

Table 20. Effect of Temperature on Hydrocarbon Product Distribution from a Non-Carbided Catalyst

	325°C	Temperature 300°C	275°C
Total Hydrocarbon yield (g/scf of (H <sub>2</sub> +CO) converted)	4.72	4.47	4.75
Percentage of material as			
C <sub>1</sub> - C <sub>3</sub>	73.9	71.3	65.8
C <sub>4</sub> +	22.9	22.4	18.5
Oxygenates	3.2	6.3	15.7

B. Incremental Induction

An incremental induction was employed in experiments FT-STW-1-9 and FT-STW-2-6. This induction procedure was similar to a procedure employed at SASOL(9). The activity of the catalysts subjected to this technique was 90% of the level, based on CO conversion at 325°C, attained in the base case. Also, the hydrocarbon fraction was composed of the lighter hydrocarbons, and the amount of the lower molecular weight hydrocarbons increased with decreasing temperatures. A greater oxygenate yield at all temperatures as compared to the base case was observed. Table 21 summarizes the above trends.

Table 21. Effect of Temperature on Hydrocarbon Product from a Incremental Induction

	325°C	Temperature 300°C	275°C
Total Hydrocarbon yield (g/scf of (H <sub>2</sub> +CO) converted)	4.66	4.05	3.91
Percentage of material as			
C <sub>1</sub> - C <sub>3</sub>	83.3	79.5	77.8
C <sub>4</sub> +	12.1	11.7	2.8
Oxygenate	4.6	8.8	19.4

C. High Temperature Induction

The taconite catalyst was carburized at a temperature of 320°C in experiment FT-STW-1-18. The catalyst was not very active (CO conversion was 29% at 325°C) following this induction treatment. The oil yield was less than 2% of the hydrocarbon product at 325°C and nonexistent at the lower temperatures.

D. Pressure Induction

The catalyst of experiment FT-STW-2-14 was induced under 300 psig pressure at a temperature of 240°C. Although the catalyst exhibited activity (72% CO conversion at 325°C), the hydrocarbon product had negligible amounts of C<sub>4</sub>+ material at any temperature. The oxygenate yield was greater, accounting for almost 33% of the hydrocarbon product at

the lowest temperature. The distribution of the hydrocarbon product as affected by temperature is shown in Table 22.

Table 22. Temperature Effect on Hydrocarbon Product Distribution of a Pressure Induced Catalyst

	325°C	Temperature 300°C	275°C
Total Hydrocarbon yield (g/scf of (H <sub>2</sub> +CO) converted)	5.29	5.81	6.01
Percentage of material as			
C <sub>1</sub> - C <sub>3</sub>	87.5	77.5	67.4
C <sub>4</sub> +	4.4	5.0	-
Oxygenate	8.1	17.5	32.6

## Reduction Conditions

The catalyst in experiment FT-STW-4-10 was reduced at a temperature of 375°C, followed by a 240°C induction period. The conversions and selectivities are very similar to the base case. Summarized in Table 23 is the hydrocarbon product distribution. The difference in the C<sub>1</sub> - C<sub>3</sub> hydrocarbon fraction at 275°C can be attributed to the poor material recovery in this test. The results indicate that a lower reduction temperature does not alter the catalyst activity or selectivity.

Table 23. Hydrocarbon Product Distribution of a Catalyst Reduced at 375°C

	325°C	Temperature 300°C	275°C
Total Hydrocarbon yield (g/scf of (H <sub>2</sub> +CO) converted)	4.9	5.0	4.9
Percentage of material as			
C <sub>1</sub> - C <sub>3</sub>	77.5	71.8	71.2
C <sub>4</sub> +	17.4	21.0	17.8
Oxygenate	5.1	7.2	11.0

## Pressure

Experiments were performed at system pressures greater than and less than that used in the base case. The pressures examined were at system pressures of 150 psig and 600 psig.

### 150 psig

Experiment FT-STW-3-9 was performed at an operating pressure of 150 psig. The activity of the catalyst while operating at this pressure was very low at all temperatures (maximum of 17% CO conversion at 325°C). The selectivity to hydrocarbons was to the lower molecular weight material.

