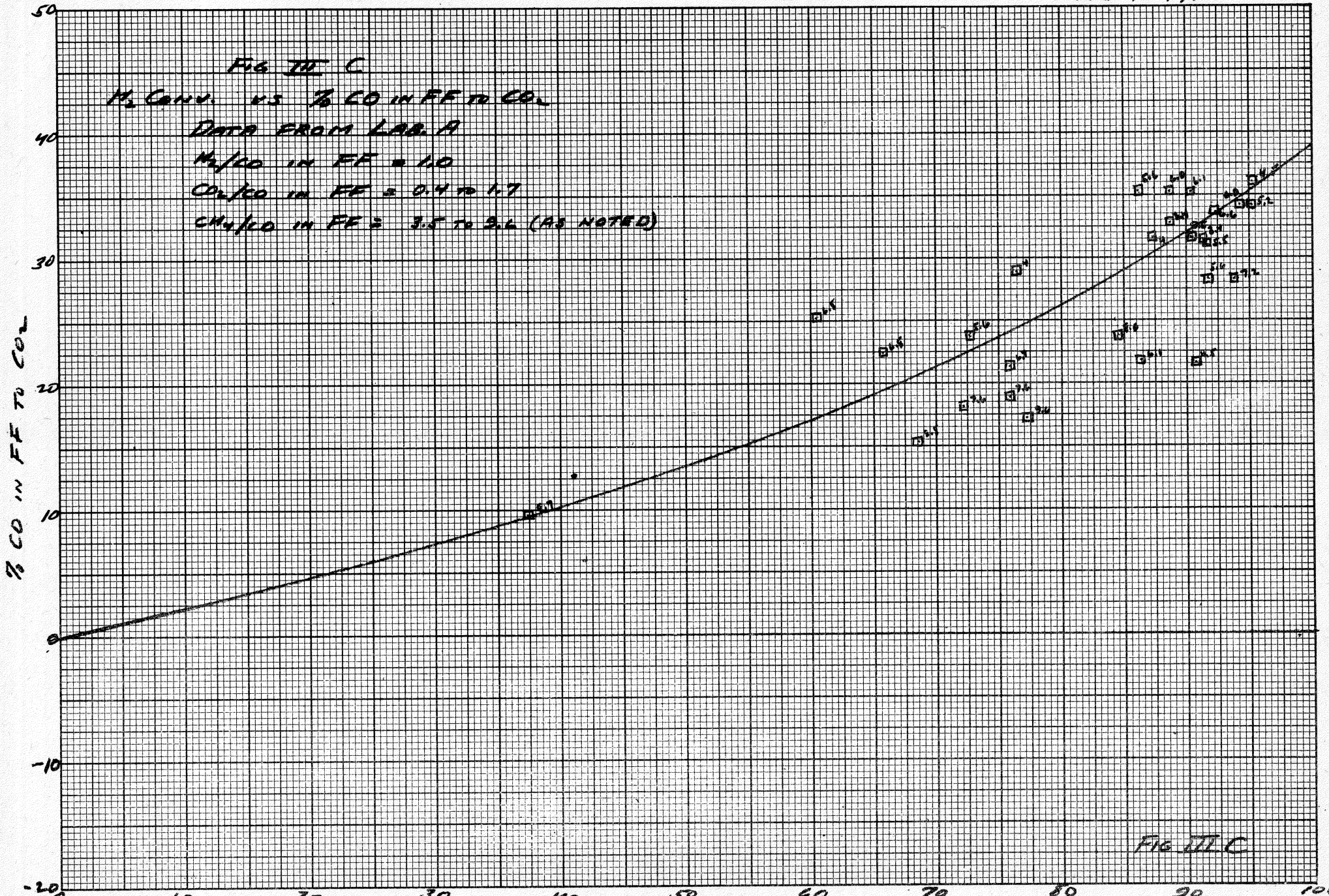


Fig III C

LPG 3/20/47

FIG. III D

H_2 CONV. VS % CO IN FF TO CO_2

CALCULATED MAXIMA

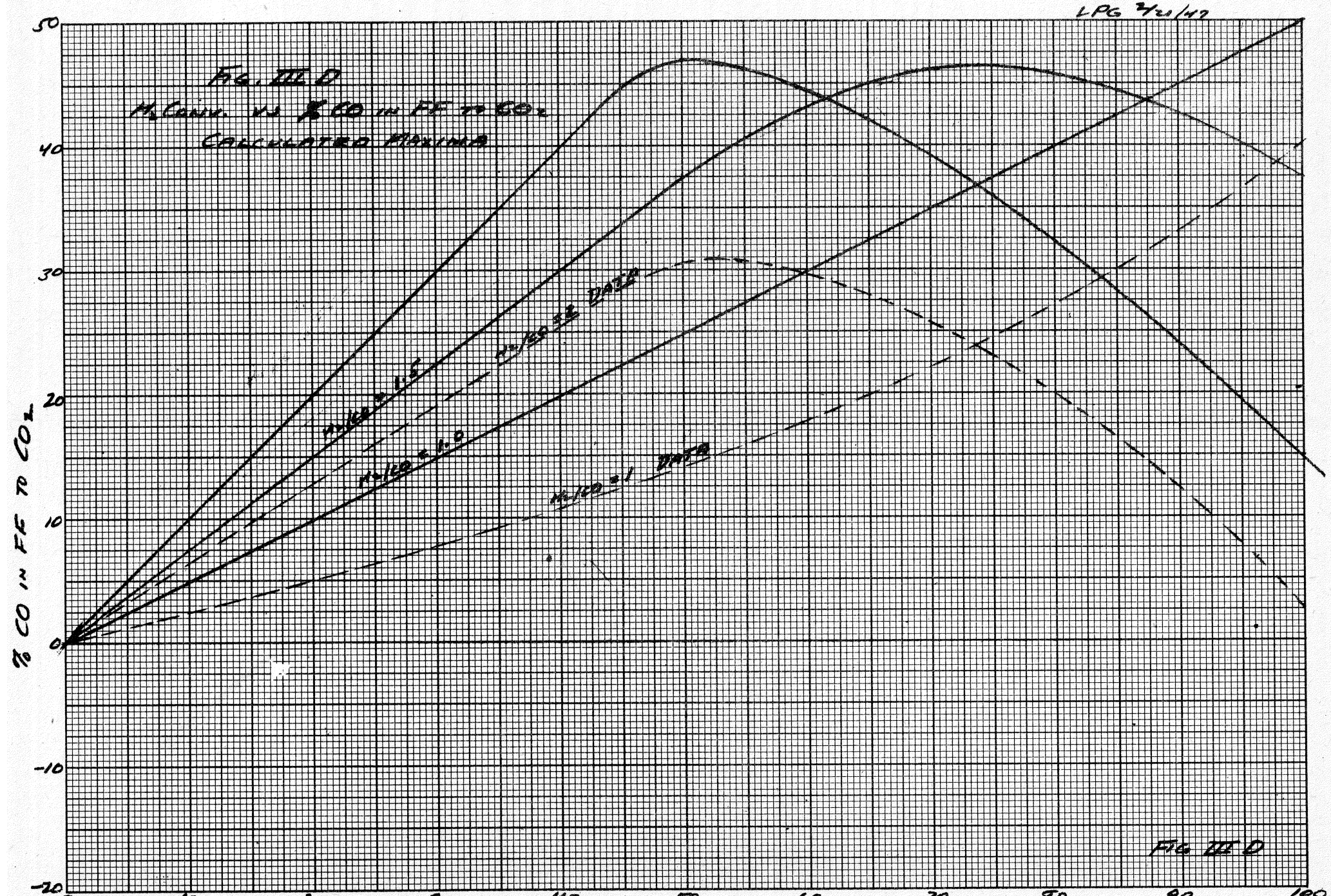


FIG III D

LPG 2/22/47

FIG. III E

H_2 CONV. VS % CO IN FF TO CO_2

H_2/CO IN FF = 1.2 TO 1.6 AS NOTED

▣ LAB. A

▣ LAB. B

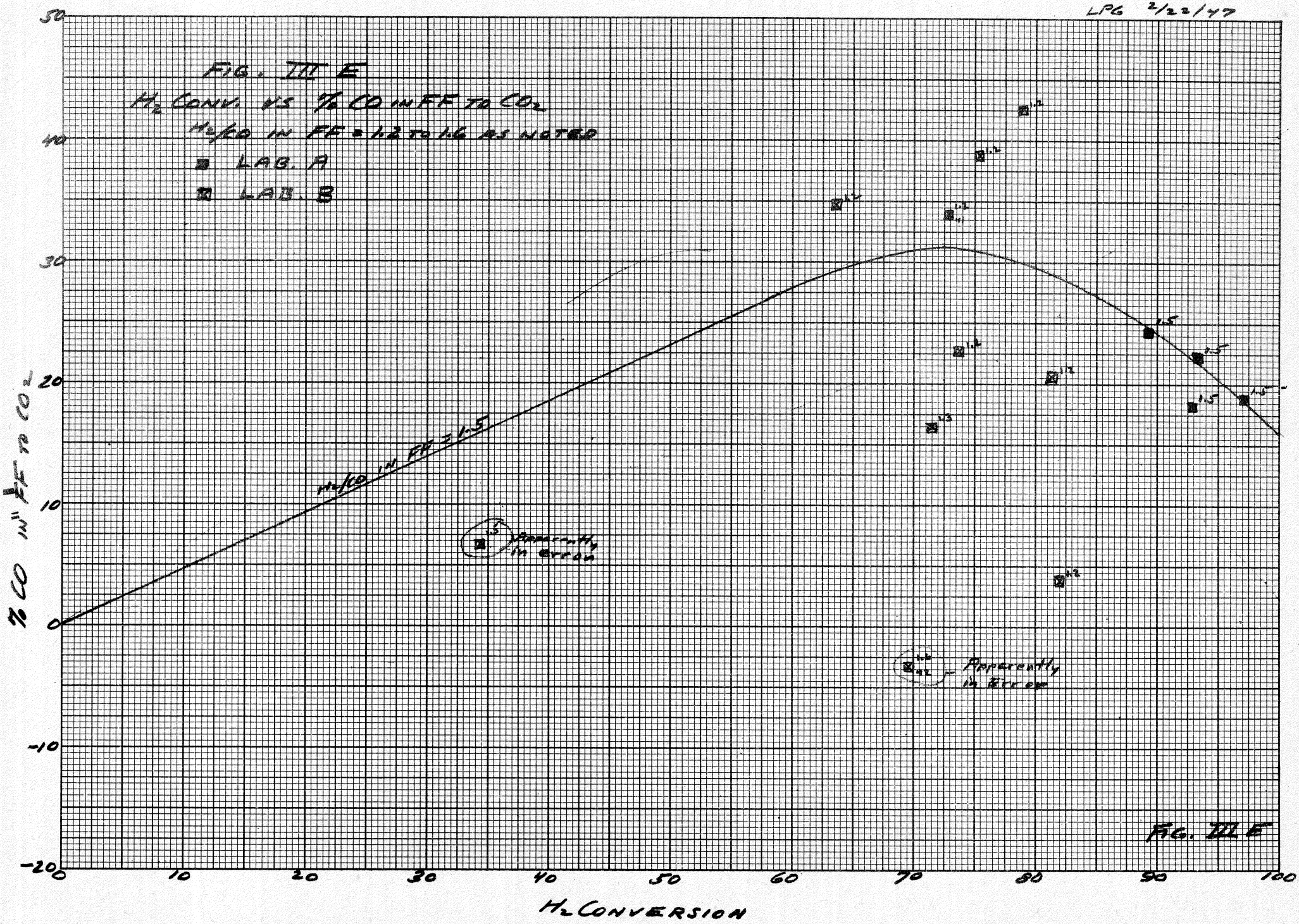


FIG. III E

LPG 2/20/47

FIG. III

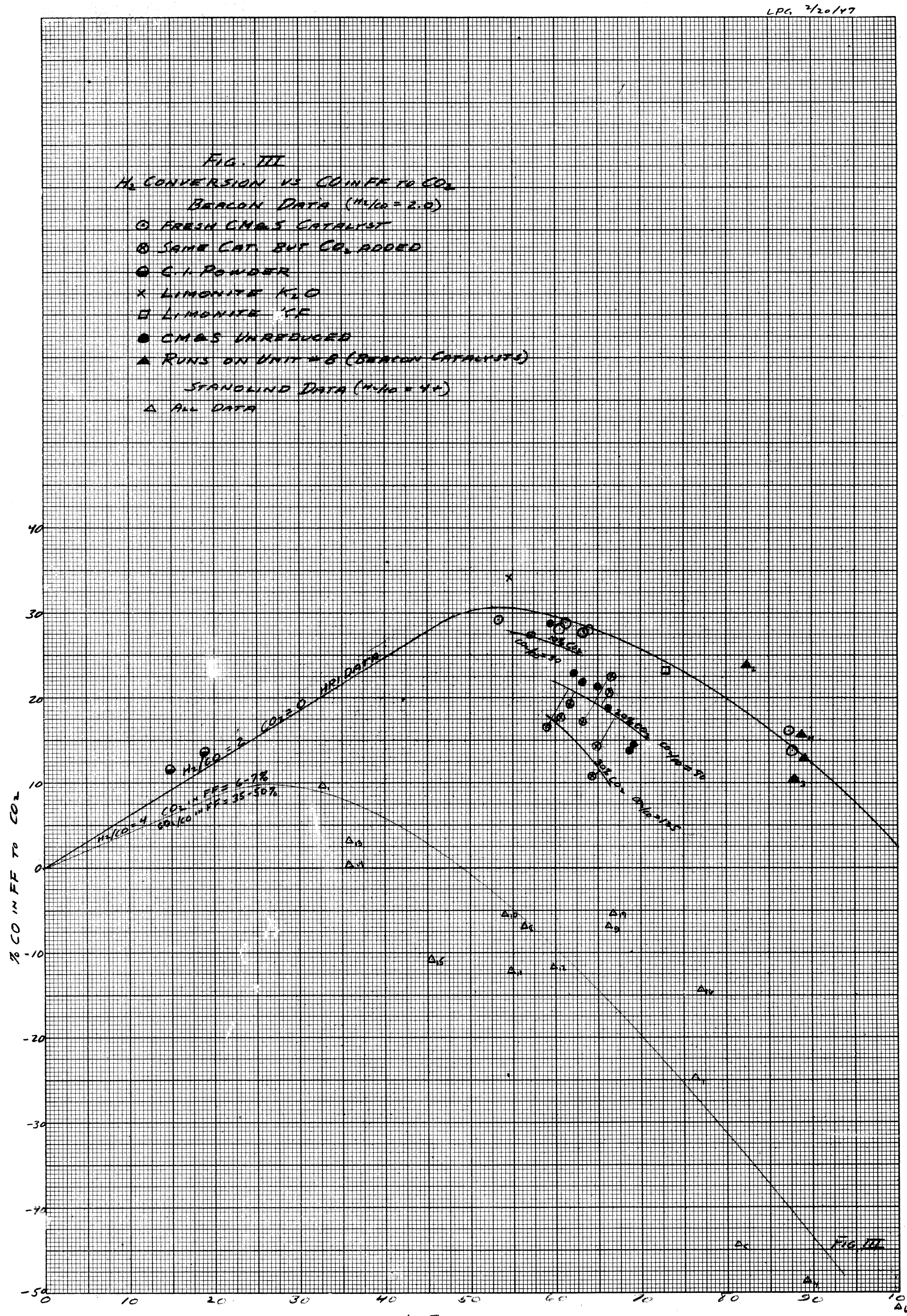
H_2 CONVERSION VS CO IN FF TO CO_2

BEACON DATA ($H_2/CO = 2.0$)

- ⊙ FRESH CMAS CATALYST
- ⊗ SAME CAT. BUT CO_2 ADDED
- ● C.I. POWDER
- × LIMONITE K_2O
- □ LIMONITE "F"
- ● CMAS UNREDUCED
- ▲ RUNS ON UNIT #8 (BEACON CATALYSTS)

STANOLIND DATA ($H_2/CO = 4+$)

- △ ALL DATA



LPG 2/26/47

FIG IX

H_2 CONV. VS CO TO C_3+

MRI & BEACON DATA

WITH CMS CATALYST

◎ MRI M SERIES

● MRI N SERIES

x MRI O SERIES

B BEACON

% CO IN FF TO C_3+ (CARBON BALANCE)

H_2 IN FF CONVERTED

FIG IX

LPE 2/26/43

FIG II B

H_2 CONV. VS CO TO C_3+

PRI DATA

DIRECT FROM SUMMARIES

⊙ M SERIES

• M SERIES

RUN NUMBERS NOTED IN ALL BUT THIRD SERIES

% CO IN FF TO C_3+ (INCL. ALC.) (DIRECT FROM SUMMARIES)

% H_2 IN FF CONVERTED

SERIES M-7,8,9

FIG II B

3/27/47 LPG

FIG. IX B

H_2 CONV. VS CO TO C_3^+

