

**TECHNOLOGY DEVELOPMENT FOR IRON
FISCHER-TROPSCH CATALYSIS**

Contract No. DE-AC22-91PC94055

Quarterly Technical Progress Report No. 4

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Prepared for

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4. Contract Objectives

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

- a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts**

- 1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts
 - Role of precursor particle size on activity.
 - Role of Cu in precipitated catalysts.
 - Define attrition resistance.
- 1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts
 - Define optimum SiO_2 .
 - Define optimum Al_2O_3 .
- 1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.
- 1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

- 2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.
- 2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.
- 2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0 Catalyst Structure and Characterization.

d. Task 4.0 Catalyst Testing.

4.1 Verify the Quality of Data Obtained from the CSTR's.

4.2 Measure Catalyst Performance.

4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.

4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

e. Task 5.0 Reports.

3. Summary of Activities

The affect of copper promotion on the activity and selectivity of hydrogen pretreated, precipitated iron Fischer-Tropsch catalysts was studied. Fischer-Tropsch synthesis was carried out in the slurry phase in one liter continuous stirred tank reactors at a space velocity of $3.1 \text{NL h}^{-1} \text{g}^{-1}(\text{Fe})$, $\text{H}_2:\text{CO}=0.7$ at either 270°C or 230°C . Catalysts with atomic compositions relative to iron of $100\text{Fe}/4.4\text{Si}/1.0\text{K}$ and $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ were used at 270°C and catalysts with the compositions of $100\text{Fe}/4.4\text{Si}/4.2\text{K}$ and $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/4.2\text{K}$ were used at 230°C . XRD and Mössbauer spectroscopy both show that the $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ catalyst contained approximately 24% $\alpha\text{-Fe}$ with the remainder Fe_3O_4 after a 24 h pretreatment with hydrogen at 220°C . Copper promotion was found to substantially increase the activity and productivity of the catalysts. Catalysts promoted with copper reached maximum activity within 100 h of synthesis while catalysts with no copper went

through an induction period. The activity of the hydrogen pretreated 100Fe/4.4Si/2.6Cu/1.0K catalyst operated at 270°C was comparable to the activity of the 100Fe/4.4Si/1.0K catalyst after pretreatment with carbon monoxide or syngas at one atmosphere pressure. However, the activity of the hydrogen pretreated 100Fe/4.4Si/2.6Cu/4.2K catalyst at 230°C was found to be substantially lower than the same catalyst pretreated with carbon monoxide or syngas at one atmosphere pressure.

4. Status, Accomplishments, Results and Discussion

A.0. - Task 1.0. Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

A.1. Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Catalysts

- Role of precursor size on activity.

A CSTR run using a fly ash sample having the desired particle size has been completed. The data show that this ash did not have sufficient activity to warrant further investigation.

- Role of Cu in precipitated catalysts.

See Task B.1.

- Define attrition resistance.

There still exists a problem with spray-drying and the formation of spherical particles in the desired size range and strength. Additional discussions with Niro Atomizer, Inc. have been made. They have suggested that some preliminary experiments be conducted prior to further work by them. They have suggested that we take the various Si supported catalysts we have prepared and place them on a flat glass plate and dry them with a flow of hot air. After drying, the crush strength of the catalysts would be determined. This procedure would be done by Niro, Inc. prior to any work they would do. They were not overly optimistic about using Si supported catalysts.

The powder sample of a commercial catalyst, C-73 from UCI and C-73 (CO-treated) were used for microhardness test. Cold molds using epoxy hardeners were used to prepare the specimens. After imbedding the particles in the epoxy, they were allow to harden. Then the epoxy molds were polished. Several particles were photographed in the optical microscope. Using a MICROMET-4 hardness tester, the microhardness measurements were made. The specimen was mounted onto the hardness tester, and a load of 25 gm was used to make the Vicker's indentation on the particles, which are 10 to 50 microns in size. The indentations were so large that they covered the entire particles. Hence, a load of 10 gm (the minimum load available) was used to make the indentations. After making the indentations the specimen was mounted on the optical microscope and the diagonal distances of the indentations were measured. The average value of about 50 indentations was taken

for measuring the Vicker's hardness, which was calculated to be 1274 kg/mm². There was no difference between the as-received and the CO-treated samples. The value of 1274 is not accurate, as the hard epoxy under the particles can also take part of the load. This introduces additional uncertainty to the calculated value. The hardness values for the three catalysts are plotted in Figure 1.

The carbided sample of C-73 that will be tested for microhardness was taken from a current CSTR run that was just completed. Currently the wax is being removed from the catalyst by extraction. A sample of this catalyst will also be sent to Sandia.

A.2. Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define Optimum SiO₂
No scheduled for further activity to report.
- Define Optimum Al₂O₃
No scheduled or further activity to report.

A.3. Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity for both High- and Low-Alpha Catalysts

No scheduled or further activity to report.

A.4. Complete the Optimization of Two Best Low-Alpha, Iron-Based Catalysts Developed During the Previous Contract

Completed.

A.5. Schedule of Activities for Next Quarter

- Conduct experiments suggested by Niro Atomizer, Inc..

- Determine the microhardness of the carbided C-73 catalyst.

B.0. - Task 2.0. Definition of Preferred Pretreatment for Both Low- and High-Alpha Catalysts

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

B.1. Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron Based Fischer-Tropsch Catalysts

The affect of copper promotion on the activity and selectivity of hydrogen pretreated, precipitated iron Fischer-Tropsch catalysts was studied. Fischer-Tropsch synthesis was carried out in the slurry phase in one liter continuous stirred tank reactors at a space velocity of $3.1 \text{NL h}^{-1} \text{g}^{-1}(\text{Fe})$, $\text{H}_2:\text{CO}=0.7$ at either 270°C or 230°C . Catalysts with atomic compositions relative to iron of $100\text{Fe}/4.4\text{Si}/1.0\text{K}$ and $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ were used at 270°C and catalysts with the compositions of $100\text{Fe}/4.4\text{Si}/4.2\text{K}$ and $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/4.2\text{K}$ were used at 230°C . XRD and Mössbauer spectroscopy both show that the $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ catalyst contained approximately 24% $\alpha\text{-Fe}$ with the remainder Fe_3O_4 after a 24 h pretreatment with hydrogen at 220°C . Copper promotion was found to substantially increase the activity and productivity of the catalysts. Catalysts promoted with copper reached maximum activity within 100 h of synthesis while catalysts with no copper went through an induction period. The activity of the hydrogen pretreated $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ catalyst operated at 270°C was comparable to the activity of the $100\text{Fe}/4.4\text{Si}/1.0\text{K}$ catalyst after pretreatment with carbon monoxide or syngas at

one atmosphere pressure. However, the activity of the hydrogen pretreated 100Fe/4.4Si/2.6Cu/4.2K catalyst at 230°C was found to be substantially lower than the same catalyst pretreated with carbon monoxide or syngas at one atmosphere pressure.

A portion of our baseline catalyst, 100Fe/4.4Si/1.0K, was impregnated with aqueous copper(II) nitrate hemipentahydrate to give an atomic composition relative to iron of 100Fe/4.4Si/2.6Cu/1.0K. Catalysts and Ethylflo 164 hydrocarbon oil were loaded into one liter continuous stirred tank reactors to give a catalyst loading of 10 weight percent. Additional potassium promotion was accomplished by adding the appropriate amount of potassium *t*-butoxide. Low alpha runs were conducted on the 100Fe/4.4Si/1.0K and the 100Fe/4.4Si/2.6Cu/1.0K catalysts at 270°C and high alpha runs were conducted on the catalysts with compositions of 100Fe/4.4Si/4.2K and 100Fe/4.4Si/2.6Cu/4.2K at 230°C.

Hydrogen pretreatments were performed at low temperature and high flow rates to minimize the production of water and decrease sintering of the metallic iron than is formed. Hydrogen flow was started at ambient conditions at a rate of 2000 sccm. The temperature of the reactor was increased to 220°C at a rate of 2°C/min at atmospheric pressure. These conditions were maintained for 24 h and then the hydrogen flow was adjusted to 1.28 NL/h/g(Fe). Carbon monoxide flow was slowly increased to 1.82 NL h⁻¹g⁻¹(Fe) over a 15 minute period to give a H₂:CO ratio of 0.7 and a total space velocity of 3.1 NL h⁻¹g⁻¹(Fe). The pressure of the reactor was slowly increased to 175 psig and the temperature increased to 270°C or 230°C at a rate of 15°C/h.

Low-Alpha Runs

A comparison of the carbon monoxide conversions for the 270°C runs is shown in Figure 2. The 100Fe/4.4Si/2.6Cu/1.0K catalyst had high initial conversion in excess of 84% and reached a maximum of 88% after 100 h of synthesis. The catalyst deactivated linearly at a rate of only 0.77%/week. The 100Fe/4.4Si/1.0K catalyst had an initial carbon monoxide conversion below 20% after the hydrogen pretreatment; however, this catalyst went through an induction period of approximately 300 h in which the carbon monoxide conversion increased to 65%. The total hydrocarbon productivity paralleled the carbon monoxide conversion and ranged between 0.45 and 0.50 g HC/g(Fe)/h for the 100Fe/4.4Si/2.6Cu/1.0K catalyst and between 0.12 and 0.37 g HC/g(Fe)/h for the 100Fe/4.4Si/1.0K catalyst (Figure 3). Hydrocarbon productivity in terms of volume of syngas feed and volume of syngas converted is shown in Figures 4 and 5, respectively. Production in terms of syngas feed follows the same trend seen for the carbon monoxide conversion; however, in terms of syngas converted the productivity was nearly the same for both catalysts. Methane selectivity was similar for both catalysts despite the differences in activity (Figure 6). The methane selectivity was constant at approximately 11% of the carbon converted to hydrocarbons after 200 h on stream. Methane and ethane selectivity was about 14-16% which is typical of low-alpha catalysts. The water-gas shift reaction quotient, $K_{app} = \frac{[CO_2][H_2]}{[CO][H_2O]}$, increased with increasing carbon monoxide conversion for the 100Fe/4.4Si/1.0K catalyst and was fairly constant at about 38-40 for the 100Fe/4.4Si/2.6Cu/1.0K catalyst (Figure 7). The water-gas shift equilibrium constant is 65 at 270°C, so equilibrium was not reached for either run.

The overall activity and productivity of the 100Fe/4.4Si/2.6Cu/1.0K catalyst pretreated with hydrogen is comparable to the 100Fe/4.4Si./1.0K catalyst when activated with synthesis gas or carbon monoxide at 270 °C and 1 atm (Table 1); however, the selectivity differs somewhat from that obtained for the carbon monoxide pretreated catalyst. In general, the hydrogen pretreated 100Fe/4.4Si/2.6Cu/1.0K catalyst and the syngas activated 100Fe/4.4Si./1.0K catalyst have very similar methane and C₁₂+ selectivities and similar water gas shift activities (K_{app}); however, the carbon monoxide pretreated 100Fe/4.4Si./1.0K catalyst produced less methane and substantially more C₁₂+ products with a lower water gas shift activity (Table 1).