### 600 psig

Experiment FT-STW-4-11 was performed while operating at a system pressure of 600 psig. The activity as measured by CO conversion was never greater than 87% of that exhibited in the base case. The CO conversions of the base case versus 600 psig operation are shown in Figure 8. The hydrocarbon yield when measured as grams per cubic meter of H<sub>2</sub> + CO converted is greater at all temperatures. As shown in Table 24, there is a large increase in oxygenated product at all temperatures over the base case and also an increasing percentage of the hydrocarbon product as the temperature is lowered. Along with the increased oxygenate yield, the C<sub>4</sub>+ fraction decreased with decreasing temperature.

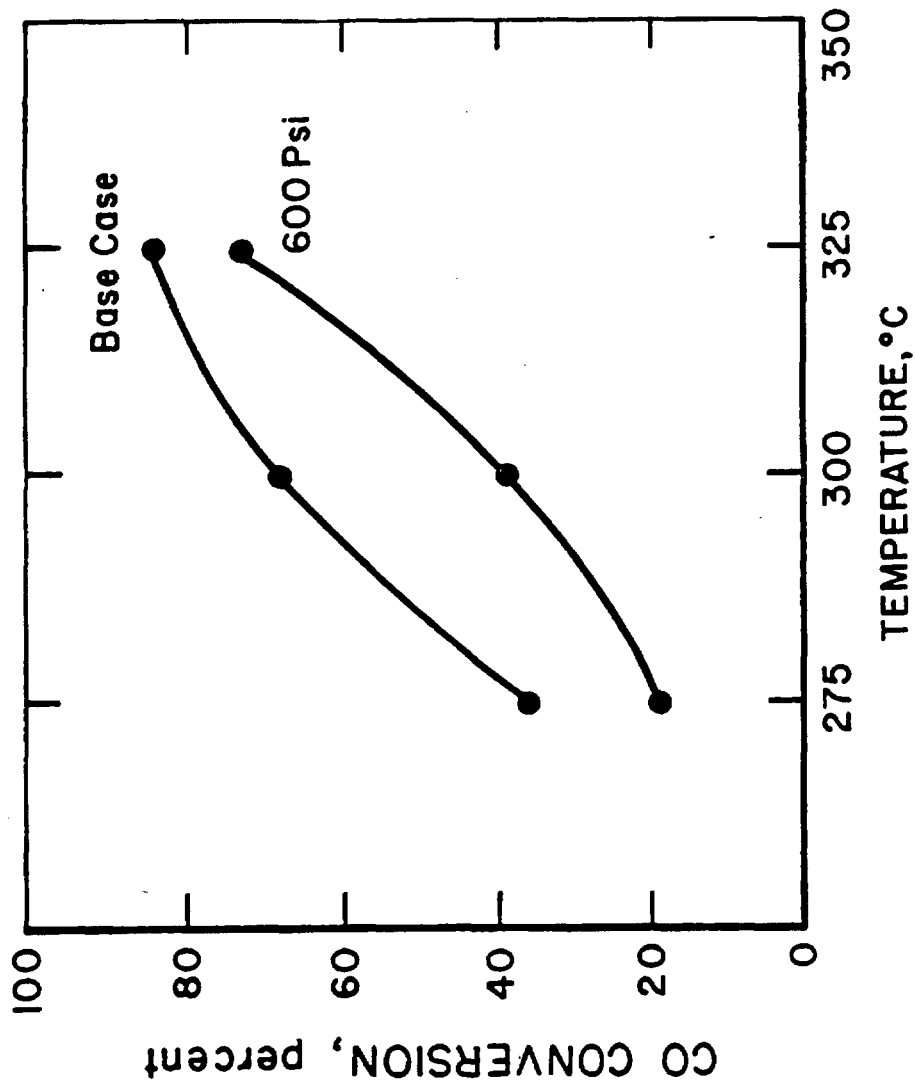


Figure 8. Effect of pressure on conversion.

Table 24. Hydrocarbon Product Distribution  
at an Operating Pressure of 600 psig

	325°C	Temperature 300°C	275°C
Total hydrocarbon yield (g/scf of (H <sub>2</sub> +CO) converted)	5.31	6.36	7.19
Percentage of material as			
C <sub>1</sub> - C <sub>3</sub>	71.3	71.3	61.3
C <sub>4</sub> +	15.0	7.7	4.9
Oxygenate	13.7	21.0	33.8

#### Exposure Velocity

The effect of exposure velocity (scfh of synthesis gas/ft<sup>2</sup> of geometric catalyst surface) on the activity and selectivity of a taconite catalyst is shown for experiments FT-STW-3-10 and FT-STW-4-12 in Table 25. Increasing the residence time results in higher conversions and heavier molecular weight hydrocarbons in the hydrocarbon fraction. The extent of the water-gas-shift reaction decreased with higher exposure velocities. However, there was a significant increase in the percentage of oxygenated material in the hydrocarbon fraction only at the lower temperature coincident with the highest exposure velocity.