LAB A DATA

□ H_2/CO IN FF = 1

■ H_2/CO IN FF = 1.5

% CO IN FF TO C_3^+ (CARBON BALANCE)

% H_2 IN FF CONVERTED

H_2/CO = 2.0 MAX. FOR 100% H_2 CONV. @ REDUCED DATA

H_2/CO = 1.0 LAB A DATA

FIG IX B

LPG 2/26/47

FIG. III C

H_2 CONV VS CO TO C_3+

BEACON DATA
WITH CO_2 OR SPECIAL CATS.

- ⊗ CM-5 CAT. CO_2 ADDED
- ● " " UNREDUCED
- ⊙ C.I. POWDER
- X LIMONITE K_2O
- □ LIMONITE KF
- △ BEACON CATALYSTS

% CO IN FF TO C_3+ (CARBON BALANCE)

0 10 20 30 40 50 60 70 80 90 100

% H_2 IN FF CONVERTED

FIG. III C

LPG 3/1/82

FIG IV

H_2 CONV VS CO TO $C_1 + C_2$'S

HRI RECALC'D. DATA:

- ⊙ 14 SERIES
- ● 19 SERIES
- X 15 SERIES

BEACON DATA:

- B CM-5 REDUCED CATALYST

% CO IN FF TO $C_1 + C_2$'S

H_2 CONVERTED

FIG V

Fig. IIA

H_2 conv. vs CO to $C_1 + C_2$'s

Log Log Data

$\alpha/\alpha_2 = 1.0$

% CO in RE to $C_1 + C_2$'s

H_2 CONVERTED

Calc. by Equation

Fig. X 4

LPG 7/27/47

Fig VI A

H_2 Conv. vs Methane Yield

MRL Data

⊙ 11 Series

● 14 Series

X 15 Series

Recirc Ratio as noted

Fig. VI A

Fig II

H_2 Conversion vs. CO in Eff to CH_4

Bergau Data

See Fig I for normal data.

% CO in Eff to CH_4

H_2 Conversion

Bergau 1.0 g/hr Cats Reduced

Bergau 0.5 g/hr Cats Red.