High-Alpha Runs

Similar results have been achieved for the 100Fe/4.4Si/4.2K and 100Fe/4.4Si/2.6Cu/4.2K catalysts when operating in a wax producing mode at 230°C. Carbon monoxide conversions are compared in Figure 8. Initial Carbon monoxide conversion for the 100Fe/4.4Si/2.6Cu/4.2K catalyst was approximately 40%. This catalyst deactivated substantially at a rate of 7.8%/week and was shut down after 410 h on stream. The 100Fe/4.4Si/4.2K catalyst had very low carbon monoxide conversion which increased from 5% to 17% during the lifetime of the run. Hydrocarbon productivity per mass of iron (Figure 9) and per volume of syngas feed (Figure 10) are consistent with the low activity of these runs; however, productivity in terms of syngas converted was similar to that described above for the active 100Fe/4.4Si/2.6Cu/1.0K catalyst (Figure 11). Methane selectivity was low for both catalysts at about 3% of the carbon converted to hydrocarbon (Figure 12). These values are slightly higher than the 2% selectivity observed for the same catalysts activated with syngas (previous

quarterly report). Water gas shift activity was far below equilibrium ($K=127$ at 230°C) as shown in Figure 13.

Catalyst Characterization

Differences in activity between the $100\text{Fe}/4.4\text{Si}/x\text{K}$ and $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/x\text{K}$ catalysts can probably be attributed to the extent of reduction of the iron oxide to metallic iron during the hydrogen pretreatment. Copper has been well established as a promoter that facilitates the hydrogen reduction of precipitated iron catalysts to $\alpha\text{-Fe}$. X-ray diffraction data (Figure 14) and Mössbauer spectroscopy (Table 2) clearly show that $\alpha\text{-Fe}$ was formed after 24 hr of hydrogen pretreatment for the $100\text{Fe}/4.4\text{Si}/2.6\text{Cu}/1.0\text{K}$ catalyst. Mössbauer spectroscopy data (Table 2) for catalyst samples withdrawn during the pretreatment show the catalyst was composed of 80% superparamagnetic material with the remainder Fe_3O_4 after the heat-up to 220°C under H_2 . The amount of the superparamagnetic component decreased throughout the pretreatment and appeared to be converted to magnetically resolved Fe_3O_4 . Metallic iron was detected in the catalyst sample taken after 10 h at pretreatment conditions. The iron composition of the catalyst after 24 h at pretreatment conditions showed 65% magnetically resolved Fe_3O_4 , 24% $\alpha\text{-Fe}$ and 11% superparamagnetic component. Identification of the superparamagnetic component has not been done yet; however, results from carbon monoxide pretreated catalysts indicate that it is small particle Fe_3O_4 . Additional catalyst samples have been removed periodically and will be analyzed by XRD, Mössbauer spectroscopy and high resolution TEM. This particular run will continue until the catalyst deactivates. Catalyst samples will be collected during the deactivation so that we may gain insight into any structural or compositional causes of deactivation. No catalyst samples could be withdrawn from

the reactor used for the 100Fe/4.4Si/1.0K run, so it is not known if any α -Fe was formed during the pretreatment. Since this catalyst underwent an induction period in which the conversion increased from 20% to 65%, it is likely that the catalyst was reduced to Fe_3O_4 during the pretreatment and then reduced to iron carbides during the subsequent synthesis.

Current and Future Work

Runs are currently being conducted on high alpha catalysts with 5 weight percent catalyst loadings. The reduced catalyst loading will decrease reactor wax production which will facilitate catalyst separation. This should enable us to make runs lasting longer than 500 h so that accurate product analyses can be obtained to verify the high alpha. Up to now we have been running 10 weight percent catalyst loadings which produce wax at a rate that overwhelms the internal filter which results in plugging of the reactor outlet. In addition, we are continuing tests on the external catalyst-wax separation tank that was reported in the previous quarterly report. Improvements have been made so that the wax removed from the reactor contains approximately 200 ppm iron.

B.2. Determine the Effect of K Content on Activation Procedures and Determinate if the Method of Addition has any Effect on Catalyst Activity and Life.

No scheduled or additional activity to report.

B.3. Physical and Chemical Changes that Occur During Pretreatment and Use

The TEM data from the University of New Mexico has not been received for the additional samples sent.

B.4. Effect of Carbon Deposition

No scheduled or further activity to report.

B.5. Schedule of Activities for Next Quarter

- Complete the H₂ pretreatment with Cu promoted catalysts.
- Start to determine the effectiveness of Ba and Zn to K as promoters.

C.0. - Task 3.0. Catalyst Structure and Characterization

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

C.1. Schedule of Activities for Next Quarter

- Continue to provide the characterization data as required.

D.0. - Task 4.0. Catalyst Testing

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

D.1. Verify the Quality of Data Obtained from the CSTRs.

This task is now completed.

D.2. Measure Catalyst Performance

A series of experiments were made to learn the viscosity of a Fischer-Tropsch reactor wax that contains catalyst. The instrument was a HBT viscometer with a Brookfield thermoseal system. A Brookfield model 64 temperature controller was utilized. A spindle number 21 was used at 100 rpm.

Two types of samples were used. For the wax without catalyst, the reactor wax collected in the 200°C trap was utilized; this represents a distillate wax in the nominal range of 200-270°C. This wax was drained from the reactor through a 0.5 μ micron sintered porous metal filter. The catalyst containing sample was the material that was collected at the end of the run and contained the wax remaining in the reactor together with the catalyst. The conditions for the reactor runs are compiled in Table 3. In all cases, the runs were not conducted for a sufficient length of time for the F.T. wax to have become a major fraction of the organic material remaining in the reactor at the end of the run. However, it should have been representative of the wax in the reactor during run 2 at LaPorte.

The viscosity of (1) a hard Fischer-Tropsch wax from Sasol, (2) a reactor wax (rewax) sample collected during run LGX 150, and (3) the distilled Allied-Signal polyethylene wax are shown in Figures 15 through 17. The initial viscosities of these materials were in the range of 10 to 36 cps at 120°C; the viscosities were in the order Fischer-Tropsch wax < reactor wax < distilled Allied-Signal oil. With increasing temperature, the viscosity declined to become immeasurably low at about 140°C for the F.T. wax and at about 225°C for the other two samples.

The viscosity of the reactor wax plus catalyst sample from the LGX 149 run was measured with increasing time at three temperatures. Thus, a sample of the material collected from the reactor was placed in the instrument and quickly heated to the desired temperature. For the measurement at 150°C, the viscosity remained essentially constant during 80 minutes at this temperature. Whereas the viscosity of the distilled Allied-Signal oil was about 20 cps at 150°C, the material containing the catalyst had a viscosity of about 150 cps at this temperature (Figure 18). The

viscosity of the catalyst containing material was lower at 190°C than at 150°C (100 vs. 150 cps, respectively); however, during the 80 minutes at 190°C the viscosity steadily increased to about 200 cps (Figure 19). At 230°C the initial viscosity was about 60 cps but it steadily increased during 80 minutes to attain a value of about 300 cps (Figure 20). The viscosity did not increase with time with the distilled Allied-Signal oil. Thus, it appears that in the presence of the iron catalyst the oil is reacting with air at temperatures above about 150°C and this leads gradually to a more viscous material.

Measurements were made with samples from the reactor from each of the runs. Because of variations such as catalyst settling, different amounts of synthesis products, etc., it is anticipated that there may be considerable variation among the composition of three samples and even among portions removed at different times from a wax/catalyst sample. Even so, each sample exhibits the same general trend as the temperature is increased. At the temperature for each data point in Figures 21 through 23, the sample was heated to that temperature, held at that temperature for 15 minutes, the viscosity was then measured and the temperature was then increased to the next higher desired temperature. In each case, the viscosity decreased with increasing temperature to attain a minimum (160-220°C) after which there was an increase in viscosity.

The lower temperature data indicate that the viscosity decreases with increasing temperature and that the presence of the catalyst increases the viscosity relative to the wax at a given temperature; both of these effects are expected. At the higher temperatures the reaction of the wax with air, presumably catalyzed by the iron, prevented reliable data to be obtained at temperatures of interest for the runs at 270°C.

D.3. Determine Stable Phases that Exist During Synthesis at High and Low CO Conversion Levels

No scheduled or additional activity to report.

D.4. Obtain Data on Rates Involved in the Interconversion of Iron Oxide and Carbide

No scheduled or additional activity to report.

D.5. Schedule of Activities for Next Quarter

- Continue efforts to improve our ability to remove wax from reactor with high-alpha Fe catalysts.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table 1

Activity and Productivity Data of Low-Alpha Catalysts

Catalyst	100Fe/4.4Si/2.6Cu/1.0K	100Fe/4.4Si/1.0K	
Pretreatment	H ₂ /220°C/0psig	CO/270°C/0psig	H ₂ :CO=0.7/270°C/0psig
Time On Stream/h	524	360	312
Space Velocity NL h ⁻¹ g ⁻¹ (Fe)	3.1	3.1	3.1
Conversion/%			
CO	86	84	87
H ₂	77	75	77
CO+H ₂	82	80	83
WGS			
CO ₂ mol%	47	45	50
H ₂ :CO usage	0.63	0.63	0.62
K _{app}	36	16	40
Productivity			
g HC Nm ⁻³	166	168	162
g C ₃ +Nm ⁻³	134	142	130
g HC g ⁻¹ (Fe)h ⁻¹	0.48	0.52	0.50
Selectivity/wt. %			
C ₁	12	8.2	11
C ₂ -C ₄	29	27	32
C ₅ -C ₁₁	43	36	46
C ₁₂ ⁺	16	29	11

Table 2

Mössbauer Data of 100 Fe/4.4 Si/2.6 Cu/1.0 K

Condition	S.P.	Fe ₃ O ₄	α -Fe	ϵ' -Fe _{2.2} C
2.25 h heat-up to 220°C H ₂ at 0 psig	80	20		
2 h at pretreatment conditions: H ₂ , 220°C, 0 psig	42	58		
10 h at pretreatment conditions: H ₂ , 220°C, 0 psig	18	72	10	
24 h at pretreatment conditions: H ₂ , 220°C, 0 psig	11	65	24	
0.25 h at pretreatment conditions: H ₂ :CO=0.7, 270°C, 175 psig	8	62	4	26