Table 25. The Effect of Exposure Velocity

Exposure Velocity (J)	24	48	96	24	48	96
Temperature (°C)	325	325	325	300	300	300
CO conversion (%)	87.2	84.1	55.1	74.0	68.1	35.8
Material Recovered						
(Percentage)						
Hydrocarbon	31.3	29.6	30.9	34.2	30.0	30.3
Water	18.4	20.6	23.0	15.5	24.3	27.1
CO <sub>2</sub>	48.5	48.7	44.3	48.3	44.6	39.4
Oxygenate	1.8	1.1	1.8	2.0	1.3	3.2
Hydrocarbon Composition (wt %)						
C <sub>1</sub> - C <sub>3</sub>	72.2	79.2	75.7	69.5	72.6	76.6
C <sub>4</sub> +	22.4	17.4	18.8	24.9	23.2	14.0
Oxygenate	5.4	3.4	5.5	5.6	4.2	9.5



## Synthesis Gas Composition

The effect of a lower ratio ( $H_2/CO$  of 0.9) synthesis gas on catalyst performance was investigated in Experiment FT-STW-3-13. In general, low ratio  $H_2/CO$  gases have been shown to shift the product distribution toward higher molecular weight hydrocarbons. However, as shown in Table 26, the difference in the hydrocarbon product distribution between using synthesis gas compositions of 2/1 and 0.9/1  $H_2/CO$  is negligible at 325°C. As indicated by the percent  $CO_2$  and water, the water-gas-shift activity of the catalyst increased at the lower synthesis gas ratio. The catalyst deactivated quickly when the temperature was dropped below 325°C and exhibited no activity at 275°C.

Table 26. Effect of Synthesis Gas Composition

Experiment No.	Base	FT-STW-3-13
Synthesis Gas ( $H_2/CO$ )	2.0/1.0	0.9/1.0
Temperature (°C)	325	325
Total Product Distribution (wt %)		
Hydrocarbon	29.6	28.3
Water	20.6	15.3
$CO_2$	48.7	54.2
Oxygenate	1.1	2.2
Hydrocarbon Distribution (wt %)		
$C_1 - C_3$	79.2	75.7
$C_4+$	17.4	17.3
Oxygenate	3.4	7.0

## Promotors

Potassium and copper as promoters to thermally sprayed taconite ore were investigated to evaluate their effect on activity and/or product distribution. Table 27 is a summary of the experiments using impregnated catalyst, along with the respective activities as measured by CO conversion.

Table 27. Summary of Experiments Using Promoted Catalysts and Activity

Experiment	Impregnating Solution	CO Conversion, %		
		325°C	300°C	275°C
FT-STW-2-15	17.8% Cu(NO <sub>3</sub> ) <sub>2</sub>	80.7	55.8	27.4
FT-STW-1-20	10.6% K <sub>2</sub> CO <sub>3</sub>	78.8	87.1	83.9
FT-STW-4-7	6.0% K <sub>2</sub> CO <sub>3</sub>	76.7	53.3	10.7
FT-STW-3-11	8.8% KNO <sub>3</sub>	75.6	45.9	18.9
FT-STW-2-10	6.0% K <sub>2</sub> CO <sub>3</sub>	74.8	56.9	24.5
FT-STW-3-12	8.9% Cu(NO <sub>3</sub> ) <sub>2</sub> + 8.8% KNO <sub>3</sub>	74.3	53.8	26.8
FT-STW-1-19	3.0% Cu(NO <sub>3</sub> ) <sub>2</sub> + 8.8% KNO <sub>3</sub>	72.2	53.4	23.5
FT-STW-4-14	17.8% Cu(NO <sub>3</sub> ) <sub>2</sub> + 8.8% KNO <sub>3</sub>	16.6	9.0	8.9
FT-STW-2-9	10.6% K <sub>2</sub> CO <sub>3</sub>	16.6	8.6	4.6
FT-STW-4-13	15.5% KNO <sub>3</sub>	12.6	5.1	5.0

The addition of a promotor generally resulted in a catalyst with activity less than that obtained with an unimpregnated catalyst. The high activity exhibited using a 10.6%  $K_2CO_3$  (FT-STW-1-20) solution is probably the result of the poor material recovery balances. This can be seen in the CO conversions of Experiment FT-STW-2-9, which are low with the same promotor concentration. Heavier loading of the promotor tended to suppress the activity of the catalyst.

