

- (a) High temperature favored $C_1 + C_2$ formation.
 - (b) Low temperatures favored selectivity to gasoline range hydrocarbons.
 - (c) High pressure decreased the yield of $C_1 + C_2$ and increased the yield of gasoline.
3. A flame-sprayed taconite catalyst can be successfully regenerated resulting in a total useful life of up to 8-9 months.
 4. A lower induction temperature (240°C) results in a greater oil selectivity.

DATA BASE RESULTS

In 1977, the R. M. Parsons Company completed a conceptual design and economic analysis of a commercial-scale coproducts plant producing about 260 million scf per day of SNG and 50,000 barrels per day of liquid hydrocarbon products(1,2). Classical Fischer-Tropsch synthesis was used to convert synthesis gas produced by a two-stage entrainment type slagging gasifier to a wide range of hydrocarbon fuels, including SNG, LPG, gasoline, diesel fuel, and fuel oil. Their analyses showed that the use of extended^A surface, tube wall reactors (TWR) in the shift and synthesis unit-processes resulted in the production of sufficient high-pressure steam to satisfy the steam requirements for the rest of the plant complex. This eliminates the requirement for a fuel-fired utility plant under normal operation and increases the predicted overall thermal efficiency to almost 70%. The basis used by Parsons for the conceptual design of the Fischer-Tropsch synthesis section of the plant relied heavily upon older Bureau of Mines studies

involving Hot Gas Recycle reactor systems. This was unavoidable, since the conceptual design was performed before the results of the preliminary investigation, discussed in this report, were available. Several key design parameters used by Parsons, such as space-time yield, catalyst life, and product distribution, required further verification.

The design was based on a catalyst life of one stream year, or 8000 operating hours. Since experiment FT-STW-2-2 operated successfully for over 6000 hours and catalyst regeneration had been successfully demonstrated, it was decided that catalyst life would not be a critical limiting factor. Furthermore, a rather conservative exposure velocity of 10 J with a CO+H₂ conversion of 80% was chosen in the design, while bench-scale experiments revealed that conversions of 70% could be obtained at exposure velocities two and one half times greater than this. The greatest design uncertainty, with respect to the synthesis section, fell in the area of product distribution or catalyst selectivity. The design product distribution is illustrated in Table 11.

Table 11. Reactor Product Distribution Used in R.M. Parsons Conceptual Design

<u>Component</u>	<u>Weight Percent</u>
C ₁ , C ₂	19.3
C ₃	4.5
C ₄	11.9
C ₅ , C ₆	13.6
C ₇ , C ₈ , C ₉	19.2
C ₁₀ to 640°F b.p.	18.8
640° to 940°F b.p.	7.3
Alcohols and Ketones	4.9
Acids	<u>0.5</u>
Total	100.0

Comparison of Table 11 with the data presented in the previous section indicates that Parsons assumed a much heavier product distribution, i.e., less C₁ and C₂ and more diesel and fuel oil, than could be achieved in the bench-scale TWR tests. Thus, it was decided to conduct a process variables study in order to determine if the design product distribution could be obtained and, if so, identify the required conditions.

The study was conducted in small, continuous-flow, tube wall type reactor systems, described previously, with about 17 grams of catalyst thermally sprayed onto a base heat exchange tube. The independent variables investigated were temperature, pressure, conversion, and synthesis gas feed composition, as well as catalyst promoters, carbonization, and reduction.

Catalyst and Catalyst Preparation

A beneficiated taconite iron catalyst was employed in the following series of tests. The ore, 100-200 mesh size, was flame-sprayed onto the heat exchange surface using the procedure described earlier. For comparison purposes, one test was conducted using a plasma-sprayed catalyst. The composition of the taconite catalyst is given in Table 12.