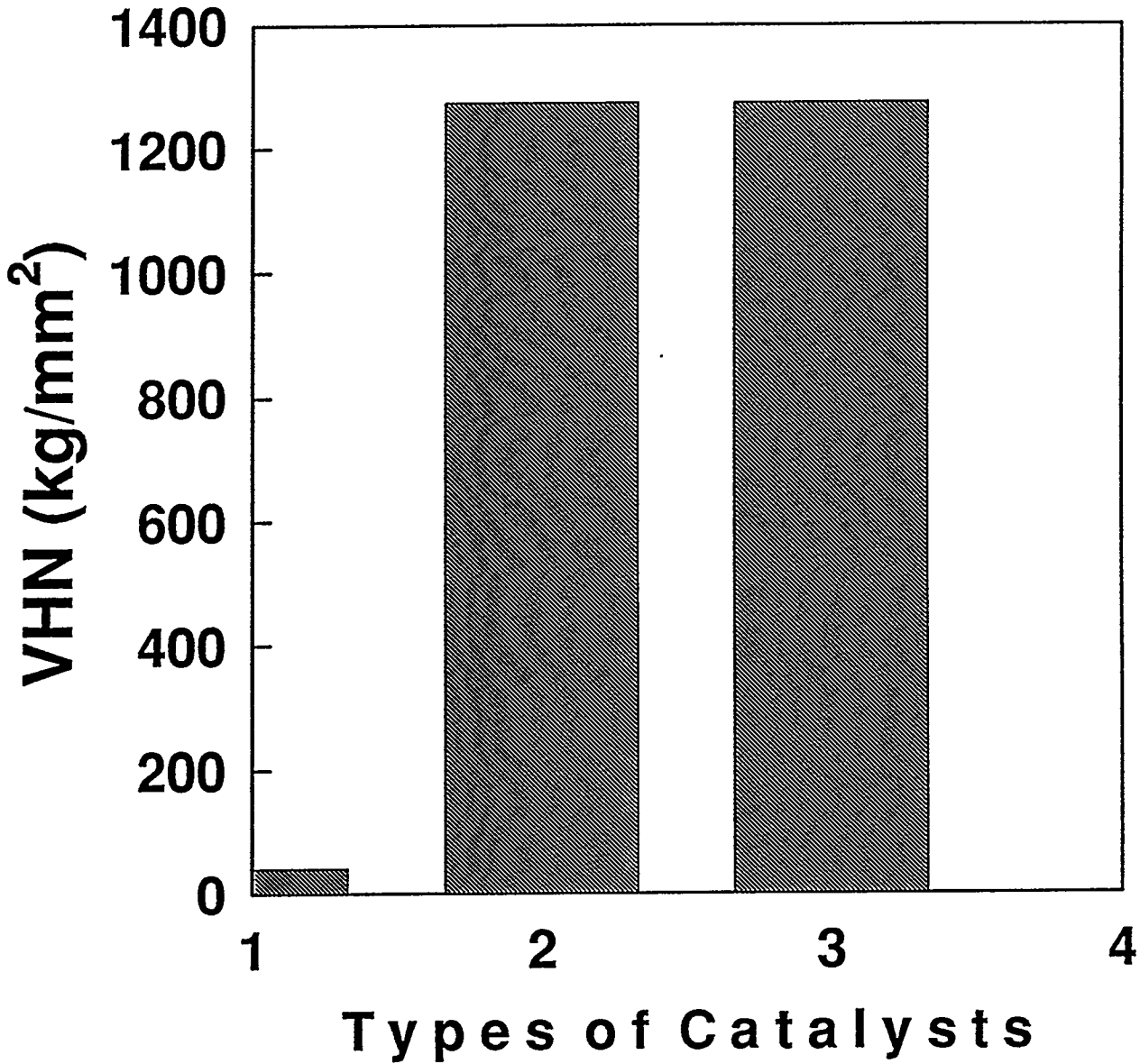
Table 3

Conditions for the Runs that Produced the Samples
Used for the Viscosity Measurements

Run	Catalyst Loading, wt.%	Startup Solvent (g)	Pretreatment	Run
LGX 148	29	Distilled Allied-Signal polyethylene oil (198 g)	CO; 270°C (~ C = 100% Fe _{2.2} C)	Variable T, P; 1100 rpm, 6 days synthesis
LGX 149	29 (20% composite 1; 80% composite 2)	Distilled Allied-Signal polyethylene oil (198 g)	CO; 270°C (~ C = 50% Fe _{2.2} C)	270°C, 175 psig, H ₂ /CO = 0.7, 2.4 NL/hr gFe, 1100 rpm, 4 days synthesis
LGX 150	29 (20% composite 1; 80% composite 2)	Distilled Allied-Signal polyethylene oil (198 g)	CO; 270°C (~ C = 100% Fe _{2.2} C)	270°C, 175 psig, H ₂ /CO = 0.7, 2.4 NL/hr gFe; 1100 rpm, 4 days synthesis

Figure 1.

Microhardness of Catalysts



1. RJO-181 (30%Fe-SiO₂)

2. C-73 - As-Received

3. C-73 - CO- Treated.

Figure 2. Comparison of carbon monoxide conversion for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270°C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

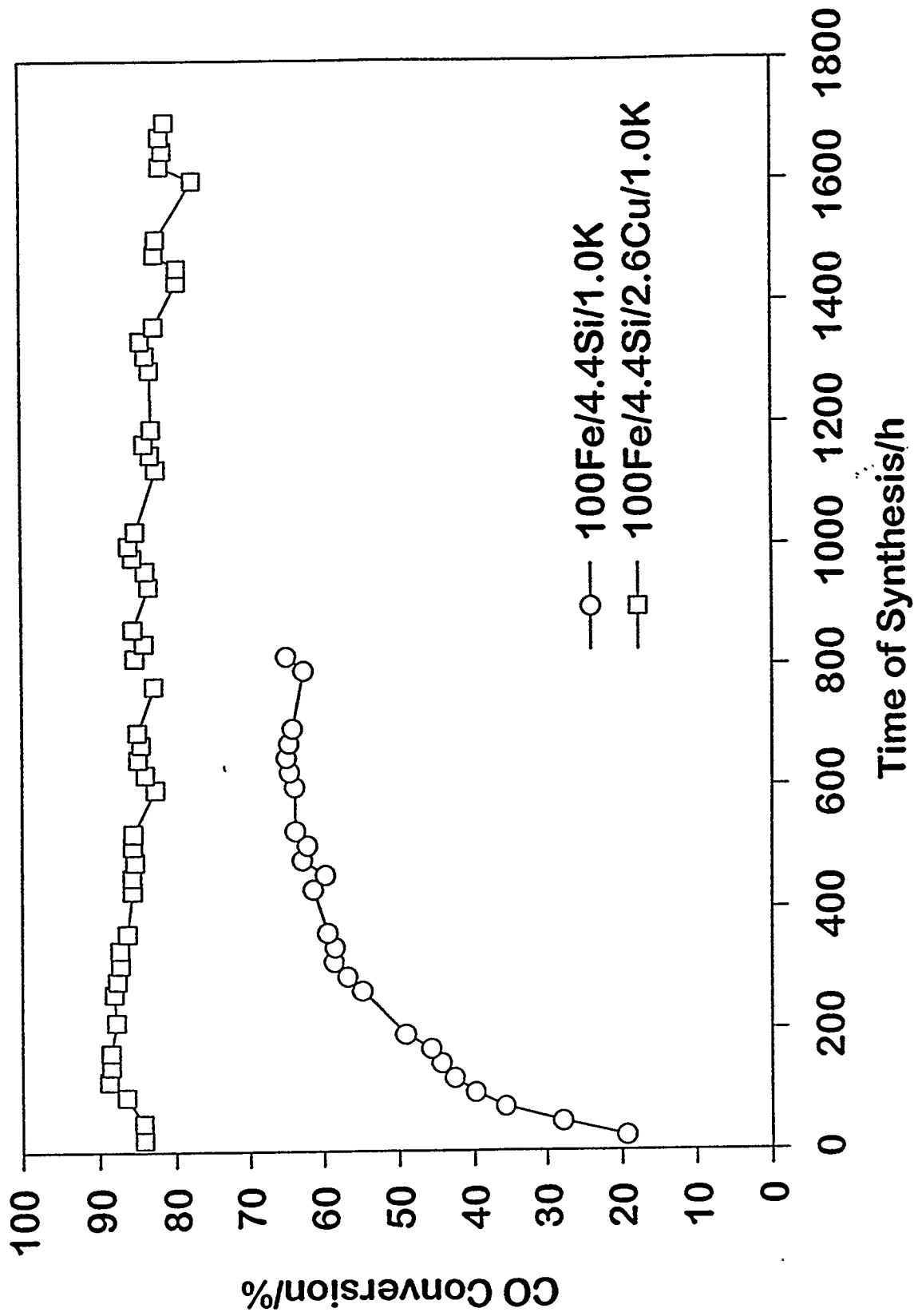


Figure 3. Comparison of FTS activity in terms of hydrocarbon production per gram of iron for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