The discussion that follows encompasses those experiments that exhibited CO conversion greater than 50% at 325°C. The total product distribution is unaffected by the addition of copper when compared to the base case. However, catalyst impregnated with potassium showed increased water-gas-shift activity at all temperatures, as reported elsewhere(12). Lowering the temperature resulted in a slight increase in the percentage of oxygenates in the product.

The specific yield of hydrocarbons (g/scf of  $(H_2 + CO)$  converted) was greater with potassium impregnated catalyst and less with a copper promotor added. The hydrocarbon fraction of the total product at 325°C was composed of higher molecular weight material when the catalyst was impregnated with potassium. The addition of copper produced a greater percentage of lighter material. As the concentration of copper in the solution increased when impregnating with both copper and potassium, the product distribution approached the distribution of a catalyst impregnated with copper only. As the temperature is lowered, the difference in the percentage of material in the  $C_4+$  fraction decreases between the base case and potassium promoted catalyst. At 275°C, the base case produced a greater percentage in this fraction. Also, as the temperature was decreased, the percentage of oxygenated material formed increased. The promoted catalysts exhibited a greater percentage of oxygenates in the total product as

temperature decreased. The maximum percentage of oxygenates recovered in the hydrocarbon product was obtained while using a copper promoted catalyst.

## SUMMARY

The effects of a number of operating parameters and catalyst variables on activity and product selectivity were investigated for a taconite ore thermally sprayed onto heat exchange surfaces. The findings from these experiments are summarized in Table 28. Within the range of operating conditions considered for a commercial scale tube wall reactor, the addition of potassium promotor had the greatest effect on increasing the average molecular weight of the hydrocarbon product. Excessive levels of potassium, however, produced a catalyst exhibiting very low activity, as already reported in the literature (13).

Under the best condition, the taconite-based flame-sprayed catalyst still produced a minimum of approximately 50 wt%  $C_1+C_2$ , while the design basis used in the R.M. Parsons' conceptual study assumed only 19.3 wt% for these components (see Table 11). Although detailed analysis of the liquid hydrocarbon product could not be obtained for the TWR tests reported here, a qualitative comparison of the product spectrum with the R.M. Parsons' design basis indicates that the marketed products would contain far more SNG and LPG and far less naphthas, diesel fuel, and fuel oil than projected in the conceptual design. The lower market value of SNG relative to the liquid products would have an adverse impact on the process economics. One alternative would be to reform the  $C_1$  and  $C_2$  fraction back to synthesis gas for recycle to the Fischer-Tropsch reactions. However, a severe penalty would be incurred in terms of thermal efficiency, and in view of the high selectivity to light gases in the synthesis reactors, this approach is not considered to be feasible.

The reactor design used in the Parsons' study employed catalyst thermally sprayed on external extended-surface heat exchanger tubes. Thus, catalyst replacement would require complete dismantling of the reactor. Although taconite ore is a comparatively inexpensive catalyst, reactor dismantling costs and the costs associated with flame-spraying the catalyst onto the heat exchange surface would render this approach prohibitively expensive.

As a result of the above findings, research studies associated with this reactor-catalyst concept were discontinued.

Table 28. Effect of Operating Parameters and Promotors on a Taconite Catalyst

Variable	Range	Result
Temperature	275° - 325°C	Lowering temperature increased molecular weight of hydrocarbon fraction.
Induction	-	Carburization is necessary.
Reduction	375° - 450°C	No observable effect.
Spraying Technique	-	Flame-sprayed catalyst more active than a plasma-sprayed catalyst.
Pressure	150-300-600 psig	Little activity at lowest pressure. Oxygenate production maximized at highest temperature. Higher molecular weight hydrocarbons produced at 300 psig.
Exposure Velocity	24-48-96 J	Lower molecular weight hydrocarbons produced with decreased residence time.
Synthesis Gas Ratio	0.9/1.0 → 2.1/1.0	No observable difference in hydrocarbon fraction at 325°C. The lower ratio syn gas deactivated the catalyst quickly after initial period of operation.

Variable	Range	Result
<b>Promotors</b>		
a. Potassium		Increase in molecular weight of hydrocarbon fraction. However, high loadings act as a poison
b. Copper		Increase in oxygenate production and in lower molecular weight hydrocarbons

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APPENDIX