HRI 1.0 g/hr

Bergau 0.5 g/hr Cats Reduced

HRI 0.5 g/hr

Fig II

98

LPG 3/2/43

Fig XI B

M. Conv. vs Methane Yield

Lab. & Data

H_2/CO = 2.0

Co/Co in FF's 25 to 30 Cm/Co in FF's 4 to 10

Recycle Ratio as Noted

% CO in FF to CH4

H_2 Conversion

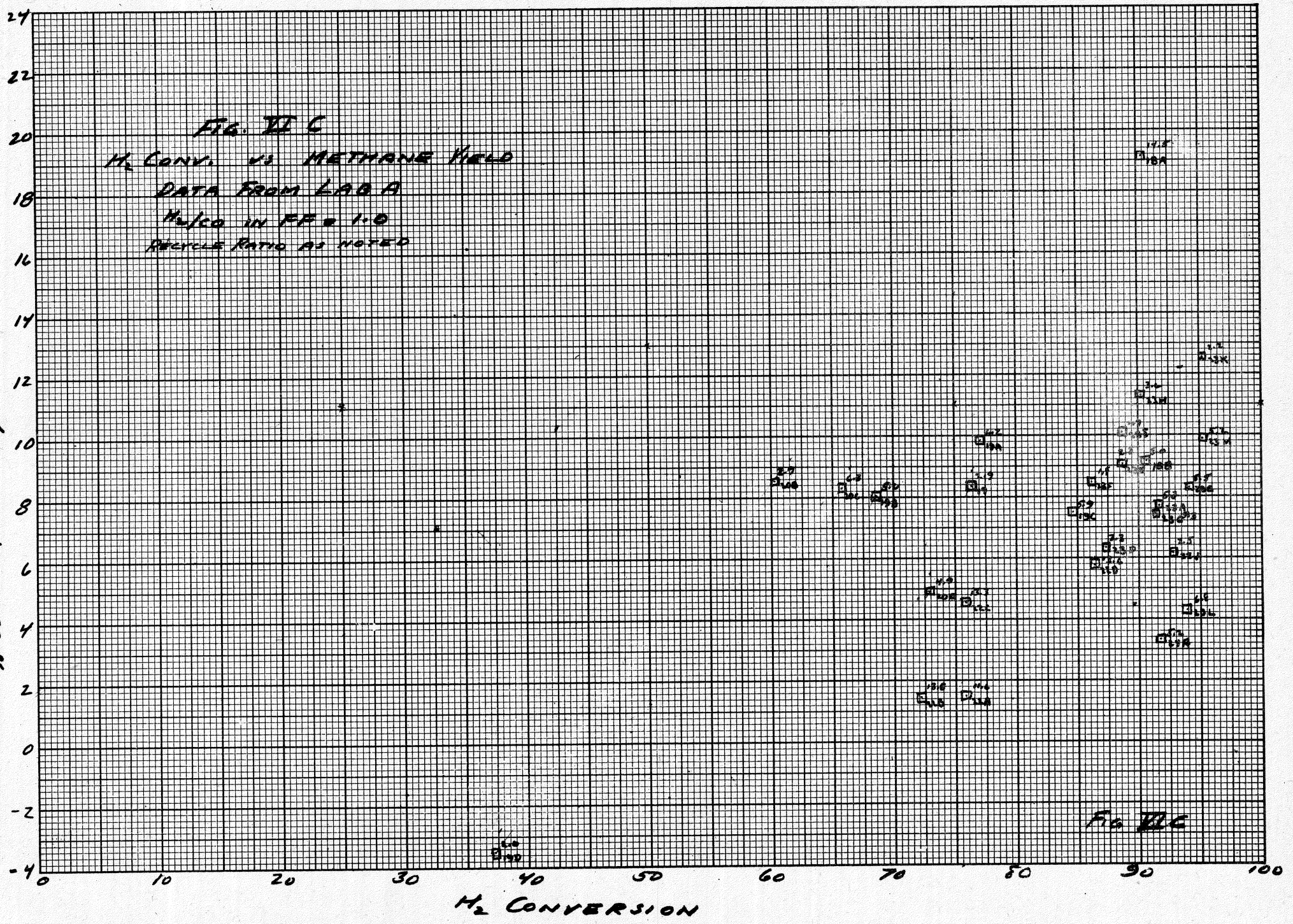


FIG. III C
H_2 CONV. VS METHANE YIELD
DATA FROM LAB A
H_2/CO IN FF = 1.0
RECYCLE RATIO AS NOTED
FIG III C
% CO IN FF TO CH4
H_2 CONVERSION
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
0
10
20
30
40
50
60
70
80
90
100