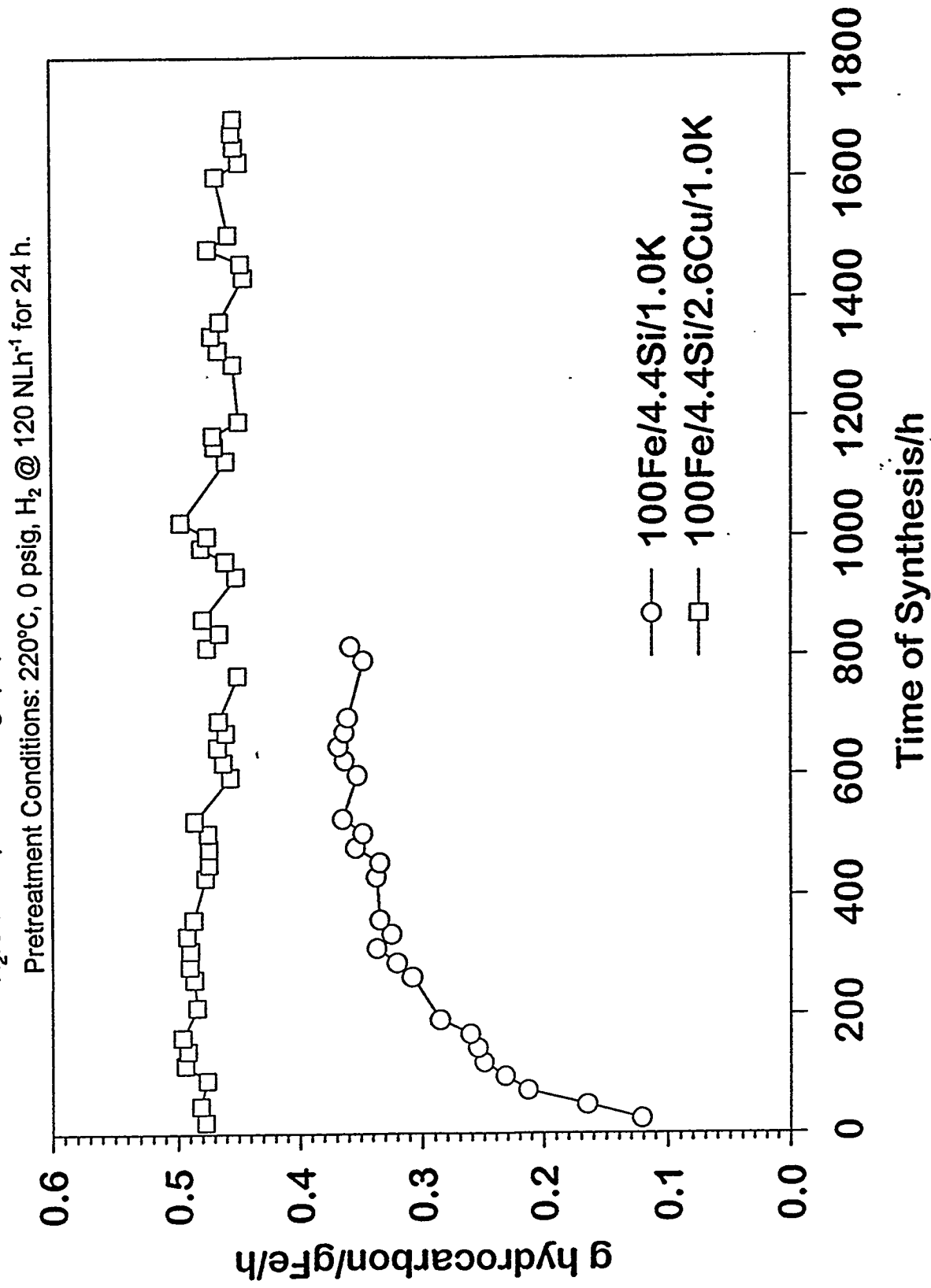


Figure 4. Comparison of hydrocarbon production per volume of syngas feed for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

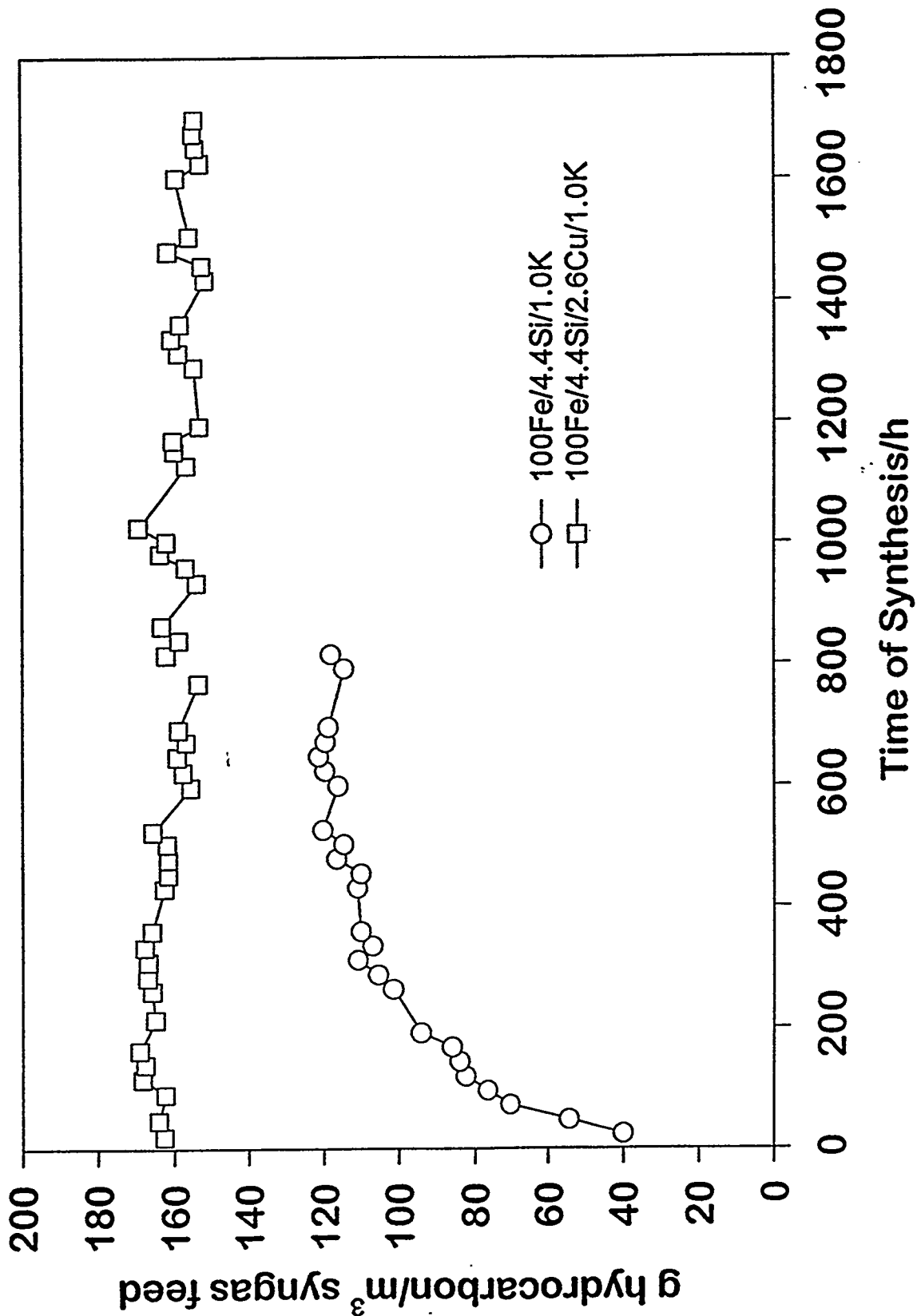


Figure 5. Comparison of hydrocarbon production per volume of syngas converted for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270°C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

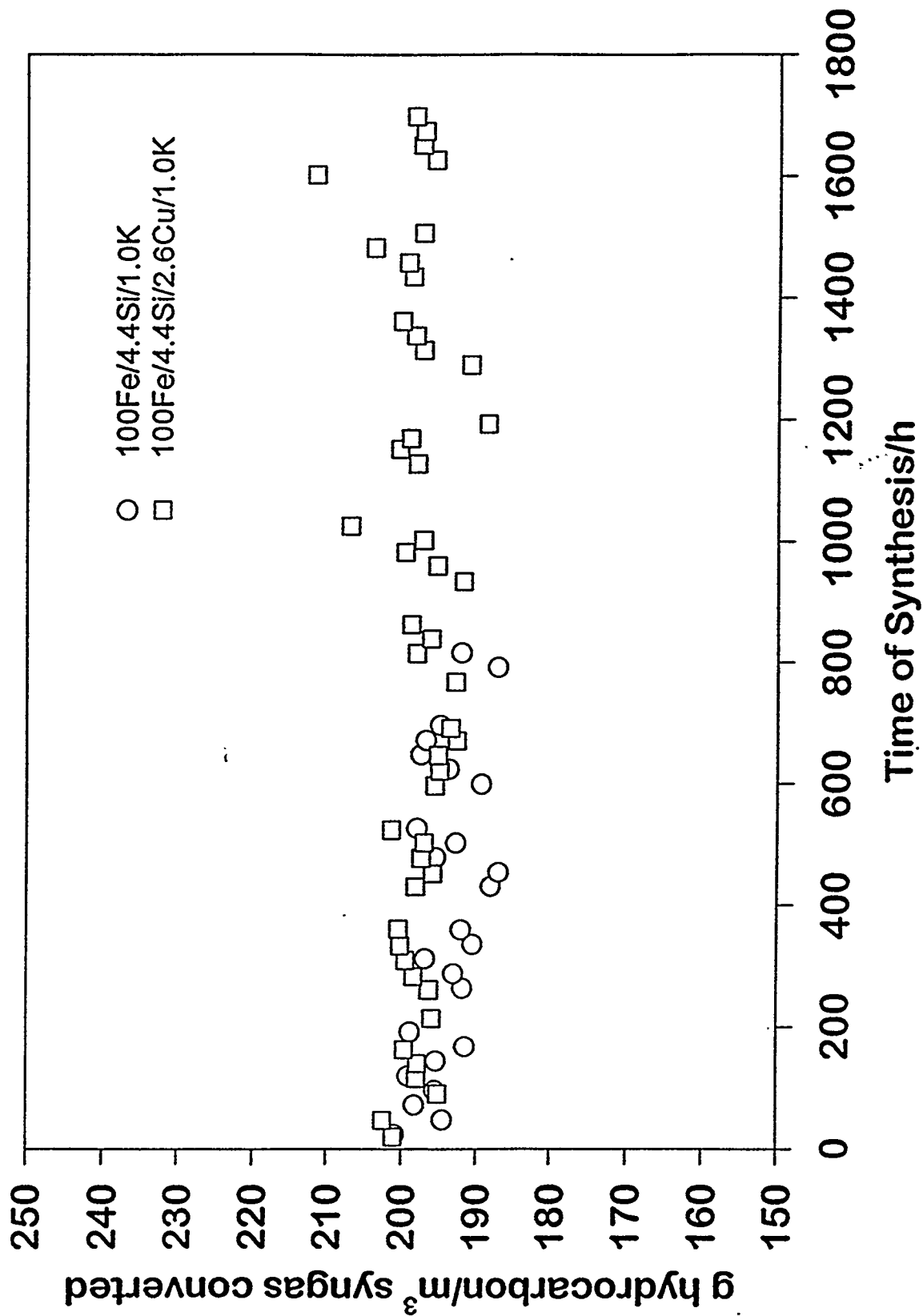


Figure 6. Comparison of methane selectivity for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270°C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