Table 12. Taconite Catalyst Composition

Element	Weight Percent
Fe	47.0 - 60.6
Al	0.1
K	0.1
Si	10.0 - 4.4
Mg	0.8 - 0.4
Cr	<0.02
Mn	0.4 - 0.2
Ti	0.1
Ca	1.7 - 0.9
V	<0.1
S	<0.1 - 0.1
Ni	<0.1
C	2.2 - 1.0
Cu	<0.02

Prior to catalyst application, the support tube was grit-blasted with aluminum oxide particles to clean and pit the surface. The grit-blasted surface was then coated with a nickel aluminide bond coat. This catalytically inactive bond coat, consisting of 95% Ni and 5% Al, was sprayed to a thickness of 0.003 inches. The catalyst was finally applied over a well-defined 3-inch section of the support tube. The spraying operation was continued, using repeated passes of the flame-spray gun, until a catalyst weight of

17 ± 0.5 grams was obtained. The configuration of the catalyst and support tube is identical to that illustrated in Figure 3 with the exception that in this series of tests, only three inches of catalyst was used.

Promotor Impregnation

The influence of potassium and copper promoters on the properties of iron Fischer-Tropsch has been established (10,11,13). Potassium is known to shift the product spectrum towards the longer chained hydrocarbons and will increase activity to some degree. On the other hand, addition of copper to iron catalysts has been found to enhance the rate of iron oxide reduction, thus enabling reduction to be carried out at lower temperatures.

Since catalyst properties and performance are sensitive to the level of chemical promoters present, a study was performed using small coupons to establish methods for controlling promotor concentrations in thermally sprayed catalyst coatings. Coupons of stainless steel were first sprayed with a bond coat and then flame-sprayed with taconite powder, usually 100-200 mesh size, to a thickness of 22.5 mil. The catalysts were impregnated with promoters by immersing the coated coupons into an aqueous solution of the metal salt.

Initial work with potassium was performed with solutions of potassium carbonate. Later, when coimpregnation of copper and potassium was studied, the nitrate salt of potassium was used. After impregnation, the coupon was dried and charged into a reduction unit. This unit consisted of a Vycor tube through which metered hydrogen flowed. The tube was surrounded by a furnace that maintained a constant temperature. Coupon samples were either reduced at 400°C until the theoretical amount of water

was removed or reduced at 450°C for a standard time of 24 hours. After the reduction, the tube containing the coupon was transported to a glove box maintained under an inert atmosphere. The coupon was then mildly oxidized in a 1% hydrogen peroxide solution for ten minutes. The sample was washed with pure ethanol for ten minutes, dried, and analyzed. Analysis for potassium or copper was performed by X-ray fluorescence.

The first set of experiments centered around increasing the potassium level by impregnation from a potassium carbonate solution. The following parameters were examined:

1. Impregnation after reduction
2. Promotor uniformity across taconite thickness
3. Carbonate solution temperature
4. Length of dip time
5. Potassium carbonate concentration.

The results of this series of tests may be summarized as follows:

1. Impregnation of potassium before reduction deposited between 0.63 - 0.76 wt%, whereas after reduction only 0.54 wt% was deposited.

2. Fluorescence measurements were taken after removing a portion of the catalyst layer. Three scrapings per sample were made. Analysis of each coupon after a scraping indicated potassium promoter was uniformly deposited throughout the taconite layer. Also, the maximum obtainable level of potassium to be impregnated is about 2 wt%.
3. Samples promoted at 90°C and 250°C showed no appreciable difference in potassium levels.
4. Increasing the soaking time of the catalyst, by as much as a factor of 18, did not affect the potassium promoter level.
5. In one sequence of tests, the concentration of the potassium carbonate solution was varied. As the potassium concentration in the solution was raised, there was a corresponding increase in the amount of potassium deposited on the catalyst. The results indicated that impregnation is not increased significantly after an optimum solution concentration. Above 12 wt% potassium in aqueous solution, the potassium in the catalyst did not vary from 1.3 wt%.

Further investigations were conducted by impregnating taconite with potassium nitrate and hydrated copper nitrate. Initial results indicated that increasing the copper nitrate concentration seemed to increase the amount of promoter deposited. However, there appeared to be some discrepancy between the X-ray fluorescence and bulk chemical analysis. On the surface of the taconite, copper is probably deposited via an electrochemical reaction. Equilibrium constant calculations indicate that such a reaction is favored. By removing and then analyzing consecutive layers of the catalyst, a

concentration gradient was found to exist through the taconite layer, with about 2 wt% on the outer surface and diminishing copper concentration towards the substrate.