Fig. XI D

H₂ Conv. vs Methane Yield

Standard Data

Run = 4

% CO in Ft to CHy

H₂ Conversion

Fig. XI D

FIG XII

CO TO CH_4 VS CO TO C_2S

BEACON DATA

SEE FIG. 1 FOR NOMENCLATURE

% CO TO CH_4

% CO TO C_2

2/6/47 LPG

FIG XII

LPG 3/22/47

Fig. III.8

CO to CH_4 vs CO to C_2S

HRI Data

⊙ M Series

● 14 Series

× 15 Series

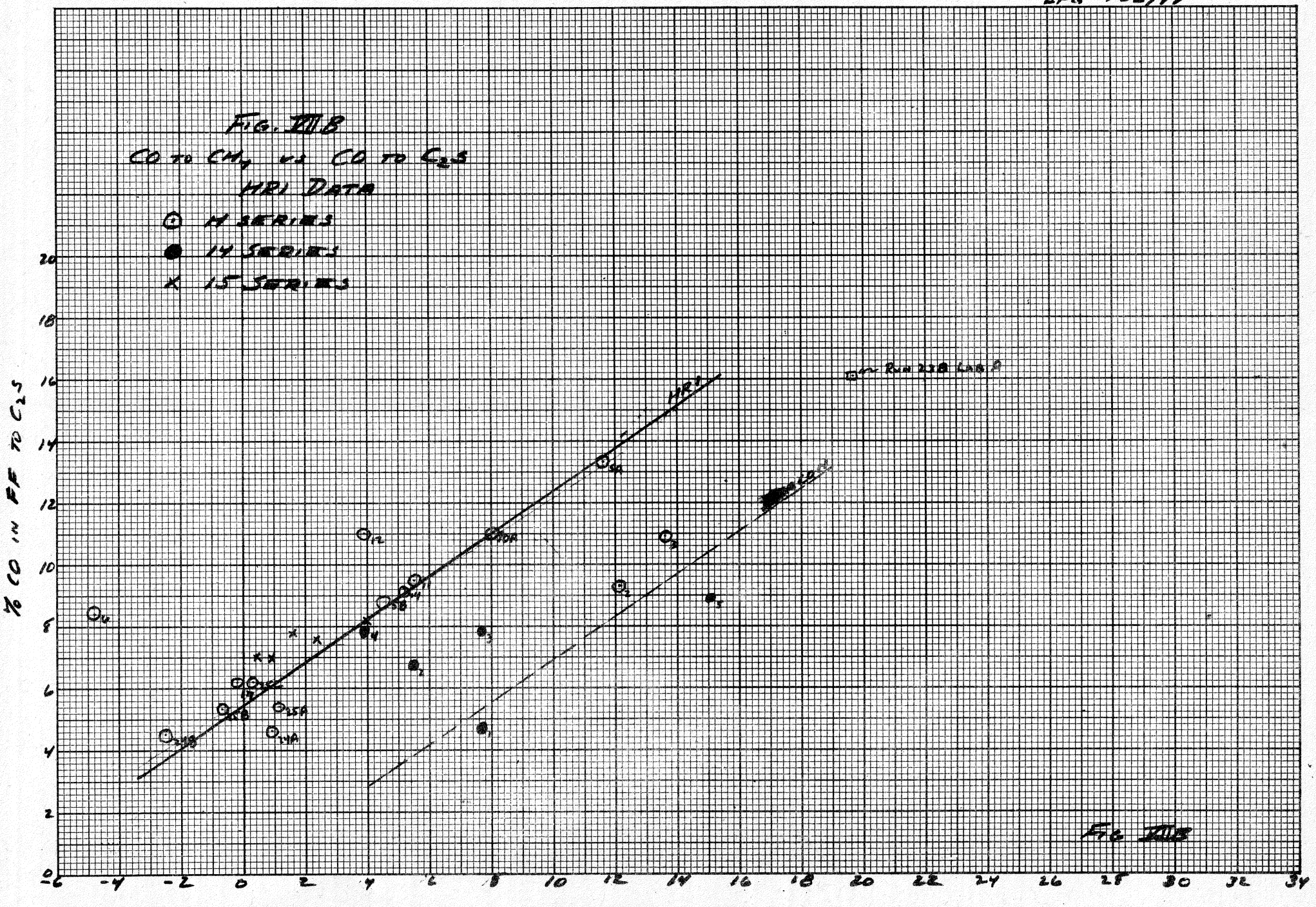


Fig. III.8

Fig VII C

CO to CH_4 vs CO to C_2's

- ☐ LAB A $H_2/CO = 1$
- ■ LAB A $H_2/CO = 1.5$
- ☒ LAB B $H_2/CO = 1.2$ to 1.6

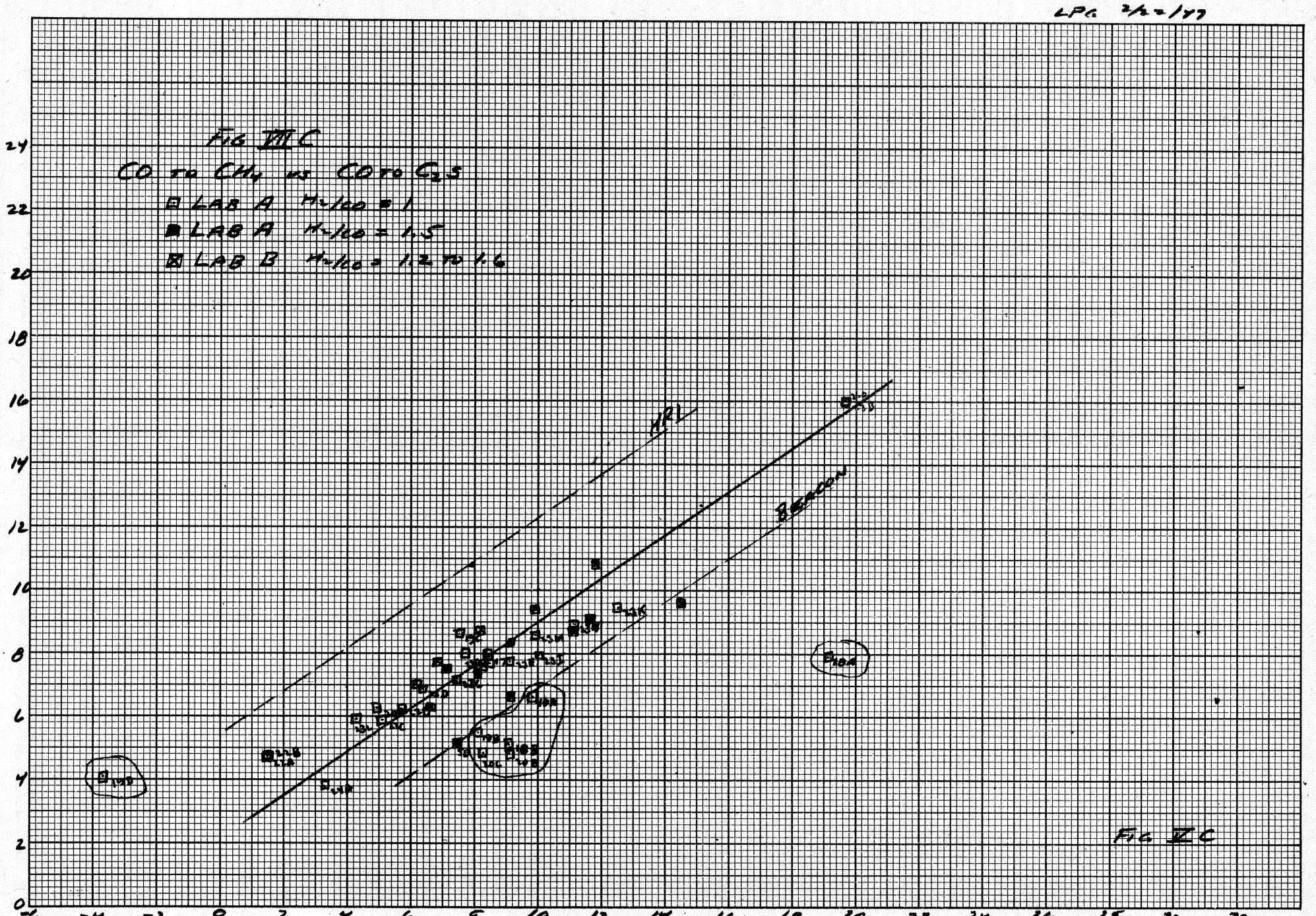


Fig VII C

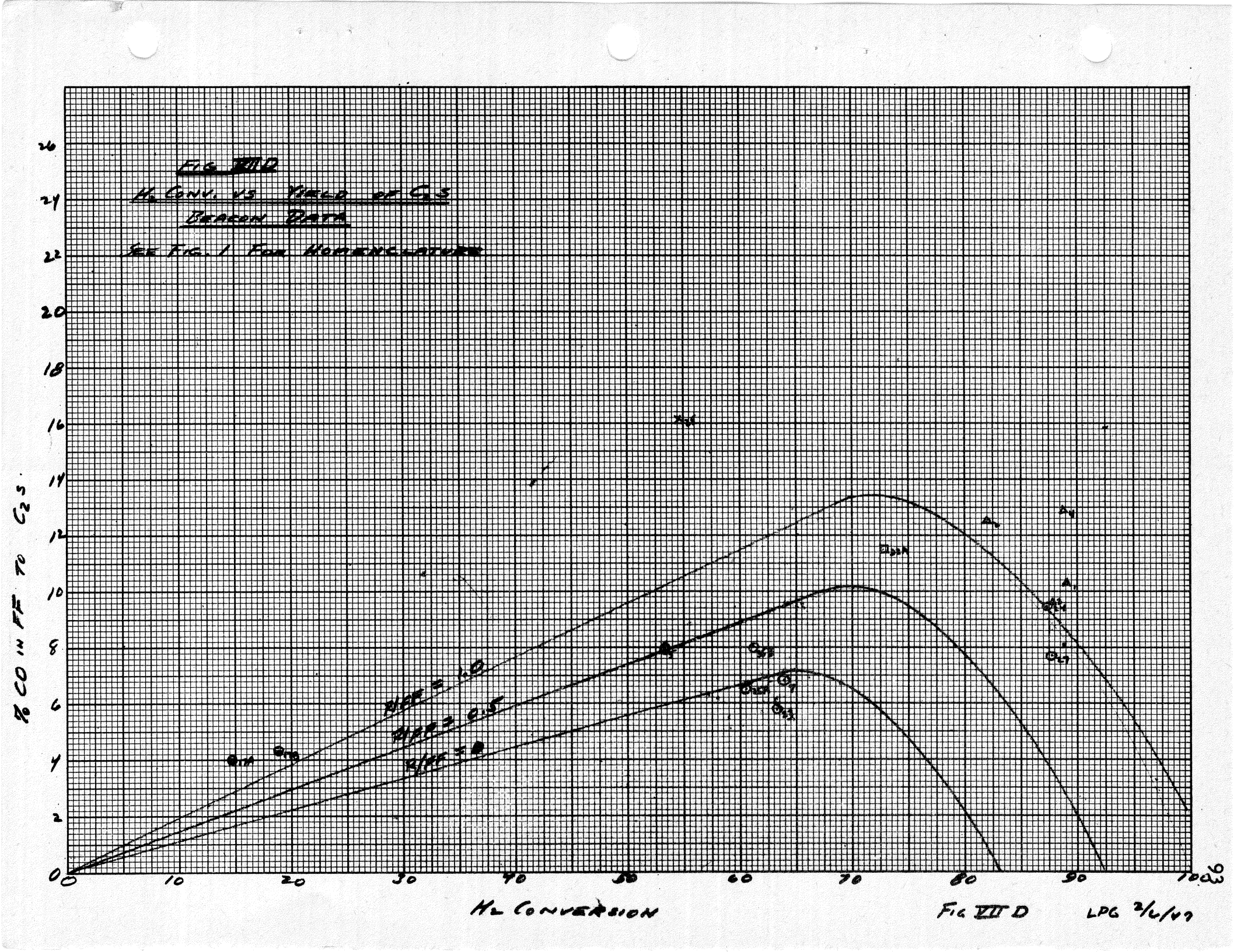


Fig VII D LPG 2/6/47

FIG. XII E

H_2 CONV. VS YIELD OF C_{2-3}

HRI DATA

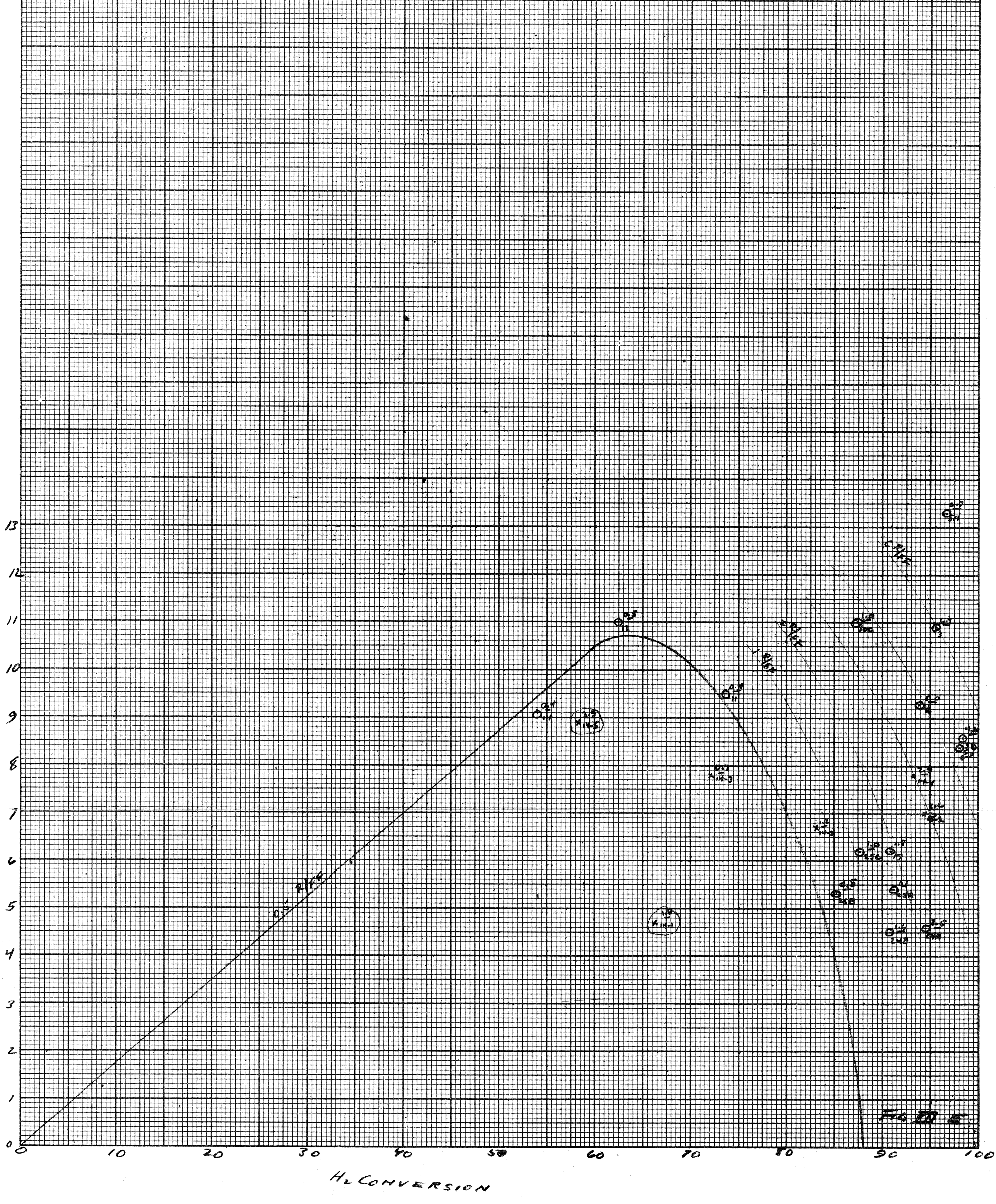


FIG XII E

LPG 3/22/47

Fig VIII

CO in FF to C_2s vs CO in FF to C_3s

- ⊙ HRI H SERIES
- ● HRI 14 SERIES
- X HRI 15 SERIES
- □ LAB A $H_2/CO = 1$
- ■ LAB A $H_2/CO = 1.5$
- ⊠ LAB B $H_2/CO = 1.2$ to 1.4
- B BEACON DATA
- X_B BEACON LINDNER K_2O
- $□_B$ " " KF
- △ BEACON CATALYSTS