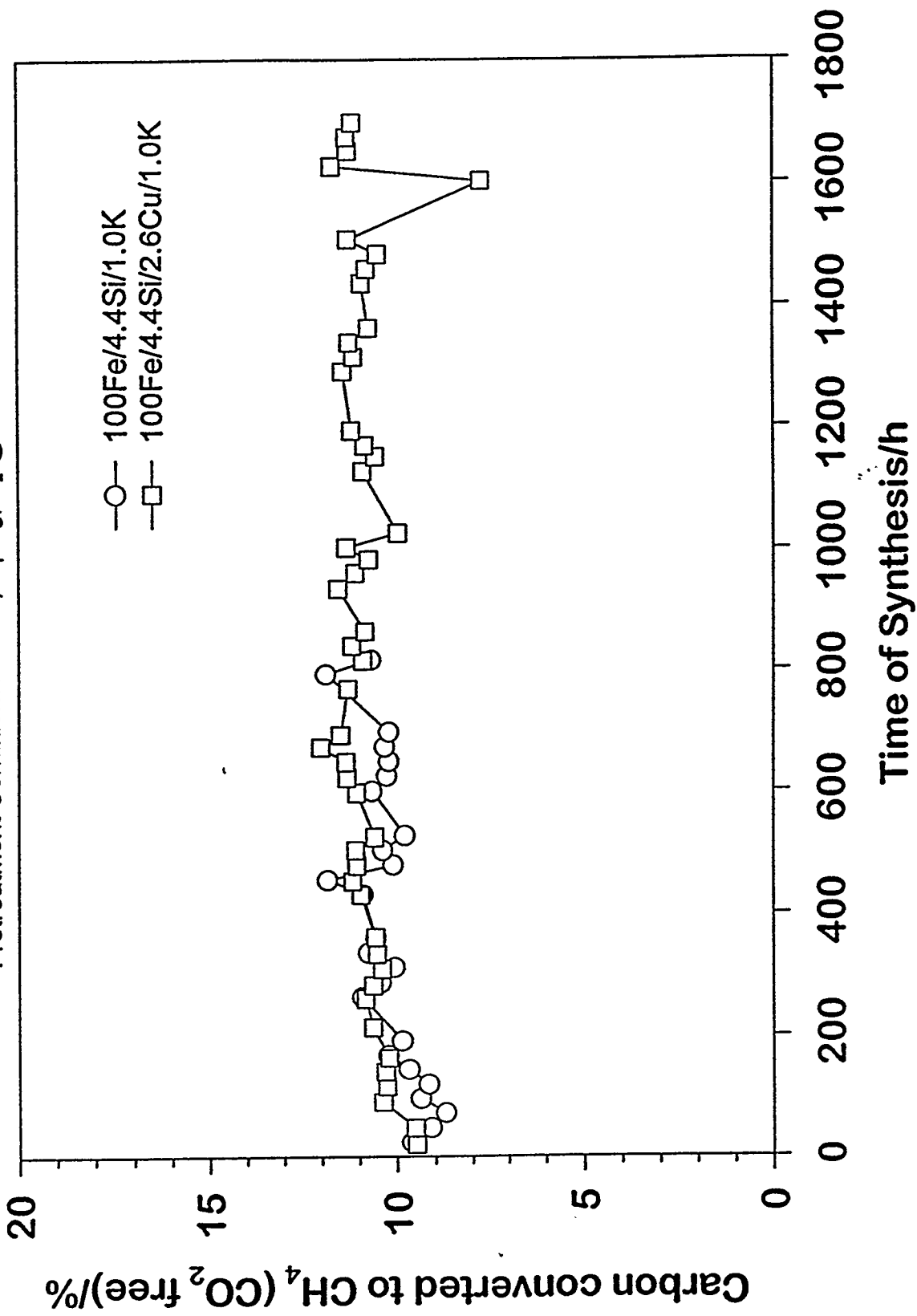


Figure 7. Comparison of water-gas shift activity for the (□) 100Fe/4.4Si/2.6Cu/1.0K catalyst and the (○) 100Fe/4.4Si/1.0K catalyst. Synthesis conditions: 270 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

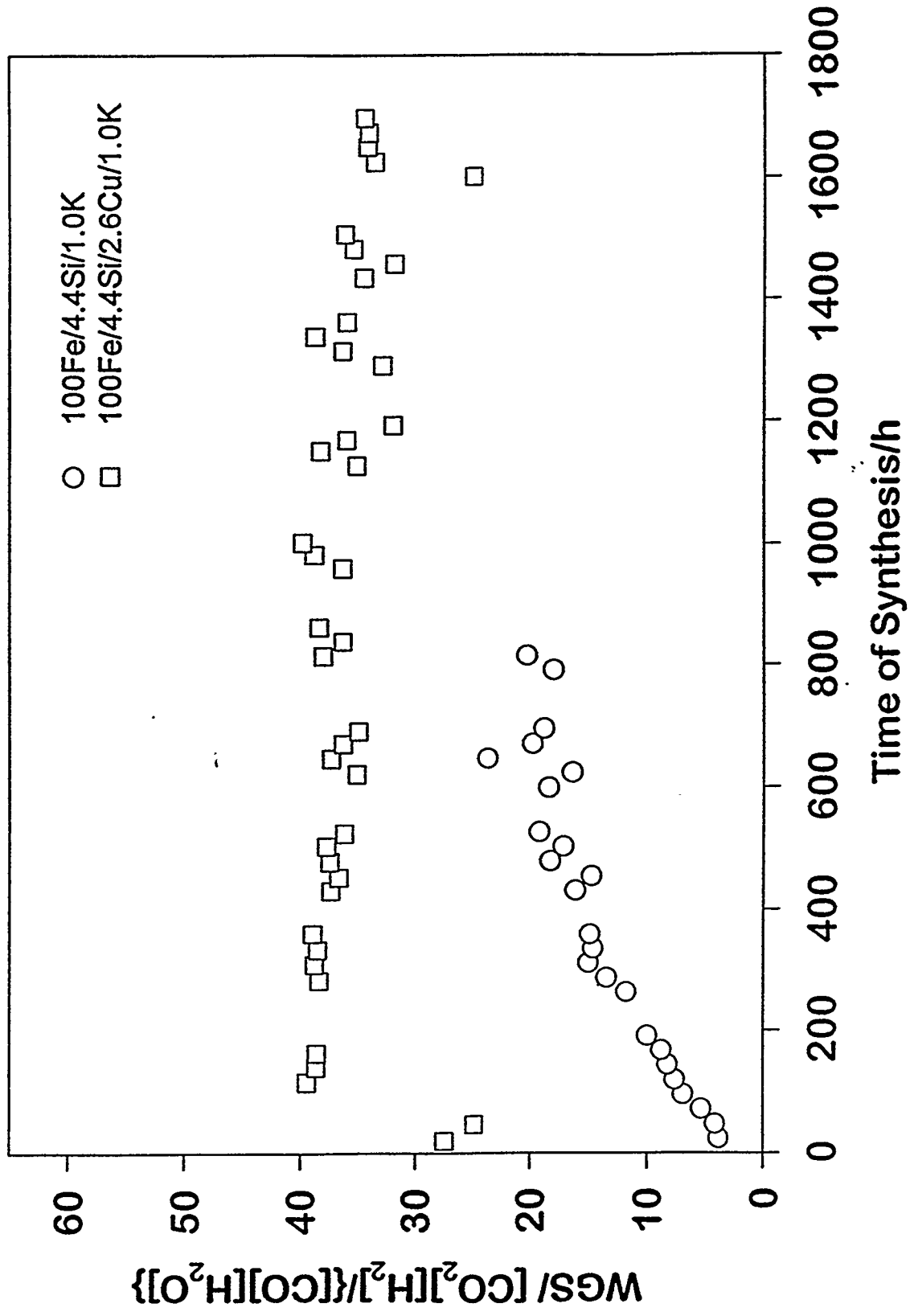


Figure 8. Comparison of carbon monoxide conversion for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe). Pretreatment Conditions: 220°C, 0 psig, H₂ @ 120 NLh⁻¹ for 24 h.

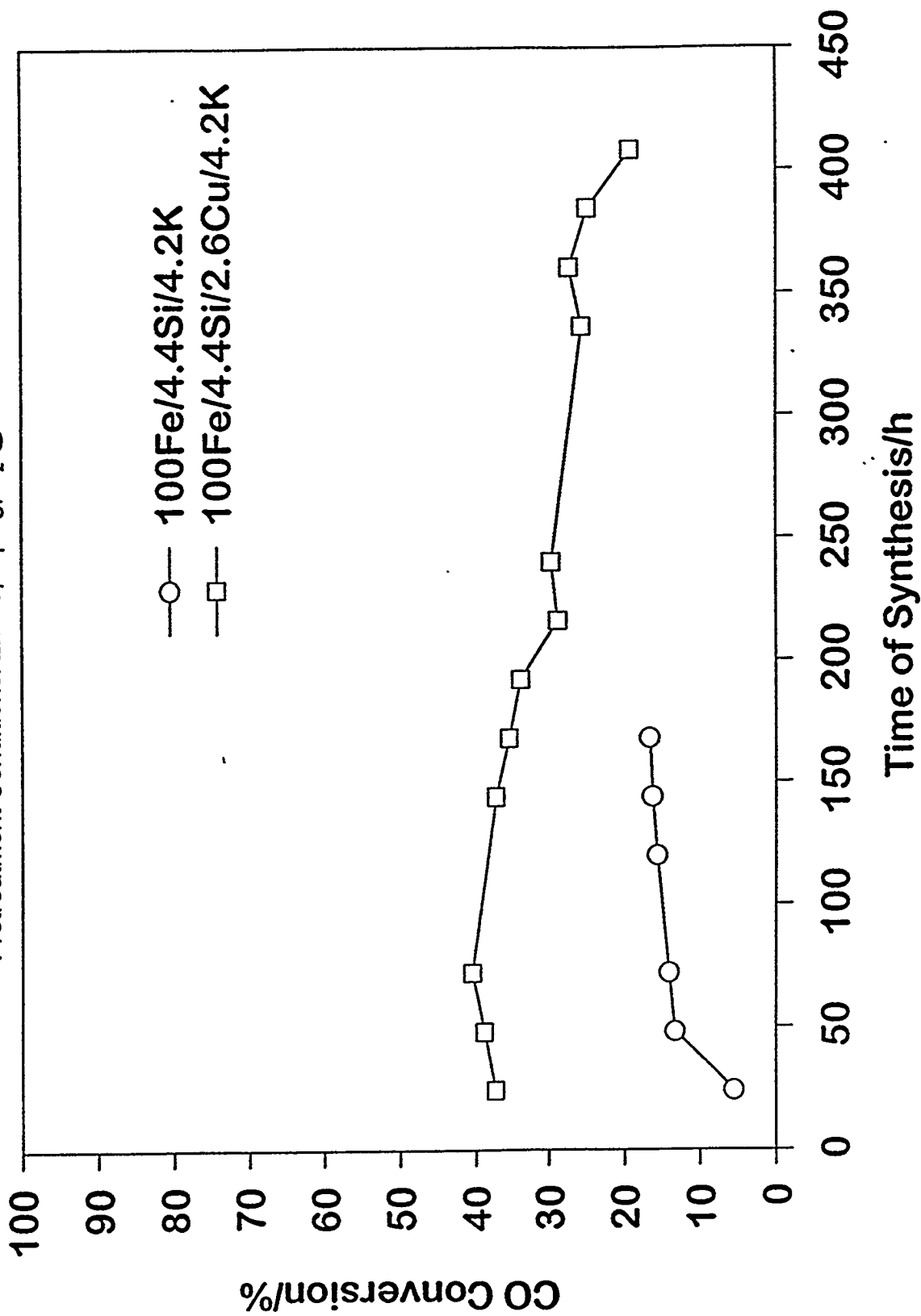


Figure 9. Comparison of FTS activity in terms of hydrocarbon production per gram of iron for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230°C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