Thermogravimetric analysis of potassium nitrate and potassium carbonate salts heated to 450°C under hydrogen indicate that the potassium nitrate decomposes to potassium but the potassium carbonate does not.

X-ray fluorescence analysis of impurity levels in unimpregnated taconite coupons indicated a negligible amount of copper, potassium, and nickel in the unpromoted samples. Samples of taconite powder, which were used in the experimental tests, were analyzed by X-ray diffraction, chemical analysis, and nitrogen adsorption. One sample was raw taconite powder, and the other was reduced taconite that had been reduced, then oxidized with hydrogen peroxide, and finally dried. Results are listed below:

Analysis	Raw Taconite Powder	Reduced Taconite
X-ray diffraction	Fe ₃ O ₄ , Quartz	Fe, Quartz
BET, m ² /g	2	12

Chemical analysis of the above raw taconite indicated a relatively high amount of silicon (10%) and low iron (47%); therefore, the inventory of taconite used for the test was reassessed. Chemical analysis of samples of the same batch from different drums showed 4.1%, 2.6%, 4.8%, and 5.3% by weight of silicon and 56.8%, 64.5%, 56.5%, and 65.7% by weight of iron, respectively. These differences emphasized the inhomogeneity of the beneficiated taconite ore as purchased, and pointed to the importance of thorough blending of the ore before use as a catalyst.

The effect of potassium and copper promotion on catalyst activity and selectivity was determined in a series of tests conducted in the bench-scale TWR systems. The catalysts were promoted with potassium or copper or a combination of the two before being installed in the reactor. The heat exchanger tube, coated with catalyst, was submerged in the solution of promotor salt(s) for a period of 10 minutes. The catalyst was then withdrawn and allowed to air-dry before being placed in the reactor.

Catalyst Activation

The active form of the catalyst was prepared by reduction under hydrogen followed by carburization with synthesis gas. Catalyst reduction was carried out at either 375°C or 450°C at atmospheric pressure and a hydrogen flow of 14 to 28 J. The catalyst was reduced for 24 hours when a reduction temperature of 450°C was employed, whereas 96 hours was required with a reduction temperature of 375°C.

Three different methods were employed for carburizing the catalyst. The catalyst was carbided either under constant operating conditions at 240°C or 320°C or by incrementally increasing both temperature and pressure until synthesis conditions were obtained. Operating parameters used for carburization are given in Table 13. A list of the tests performed, along with catalyst parameters and activation procedures, is shown in Table 14.

Table 13. Carburization Parameters

I. Carburization Under Constant Conditions

Temperature	240°C or 320°C
Pressure	atmospheric
Gas mixture	2.1 H ₂ /CO
Flow rate	3.45 scfh = 48 J
Duration	72 hours

II. Incremental Carburization

1. Increase system pressure to 45 psig with hydrogen while maintaining a temperature of 180°C.
2. Introduce synthesis gas (2.1 H₂/CO) at a flow rate of 3.45 scfh (48 J) and maintain the 45 psig, 180°C condition for 16 hours.
3. Increase temperature to 200°C and maintain for 16 hours.
4. Increase the temperature to 225°C and maintain for 16 hours.
5. Increase the pressure to 130 psig and maintain for 16 hours.
6. Increase the pressure to 215 psig and maintain for 16 hours.
7. Increase the pressure to 300 psig and maintain for an additional 16 hours. This completes the induction procedure, and the temperature is then increased to synthesis condition.