% CO in FF to C_3s

% CO in FF to C_2s

Fig VII

FIG 12

% CO TO CH_4 vs % UNSAT. IN C_{25}

BEACON DATA

See Fig. 1 FOR NOMENCLATURE

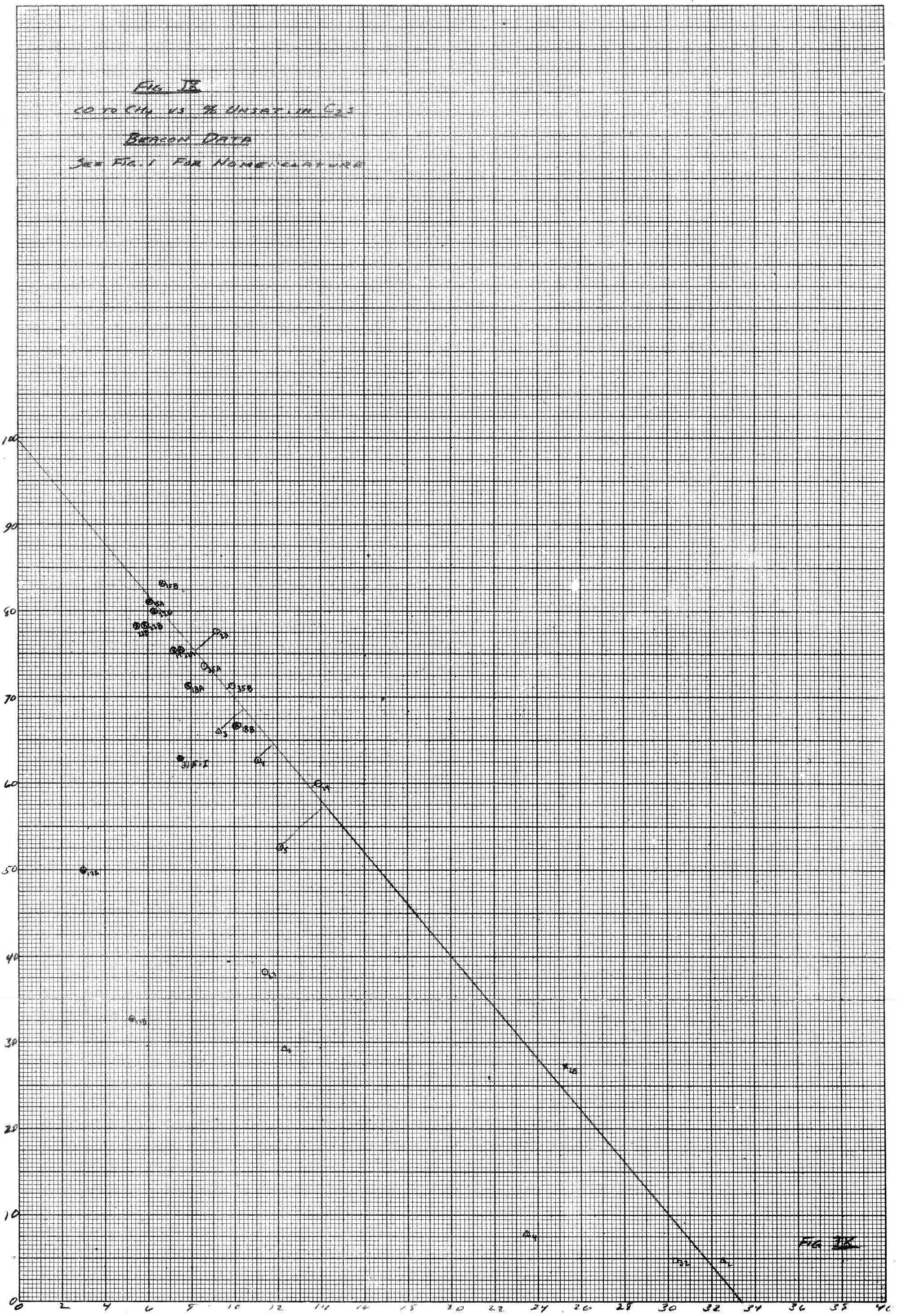


FIG 12K

LPG 4/10/47

96

LPG 2/24/47

Fig IX A

CO to CH_4 vs % Unsat. in C_2's

HRI Data

⊙ H Series

● 14 Series

× 15 Series

% Unsats in C_2's

% CO in FF to CH_4

Fig. VIII

Fig IX A

97

LPG 2/9/47

FIG. X

% UNSAT IN C_{25} VS % UNSAT IN C_{35}

NRI DATA:

⊙ M SERIES

● M SERIES

X M SERIES

BEACON DATA:

B CMC5 REDUCED CAT.

⊗ " " " COL MODED

◒ C.I. POWDER

X_B LIMONITE K_2O

□ LIMONITE RE

△ BEACON CATALYSTS

% UNSATS IN C_{35}

% UNSATS IN C_{25}

FIG X

100

Fig XL

% UNSATS IN C_2S VS % UNSATS IN C_4AF

HRI DATA:
- ⊙ H SERIES
- ● M SERIES
- X L SERIES

BEACON DATA:
- B CMAS REDUCED CATALYST
- ⊛ " " " CO_2 ADDED
- ◎ C.L. POWDER
- X_B LIMONITE K_2O
- □ LIMONITE RE
- △ BEACON CATALYSTS

HRI

BEACON

% UNSAT IN C_4AF

% UNSAT IN C_2S

Fig XI

Fig XII

% Unsats in C_{3}s vs % Unsats in C_{3}s

See Fig. IX for nomenclature

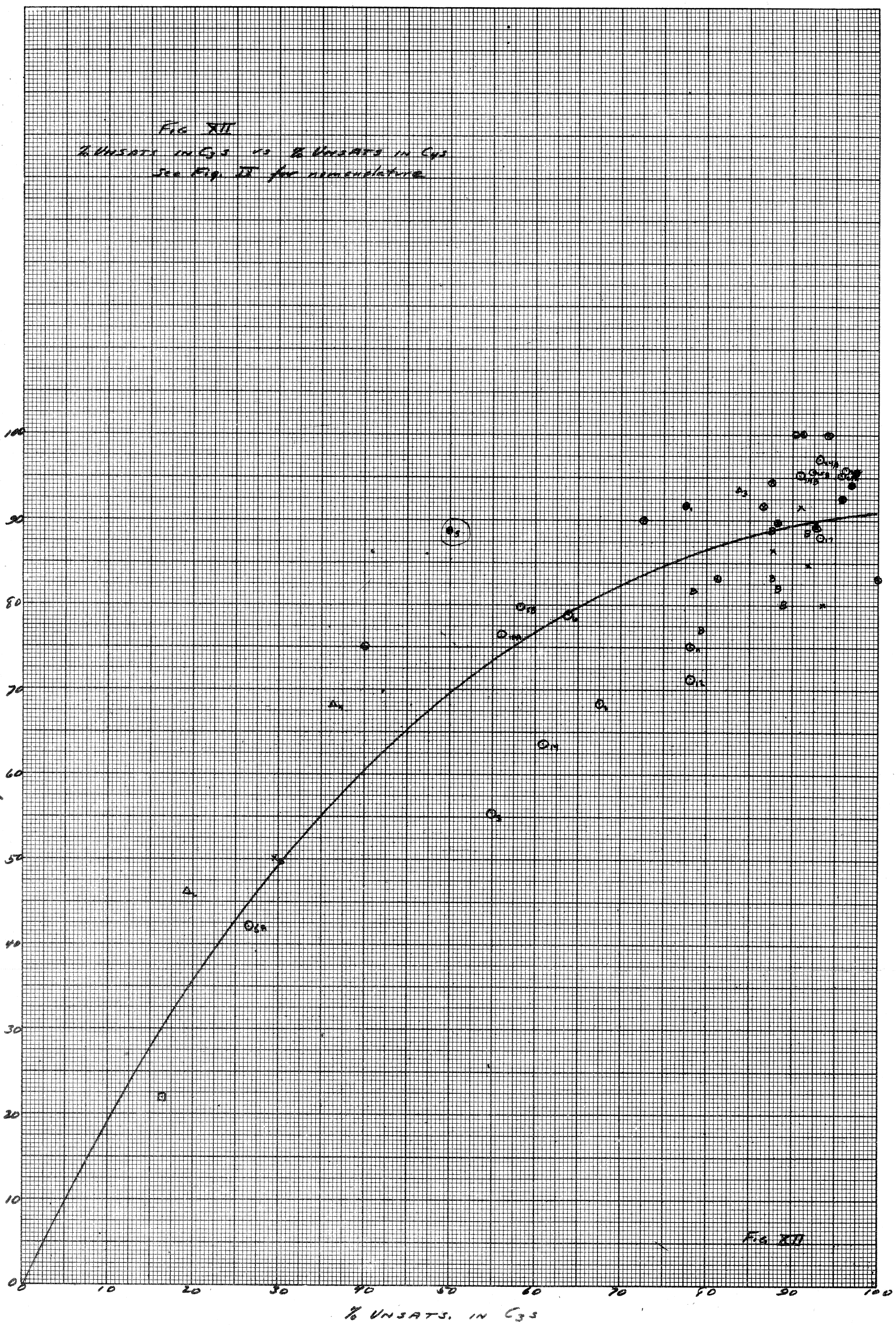
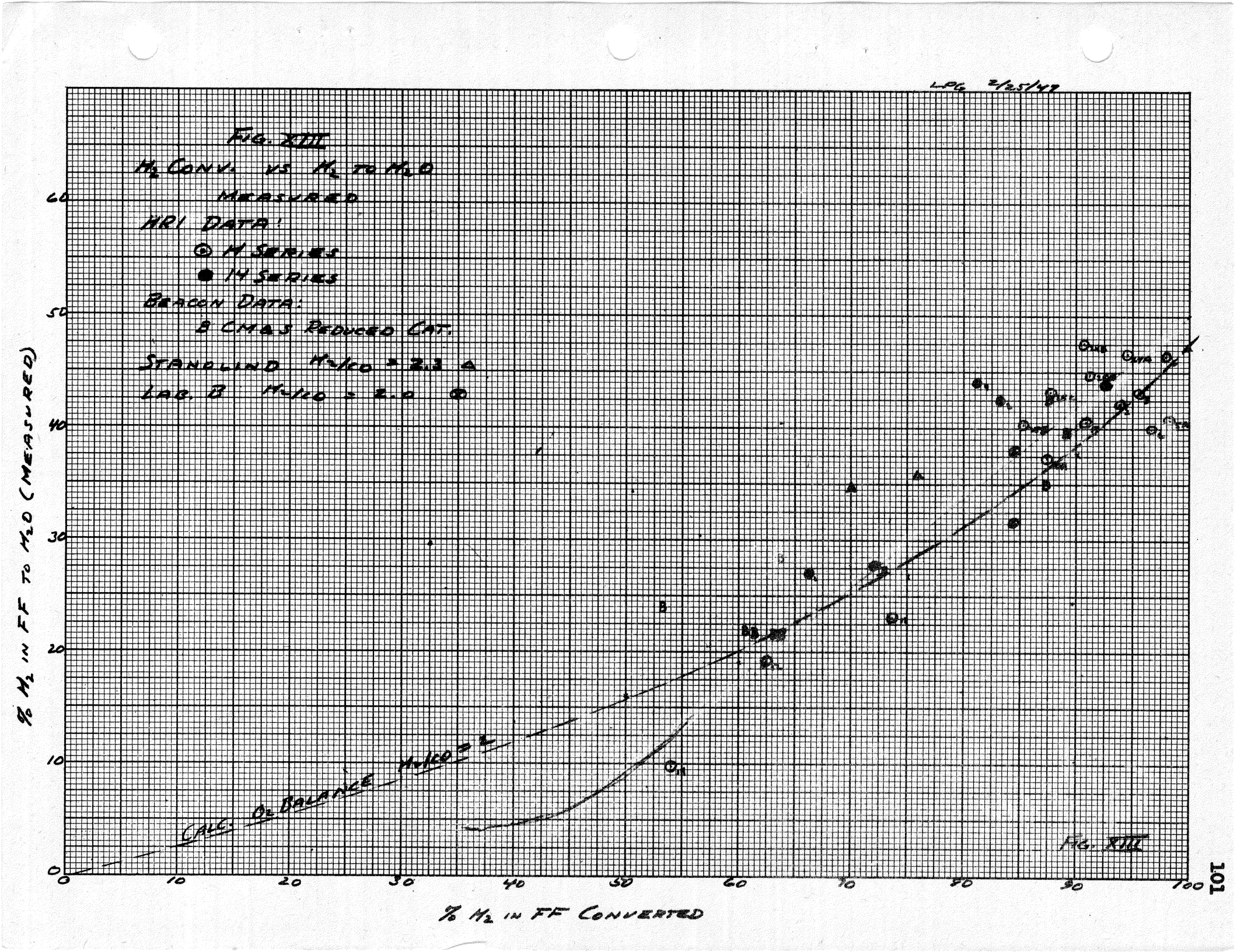