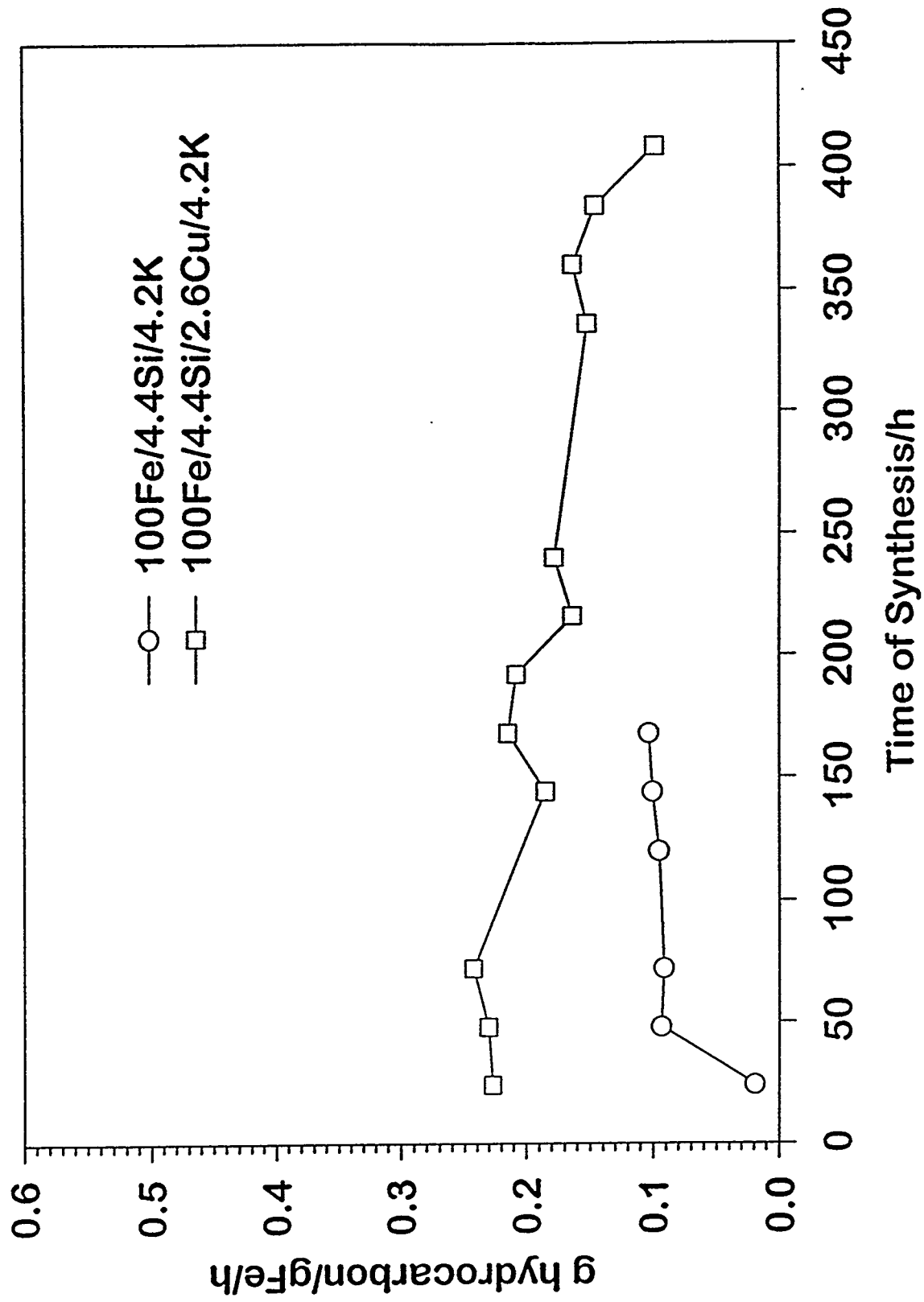


Figure 10. Comparison of hydrocarbon production per volume of syngas feed for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

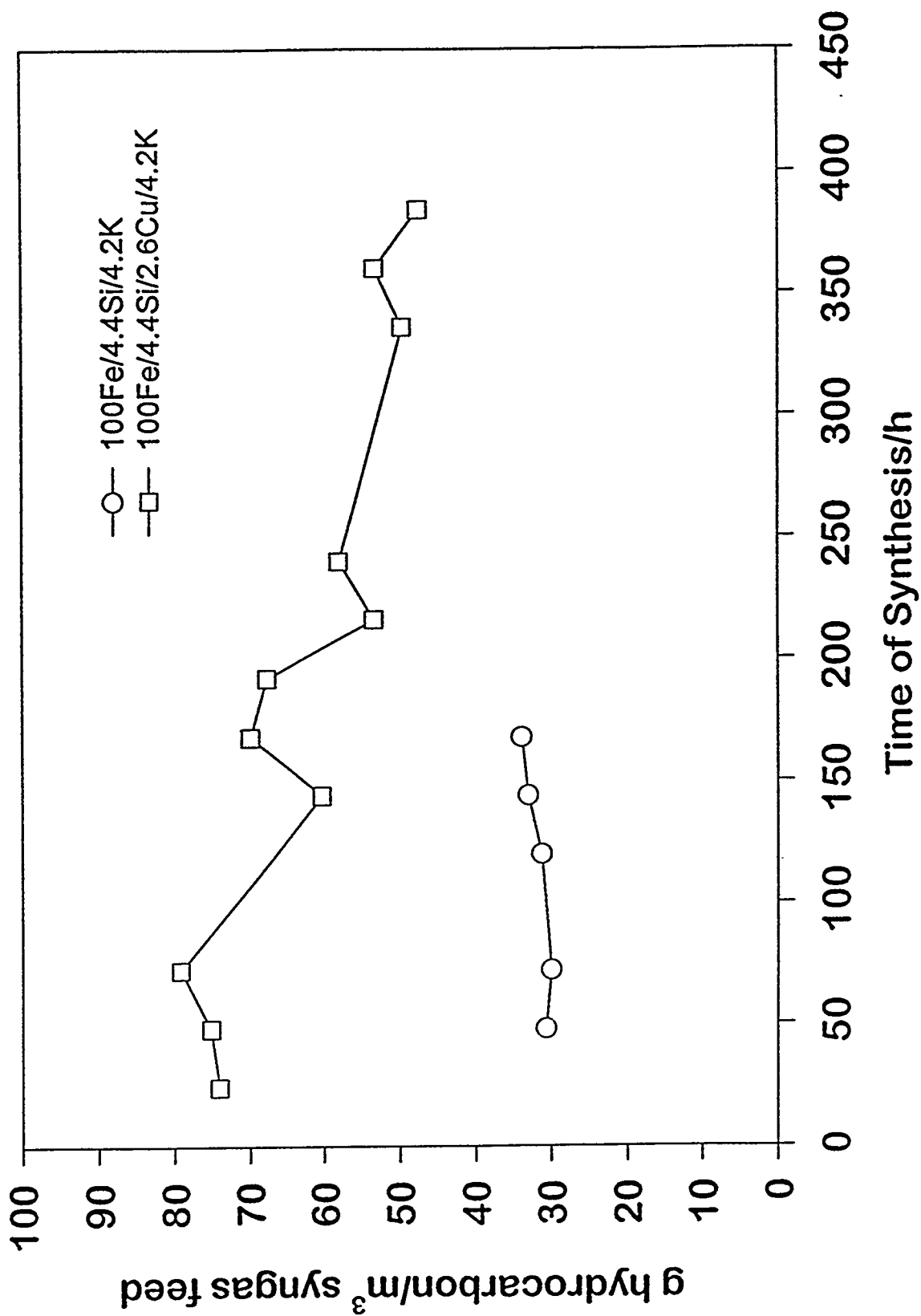


Figure 11. Comparison of hydrocarbon production per volume of syngas converted for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

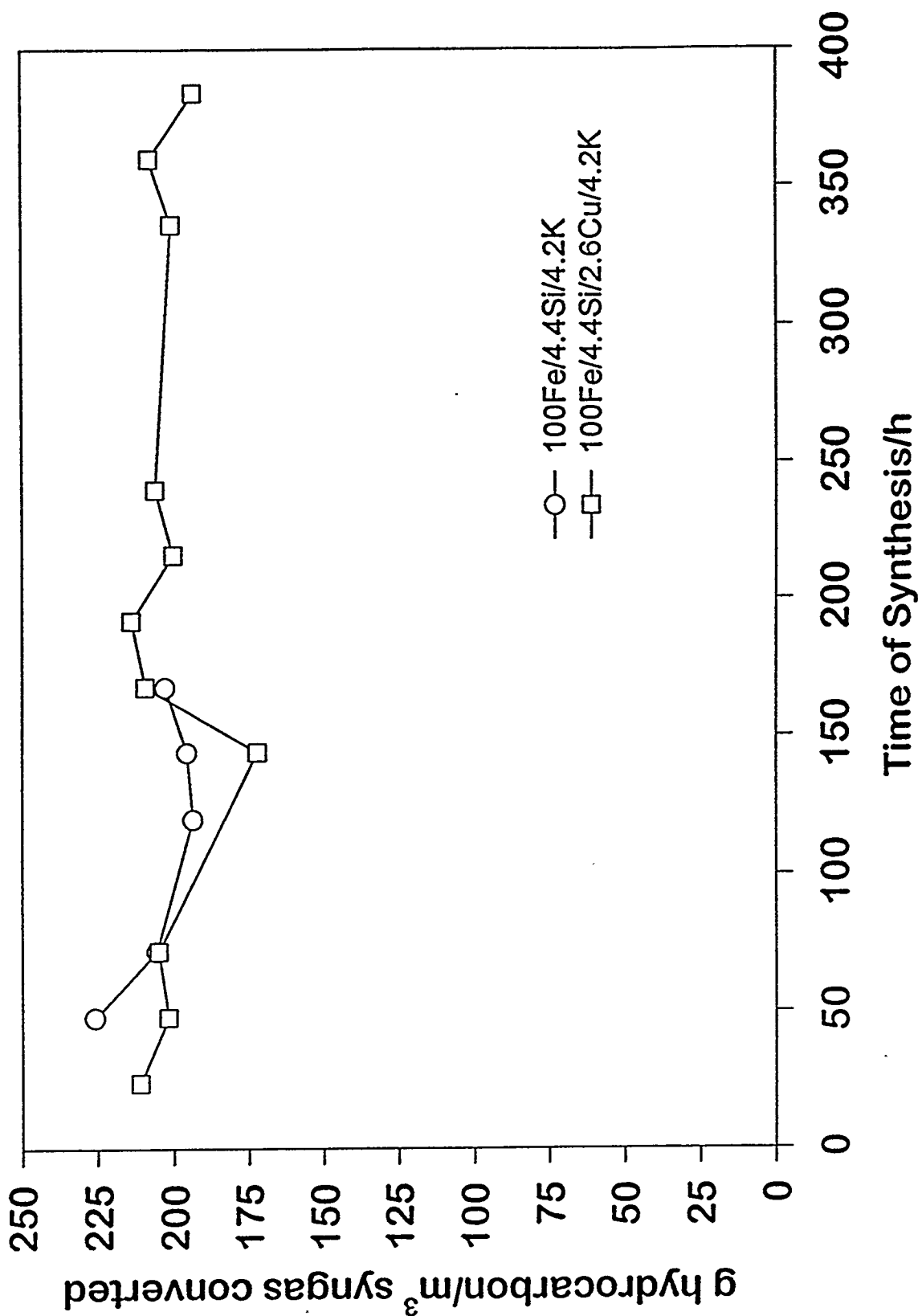


Figure 12. Comparison of methane selectivity for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230° C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