Table 14. Summary of Experiments and Methods of Activation

Experiment No.	Weight (g)	Thickness x10 ⁻² (in.)	Catalyst	Activation Procedure		Temp. (°C)	Duration (hours)	Technique or Temp.
				Reduction	Induction			
FT-STW-1-7	17.0	4.7				450	24	240°C
FT-STW-2-4	18.0	5.3				450	24	240°C
FT-STW-1-6	16.2	4.6				450	24	--
FT-STW-4-3	17.2	4.1				450	24	--
FT-STW-1-9	16.5	4.0				450	24	Incremental
FT-STW-2-6	17.5	4.6				450	24	Incremental
FT-STW-1-18	17.5	3.7				450	24	320°C
FT-STW-2-14	16.5	3.7				450	24	240°C/300 psig
FT-STW-4-10	16.5	4.6				375	96	240°C
FT-STW-3-14	17.0	4.0				450	24	240°C
FT-STW-3-9	16.5	4.2				450	24	240°C
FT-STW-4-11	17.0	4.3				450	24	240°C
FT-STW-3-10	16.5	3.5				450	24	240°C
FT-STW-4-12	17.5	3.6				450	24	240°C
FT-STW-3-13	17.0	4.9				450	24	240°C
FT-STW-2-15	17.5	4.7	17.8% Cu(NO ₃) ₂			450	24	240°C
FT-STW-1-20	17.0	4.2	10.6% K ₂ CO ₃			450	24	240°C

Table 14. Summary of Experiments and Methods of Activation (Continued)

Experiment No.	Weight (g)	Thickness $\times 10^{-2}$ (in.)	Catalyst	Activation Procedure		
				Impregnation	Reduction	Induction
				Temp. (°C)	Duration (hours)	Technique or Temp.
FT-STW-4-7	17.0	5.5	6.0% K_2CO_3	450	24	240°C
FT-STW-3-11	17.5	3.9	8.8% KNO_3	450	24	240°C
FT-STW-2-10	17.0	5.8	6.0% K_2CO_3	450	24	240°C
FT-STW-3-12	17.5	3.9	8.9% $Cu(NO_3)_2 + 8.8\% KNO_3$	450	24	240°C
FT-STW-1-19	17.0	4.0	3.0% $Cu(NO_3)_2 + 8.8\% KNO_3$	450	24	240°C
FT-STW-2-17	17.5	4.1	3.0% K_2CO_3	450	24	240°C
FT-STW-2-9	17.0	5.1	10.6% K_2CO_3	450	24	240°C
FT-STW-4-13	17.5	3.8	15.5% KNO_3	450	24	240°C
FT-STW-4-14	17.5	4.6	17.8% $Cu(NO_3)_2 + 8.8\% KNO_3$	450	24	240°C

Synthesis Operation

Following the catalyst reduction and/or induction, a standard operating schedule was followed. Synthesis gas was introduced into the reactor at the synthesis operating pressure and exposure velocity and at a temperature of 325°C. The schedule then employed is detailed in Table 15.

Table 15. Standard Operating Schedule

Period Designation	Operating Temperature	Duration
Pre-Period	325°C	120 hours
A	325°C	72 hours
B	300°C	72 hours
C	275°C	72 hours

Exposure velocity was 48 J unless otherwise specified.

Discussion of Results

This section begins with an examination of the experiments defined as the "base case." Results of these experiments are presented in terms of activity, total product distribution, and hydrocarbon product distribution. The hydrocarbon product is detailed in terms of a gaseous fraction, an aqueous oxygenated product, and an oil component. Subsequent parts of this section discuss the various parametric studies and their influence on activity and selectivity in deviating from the "base case" results. The parameters to be reported include the following:

1. Induction Treatments
2. Reduction Conditions

3. Spraying Technique
4. Pressure
5. Exposure Velocity
6. Synthesis Gas Ratio
7. Promoters

A summary of the experiments performed and the specific parameters evaluated is shown in Table 16. Also provided in this table is a reference list of the detailed experimental data from each test. These data are included in the Appendix.

Base Case

The catalyst (taconite) used to establish the base case was subjected to a 450°C, 300 psig, 24-hour hydrogen reduction period followed by a 240°C, atmospheric pressure, 72-hour induction treatment with synthesis gas before starting initial synthesis conditions. The results of these experiments clearly demonstrate reproducibility (see Experiments FT-STW-1-7 and FT-STW-2-4, Appendix). The effect of temperature on catalyst activity and selectivity is described below.

The catalyst activity and, hence, the total product yield composed of hydrocarbons, carbon dioxide, water, and the water soluble oxygenates decreased with lower temperatures. Although the overall product yield decreased, the hydrocarbon specific yield (including oxygenates), when defined as grams of hydrocarbon recovered per standard cubic foot of hydrogen plus carbon monoxide converted, remained constant throughout the temperatures explored. The carbon dioxide and water fractions follow the water gas shift reaction as affected by temperature, carbon dioxide increasing with higher temperature.