Fig XII


LPG 2/25/47
Fig. XIII
H2 Conv. vs H2 to H2O Measured
HRI Data:
M Series
14 Series
Beacon Data:
8 CM&S Reduced Cat.
Standlind H2/CO = 2.3
Lab. B H2/CO = 2.0
Calc: O2 Balance H2/CO = 2
% H2 in FF to H2O (Measured)
% H2 in FF Converted
0
10
20
30
40
50
60
70
80
90
100
Fig. XIII
101

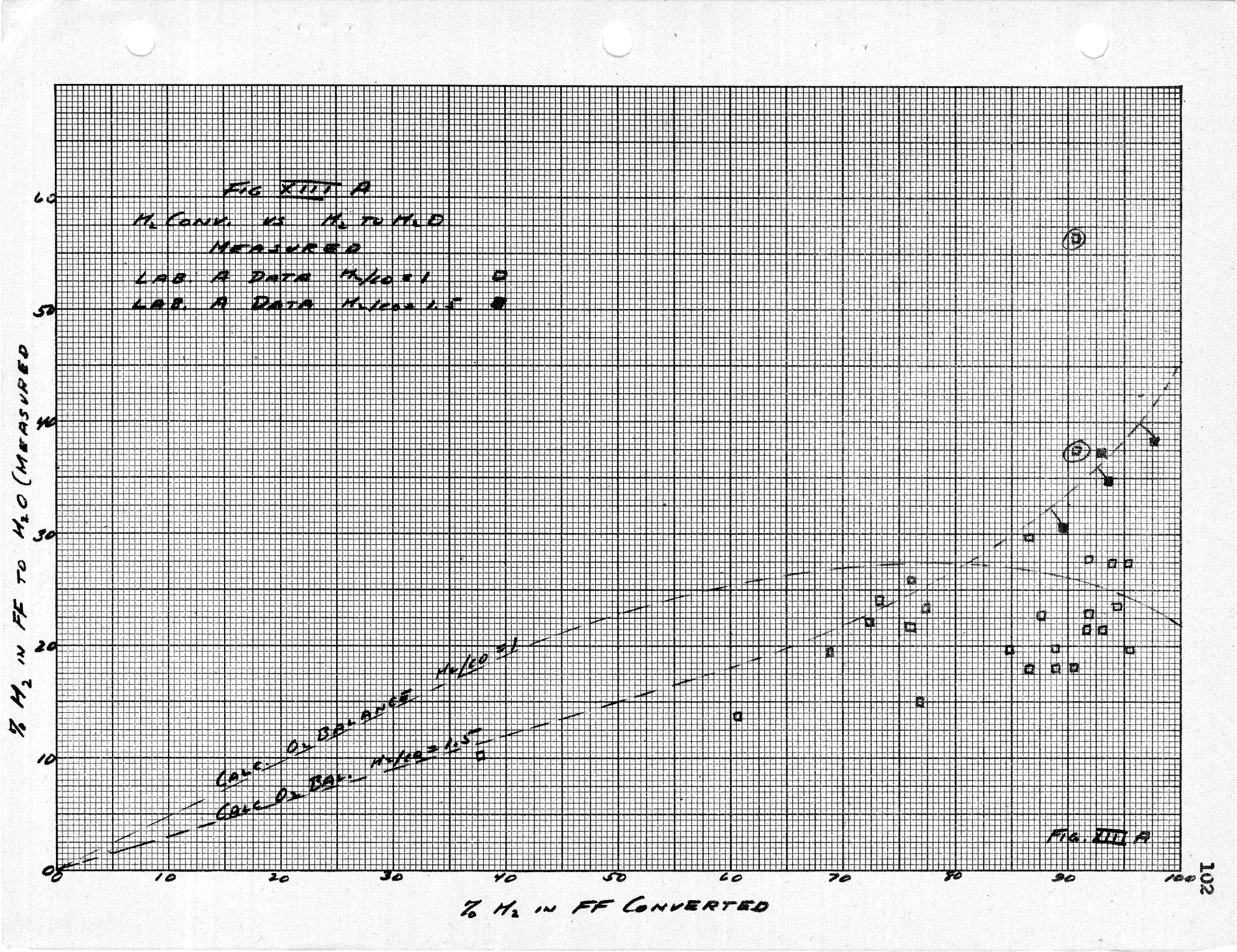


FIG XIII A
H_2 CONV. VS H_2 TO H_2O
MEASURED
LAB. A DATA $H_2/CO = 1$
LAB. A DATA $H_2/CO = 1.5$
CALC. O₂ BAL. $H_2/CO = 1$
CALC O₂ BAL. $H_2/CO = 1.5$
% H_2 IN FF TO H_2O (MEASURED
% H_2 IN FF CONVERTED
0
10
20
30
40
50
60
70
80
90
100
FIG. XIII A

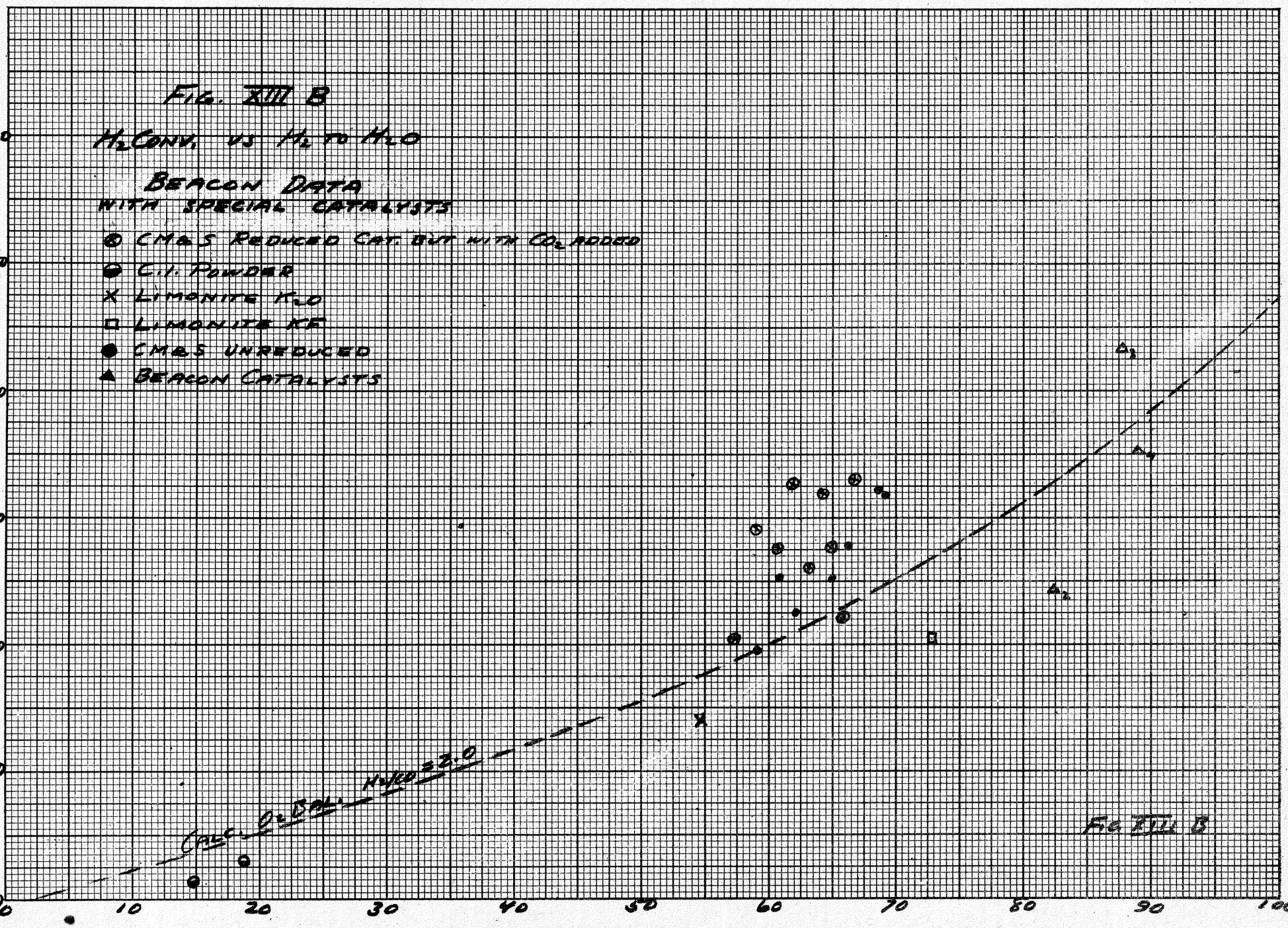


FIG. XIII B
H2 CONV. VS H2 TO H2O
BEACON DATA
WITH SPECIAL CATALYSTS
CM&S REDUCED CAT. BUT WITH CO2 ADDED
C.I. POWDER
LIMONITE K2O
LIMONITE KF
CM&S UNREDUCED
BEACON CATALYSTS
CALC. O2 BAL. H2/CO = 2.0
% H2 IN FF TO H2O
% H2 IN FF CONVERTED
0
10
20
30
40
50
60
70
80
90
100