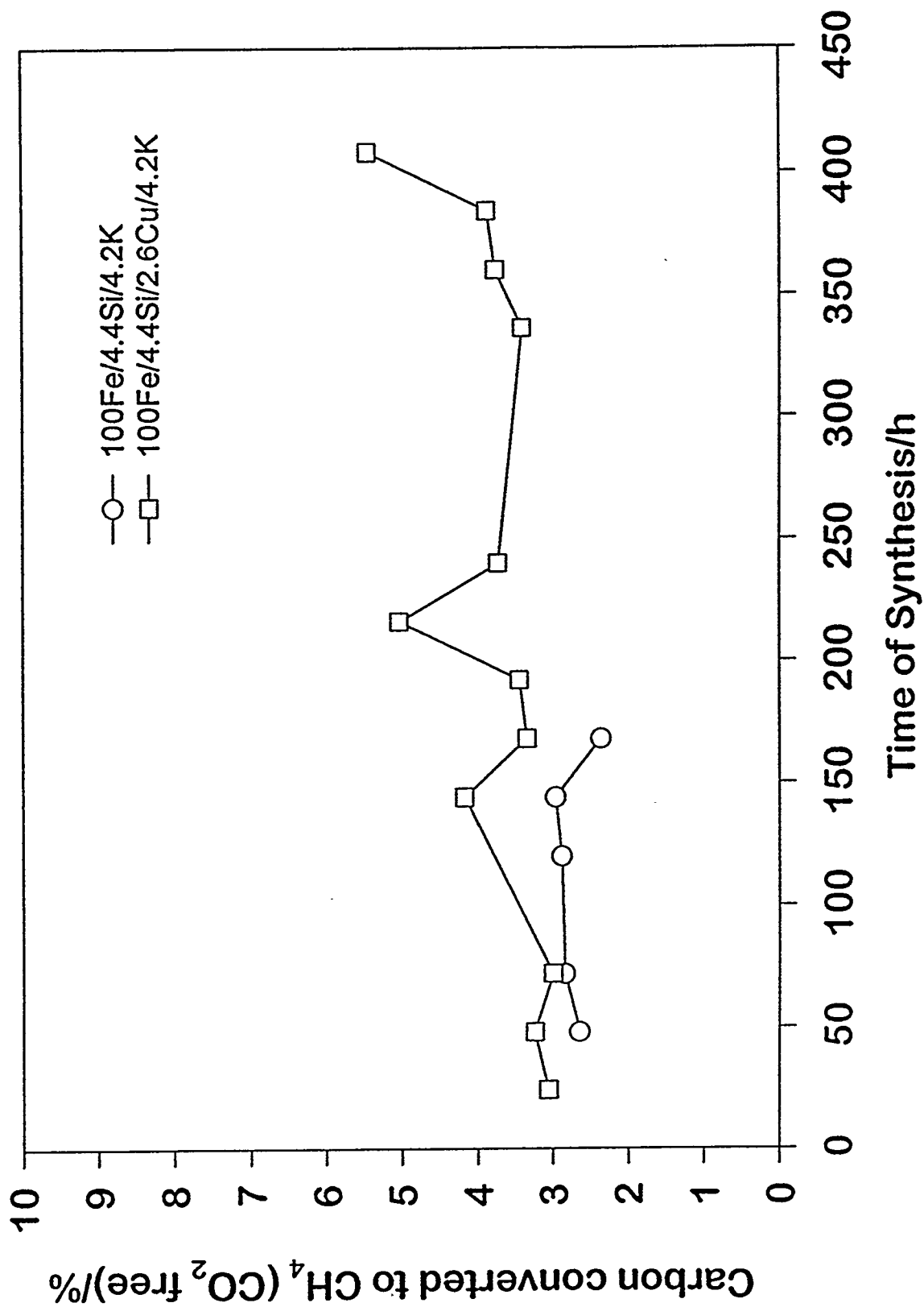


Figure 13. Comparison of water-gas shift activity for the (□) 100Fe/4.4Si/2.6Cu/4.2K catalyst and the (○) 100Fe/4.4Si/4.2K catalyst. Synthesis conditions: 230 °C, 175 psig, H₂:CO=0.7, 3.1 NL h⁻¹g⁻¹(Fe).

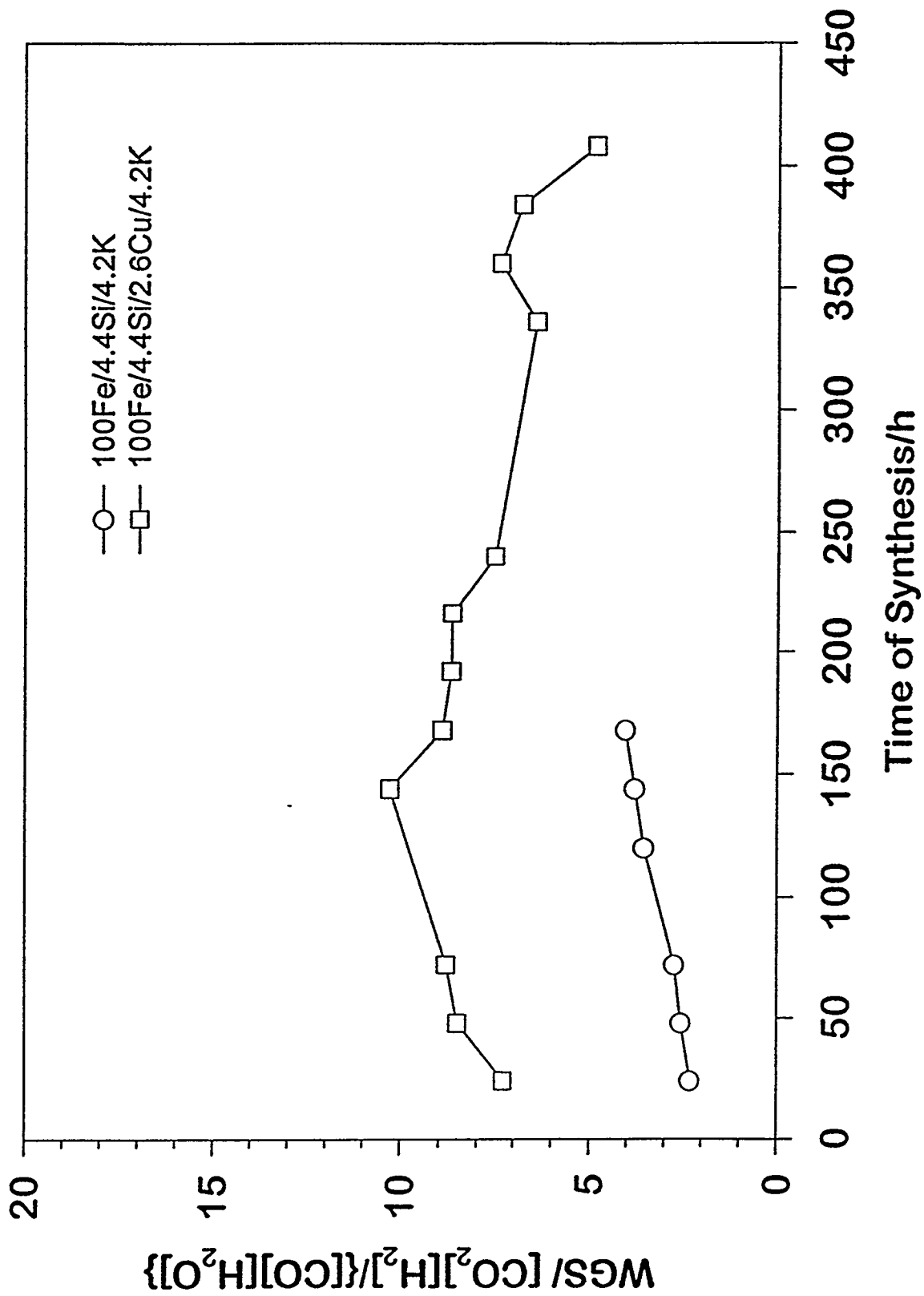


Figure 14. X-ray diffraction results of 100Fe/4.4Si/2.6Cu/1.0K catalyst after 24 pretreatment with hydrogen at 220°C, 2000 sccm, and 0 psig. Catalyst is composed of α -Fe and Fe_3O_4 .