Table 16. Summary of Experiments, Parameters, and a Listing of the Results

Experiment	Parameter	Table of Results*
FT-STW-1-7	Base Case	17,18
FT-STW-2-4	Base Case	17,18
FT-STW-1-6	Induction - Non-Carbided	20
FT-STW-4-3	Induction - Non-Carbided	20
FT-STW-1-9	Induction - Incremental	21
FT-STW-2-6	Induction - Incremental	21
FT-STW-1-18	Induction - High Temperature	--
FT-STW-2-14	Induction - Pressure	22
FT-STW-4-10	Reduction - Low Temperature	23
FT-STW-3-14	Spraying - Plasma	19
FT-STW-3-9	Pressure - 150 psi	--
FT-STW-4-11	Pressure - 600 psi	24
FT-STW-3-10	Exposure Velocity - 24 J	25
FT-STW-4-12	Exposure Velocity - 96 J	25
FT-STW-3-13	Synthesis Gas - 0.9/1.0 - H ₂ /CO	26
FT-STW-2-15	Promotor - Cu(NO ₃) ₂	27
FT-STW-1-20	Promotor - K ₂ CO ₃	27
FT-STW-4-7	Promotor - K ₂ CO ₃	27
FT-STW-3-11	Promotor - KNO ₃	27
FT-STW-2-10	Promotor - K ₂ CO ₃	27
FT-STW-3-12	Promotor - Cu(NO ₃) ₂ + KNO ₃	27
FT-STW-1-19	Promotor - Cu(NO ₃) ₂ + KNO ₃	27
FT-STW-4-14	Promotor - Cu(NO ₃) ₂ + KNO ₃	27
FT-STW-2-9	Promotor - K ₂ CO ₃	**
FT-STW-4-13	Promotor - KNO ₃	**

* Entire experimental data and results are tabulated in the Appendix.

** Complete results not presented because of poor activity; see Table 27 (Experiments Using Promoted Catalyst).

As suggested previously, the percentage of hydrocarbons in the total product yield increases with decreasing temperature. The hydrocarbon fraction as shown in the oil distillate fractions of Table 17 also became heavier with lower temperatures. The aqueous oxygenates composed of mainly methanol-ethanol-propanol increased significantly at the lowest temperature. These trends are shown in Tables 17 and 18 and in Figure 6.

Table 17. Effect of Temperature on Oil Fraction Distribution*

Boiling Range Distribution	325°C	Temperature 300°C	275°C
≤ 204°C	76.5	70.2	63.0
204° - 316°C	19.3	22.8	26.3
316° - 450°C	3.6	6.1	9.1
>450°C	0.6	1.0	1.5

*Values represent the average of the two experiments.

Table 18. Base Case Product Distribution as Affected by Temperature*

	325°C	Temperature 300°C	275°C
Hydrocarbon yield (g/scf of (H ₂ +CO) converted)	4.98	4.74	4.89
Percentage of material as			
C ₁ - C ₃	79.2	72.6	63.5
C ₄ +	17.4	23.2	25.0
Oxygenate	3.4	4.2	11.5

*Values represent the average of the two experiments.