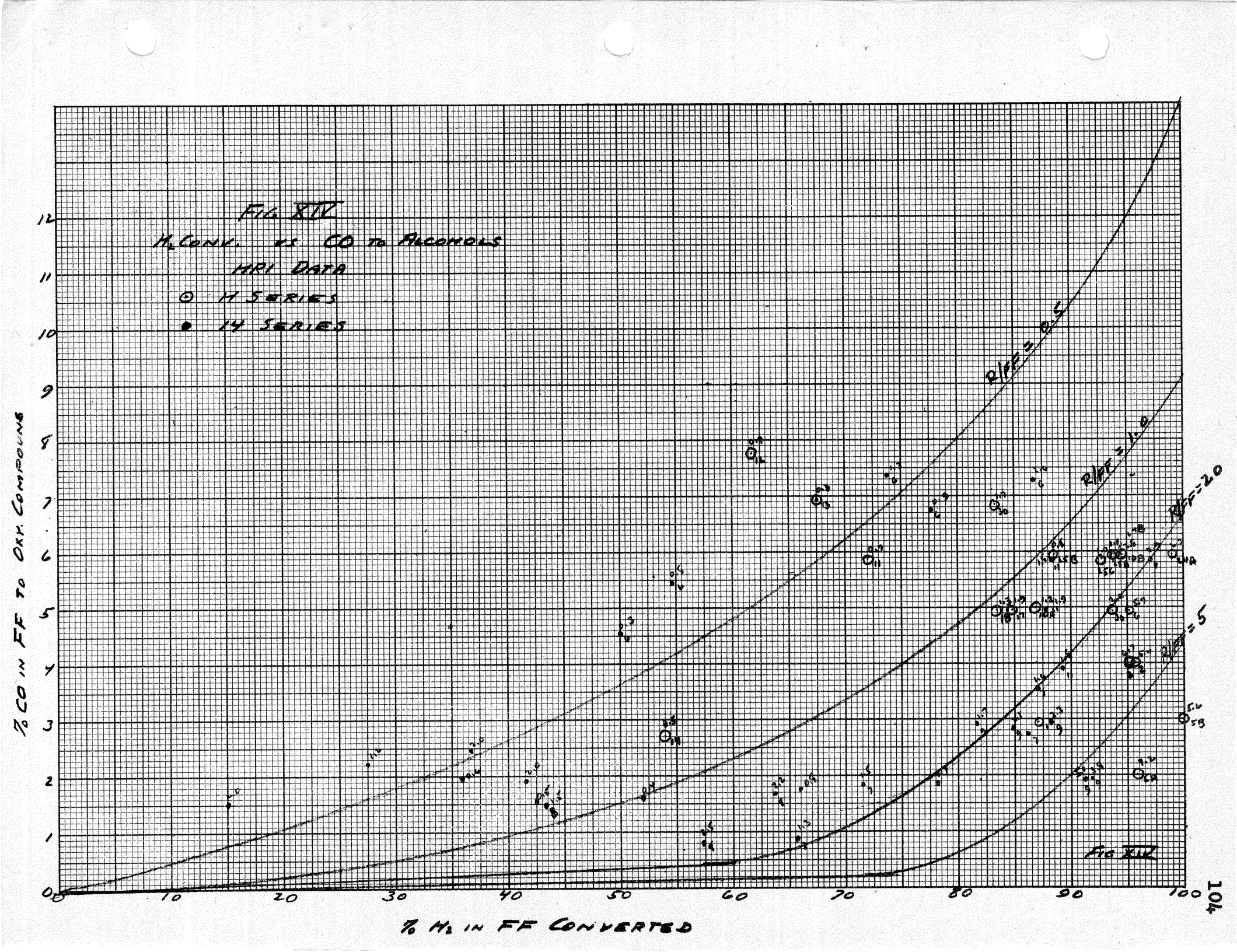


FIG. XIV
H₂ CONV. VS CO TO ALCOHOLS
HRI DATA
H SERIES
14 SERIES
% CO IN FF TO OXY. COMPOUNDS
% H₂ IN FF CONVERTED
FIG XIV
104

LPG 9/15/46

FIG XV

H_2 Conv	#3	REF
○ MRI	M-SERIES	
● MRI	14-SERIES	
× MRI	15-SERIES	
B Beacon Cmrs Red.		

	M-SERIES	14-15 SERIES
Press	192 - 235 psig	202 - 220
V_{H_2} in FF	12 - 17%	12 - 18
CO_2 % in FG	0 - 7.0	5.3
CH_4 in FF	1.6 - 3.9	1.4 - 2.9
Temp.	592 - 650	610 - 640
H_2/CO	1.8 - 2.34	1.91 - 2.08

R/FF

H₂ CONVERSION

FIG. XV

LRG 2/15/46

FIG XV A

H_2 CONV. VS R/FE

HR1 14 SERIES
FROM SUMMARIES

	14-6	14-7	14-8	14-9	14-11
TEMP.	645-664	645-655	645-655	545-585	550-603
PRESS.	130-200	250	150-215	250-255	255
H_2/CO	2-2.1	1.8-1.9	2.0	1.9-2.0	1.9-2.0
#/HR/CU FT	32-57	17-32	20-103	9-18	17-18
CO_2 % IN FE	5.8	4.0	5.6	5.5	
CH_4 % IN FE	1.9	1.5	2.2	2.2	

LAB A RUN 23B

R/FE

H_2 CONVERSION

FIG XV A

Fig XV B

H_2 Conv. vs R/EF

□ LAB A $H_2/CO = 1.0$

■ LAB A $H_2/CO = 1.5$

⊠ LAB B $H_2/CO = 1.7$ to 1.6

△ STANOLIND $H_2/CO = 3.4$ to 5.1

▲ STANOLIND $H_2/CO = 2.3$

LAB A EARLY RUNS 550°F

LAB B EARLY RUNS 600°F

LAB A LATER RUNS 600°F

STANOLIND 600° 160# $H_2/CO = 3.4$ to 5.1

BF CONV. 650° 2.0# $H_2/CO = 2$ to 2.5

R/EF

H_2 CONVERSION %

Fig. XV B

FIG XVI

R/FF vs TOTAL FEED COMP.