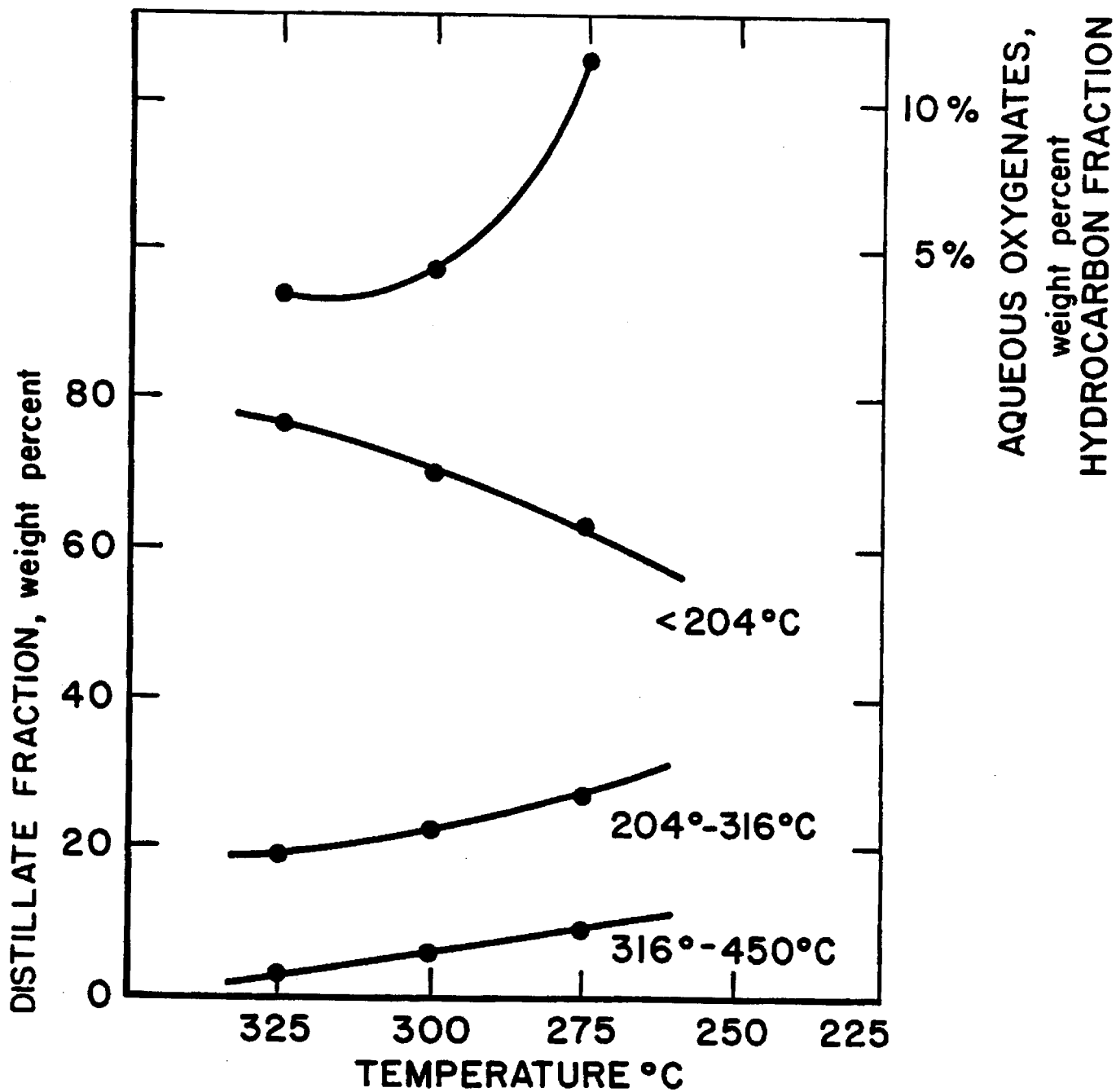


Figure 6. Effect of temperature on product distribution in C_5^+ hydrocarbons and aqueous oxygenates.

Spraying Technique

The base case catalyst was applied to the support tube using an oxygen-hydrogen flame-spray method. The catalyst in Experiment FT-STW-3-14 was applied using a plasma-spray technique. The results of FT-STW-3-14 indicated that catalyst applied by the plasma-spray method is not as active as a flame-sprayed catalyst. The hydrocarbon product as shown in Table 19 is composed of the lighter molecular weight hydrocarbons. Also, the hydrocarbon distribution is not greatly altered by operating temperature as exhibited in the base case.

Table 19. Hydrocarbon Distribution from a Plasma-Sprayed Catalyst

	325°C	Temperature 300°C	275°C
Hydrocarbon yield (g/scf of (H ₂ +CO) converted)	4.48	4.06	3.46
Percentage of material as			
C ₁ - C ₃	81.9	76.7	79.3
C ₄ +	13.5	14.1	12.5
Oxygenate	4.6	8.2	8.2

Induction Treatments

Experiments were performed to determine the advantage of induction and to evaluate various carburization procedures. The experiments to be discussed are the following:

- A. Non-carbided catalyst
- B. Incremental induction
- C. High temperature induction
- D. Pressure Induction

The experimental conditions for the various induction treatments were discussed in an earlier section.