HRI & BEACON DATA

H_2/CO IN FF = 2

% C_2^+ IN TOTAL FEED

% MATERIAL OTHER THAN H_2, CO, CO_2 & CH_4 IN TOTAL FEED

% CO_2 IN TOTAL FEED

% C_2^+ IN TOTAL FEED

% CH_4 & C_2S IN TOTAL FEED

% H_2 IN TOTAL FEED

% CO IN TOTAL FEED

R/FF

Ratio = 2.5

Ratio = 2.0

Fig XVI

FIG. XVII

% CO IN TOTAL FEED

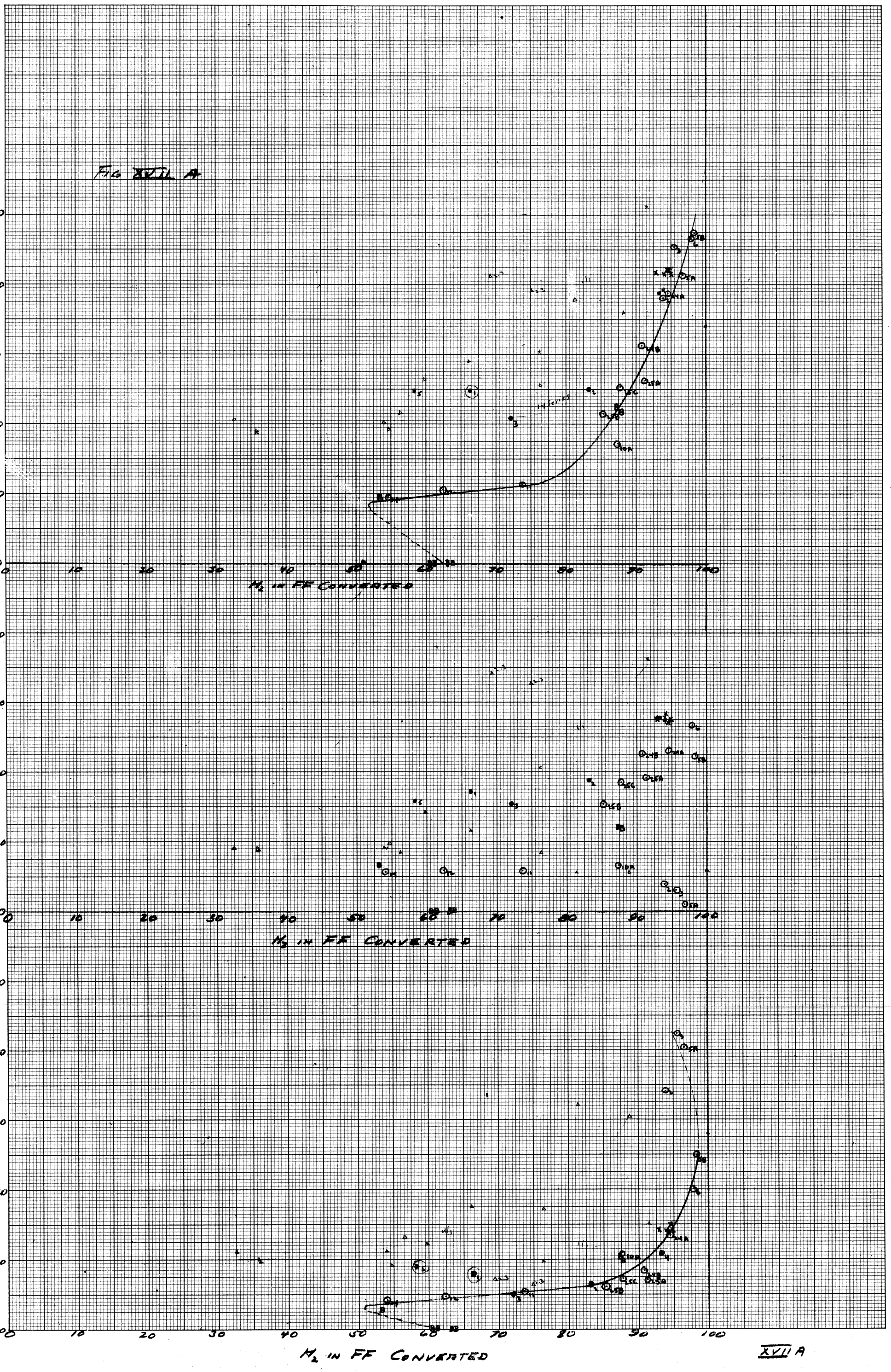
% H_2 IN FF CONVERTED

% H_2 IN TOTAL FEED

% H_2 IN FF CONVERTED

XVII

Fig XVII A



XVII A

FIG. XVII B

H_2/CO CONSUMED

2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0

0 10 20 30 40 50 60 70 80 90 100

% H_2 IN FF CONVERTED

H_2/CO IN TOTAL FEED

7
6
5
4
3
2
1
0

0 10 20 30 40 50 60 70 80 90 100

% H_2 IN FF CONVERTED

% MATERIAL OTHER THAN H_2, CO, CO_2 + CH_4 IN TOTAL FEED

32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0

0 10 20 30 40 50 60 70 80 90 100

% H_2 IN FF CONVERTED

XVII B

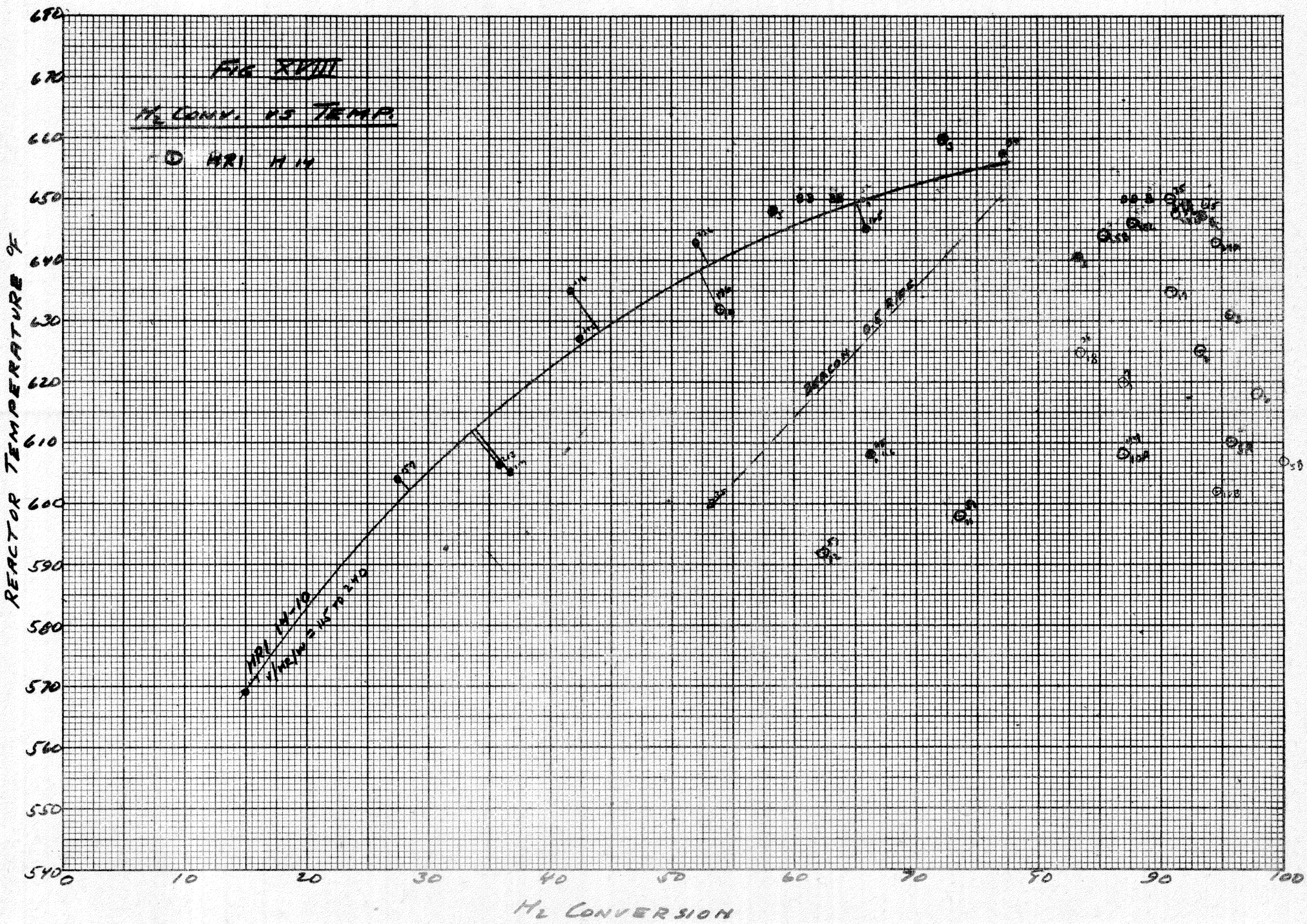


FIG XVIII
H2 CONV. VS TEMP.
HRI H 14
HRI 14-10
V/HR/W = 115 TO 240
BEACON 0.5 RISE
REACTOR TEMPERATURE °F
H2 CONVERSION
680
670
660
650
640
630
620
610
600
590
580
570
560
550
540
0
10
20
30
40
50
60
70
80
90
100

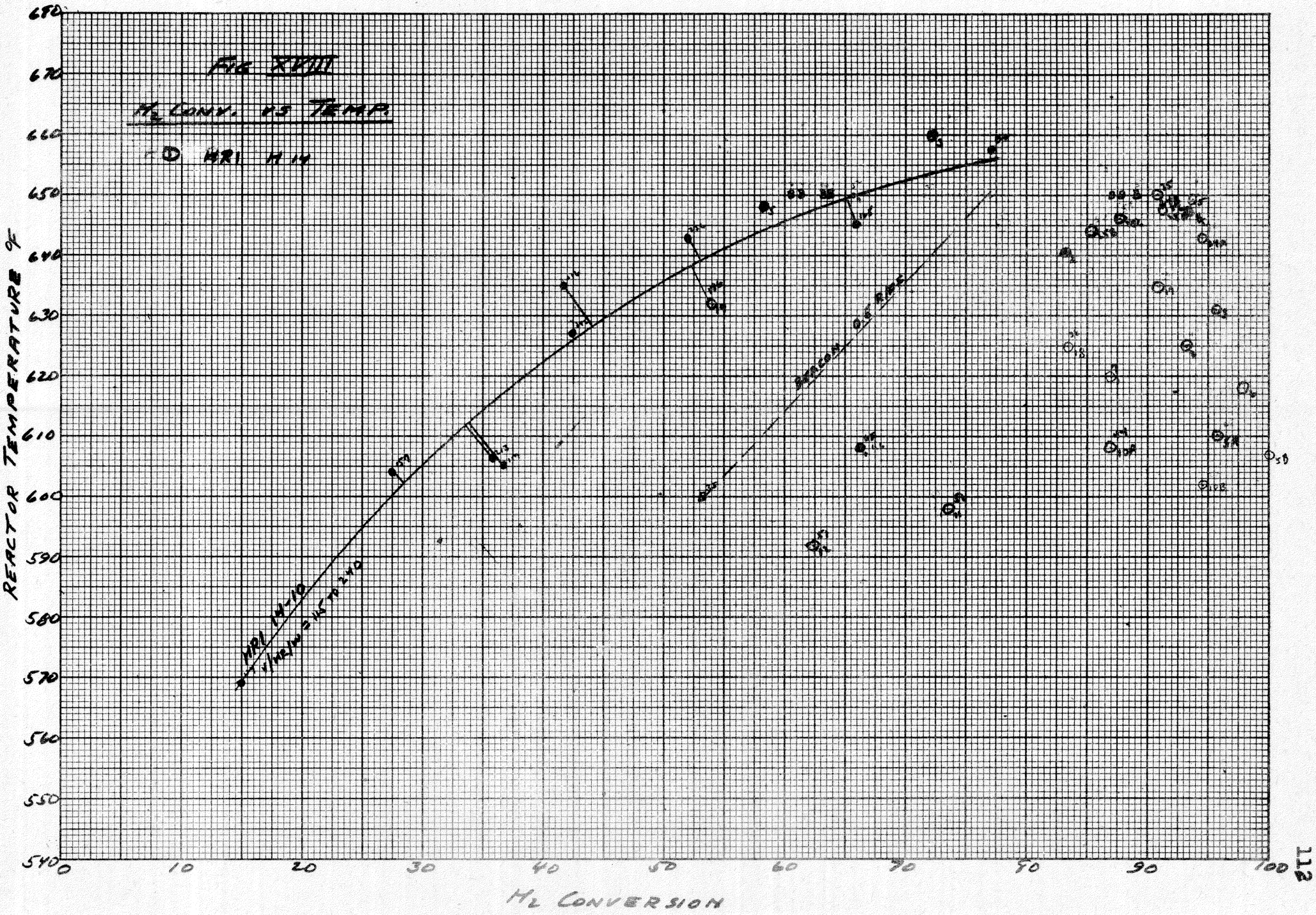


FIG XVIII
H2 CONV. VS TEMP.
HRI H 14
HRI 14-10
V/HR/W = 115 TO 240
BEACON 0.5 RIFF
REACTOR TEMPERATURE °F
H2 CONVERSION
680
670
660
650
640
630
620
610
600
590
580
570
560
550
540
0
10
20
30
40
50
60
70
80
90
100

FIG. XVIII A

H_2 Conv. vs Temp.

STANDARD DATA ▲

LAB. A $H_2/CO = 1$ □

LAB. B $H_2/CO = 2$ ●

LAB. B $H_2/CO = 2.0$ runs 11 - 12

REACTOR TEMPERATURE °F

660 650 640 630 620 610 600 590 580 570 560 550 540

0 10 20 30 40 50 60 70 80 90 100

H_2 CONVERSION