- A. Non-carbided catalyst

Experiments FT-STW-1-6 and FT-STW-4-3 were performed without carburizing the catalyst. Results indicate that a catalyst not subjected to an induction treatment was not as active as a base case carburized catalyst. This is illustrated in Figure 7; CO conversion was 17% less at 325°C when compared to the base case. Unlike the base case, the C₄₊ fraction of hydrocarbons decreased as the temperature was lowered. These trends are presented in Table 20. The conclusion from these experiments is that the beneficial effect of a base case induction procedure is to develop a more stable and active catalyst.

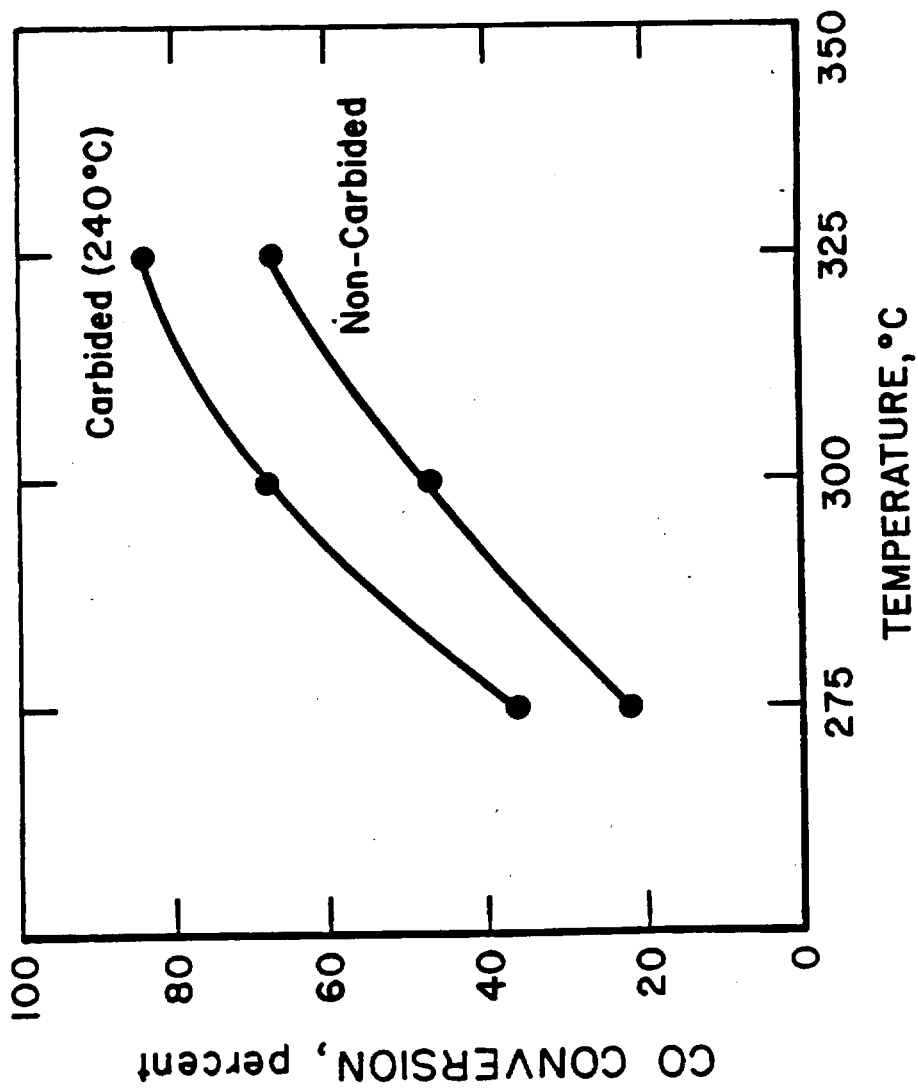


Figure 7. Effect of carbiting on activity.