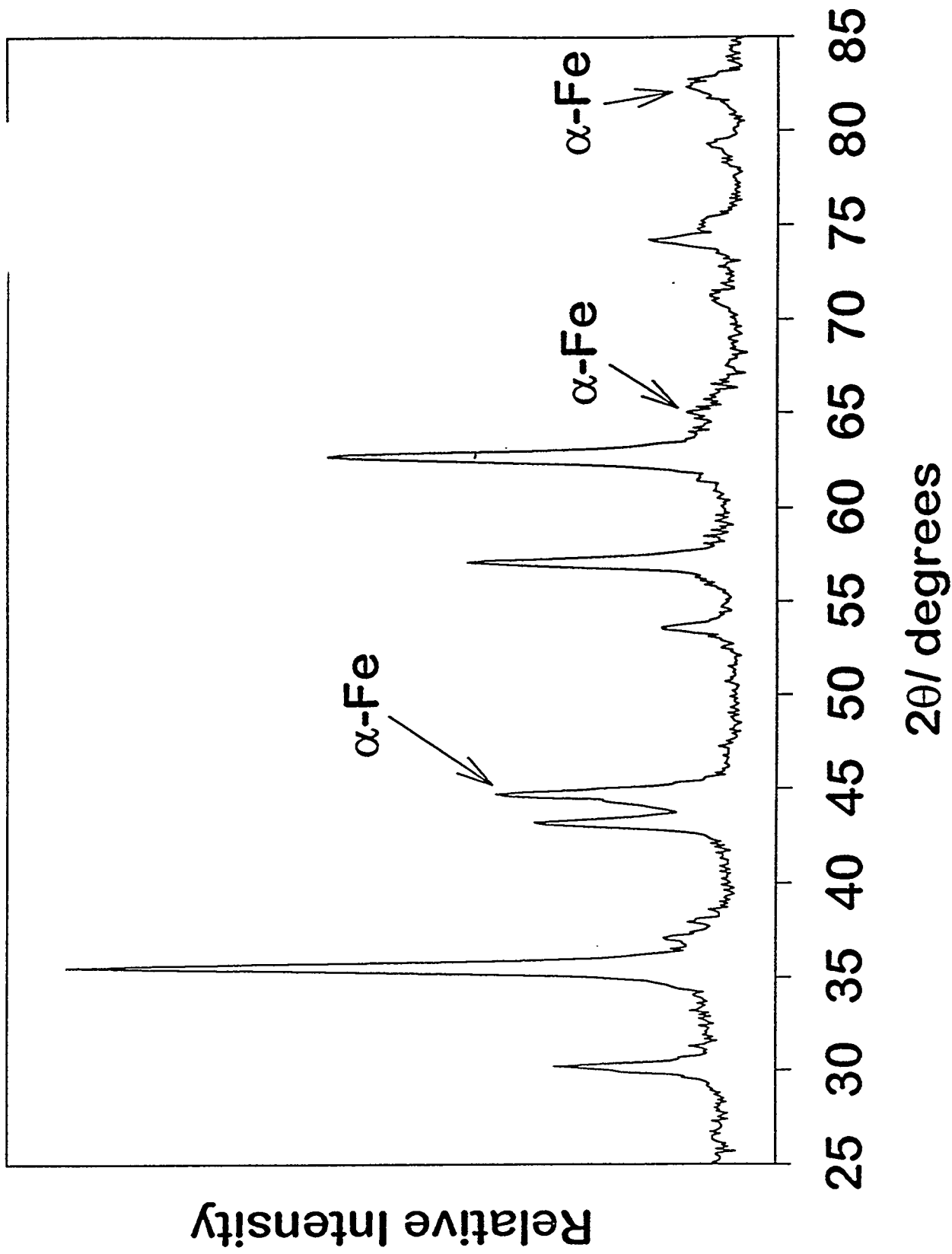


Figure 15. F.T.WAX VISCOSITY vs TEMPERATURE

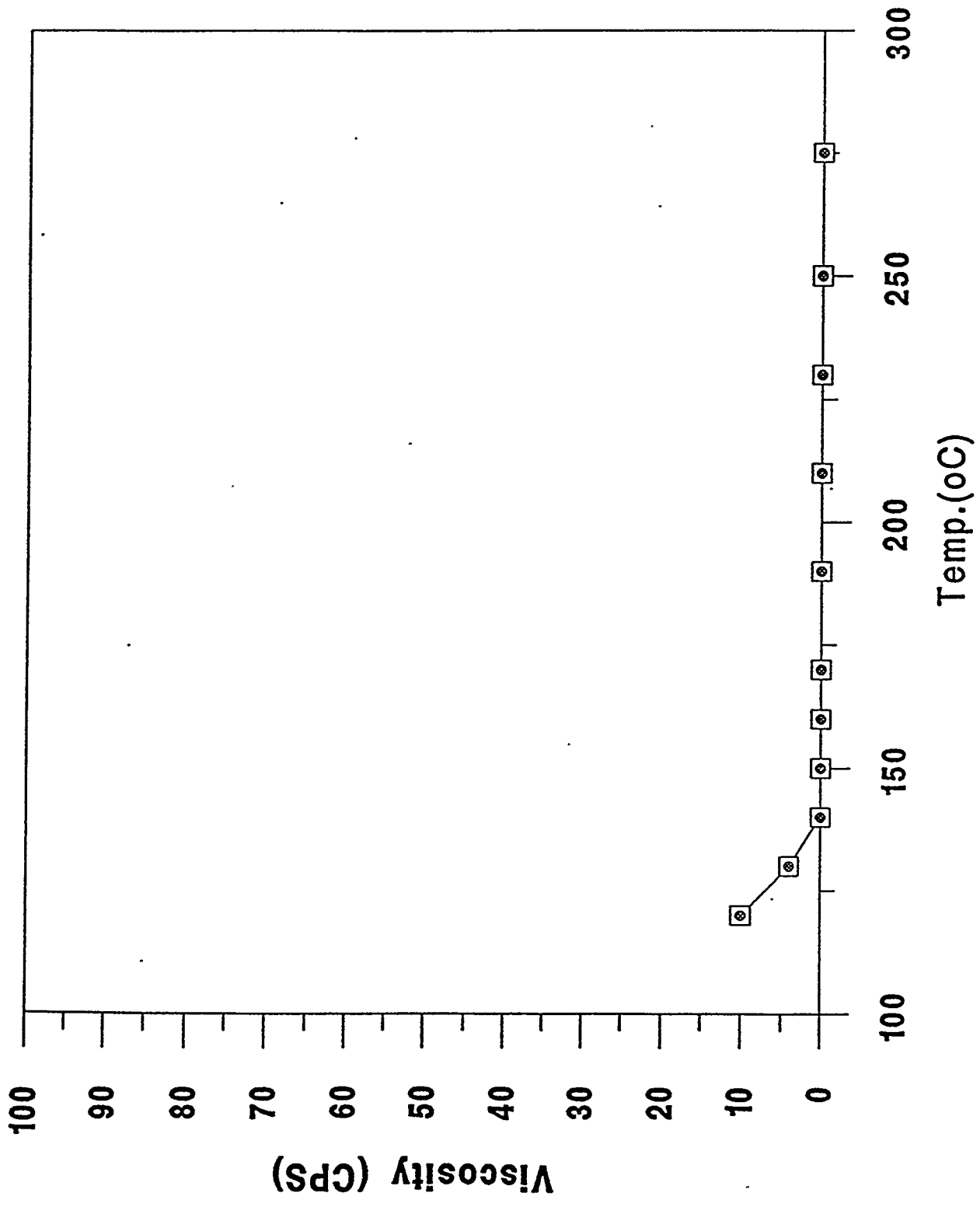


Figure 16. VISCOSITY (LGX150 REWAX) vs TEMP.

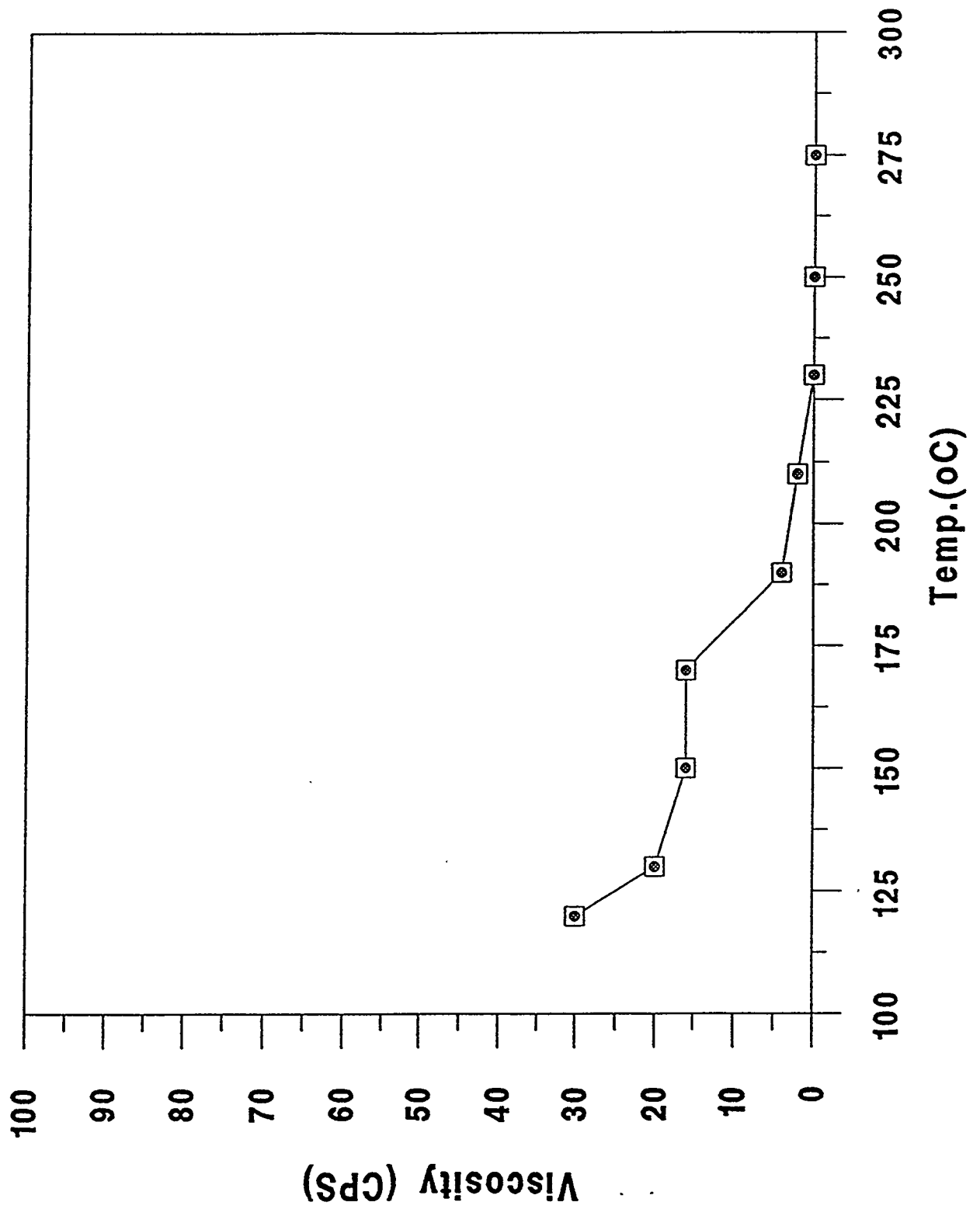


Figure 17. POLYETHYLENE VISCOSITY vs TEMPERATURE

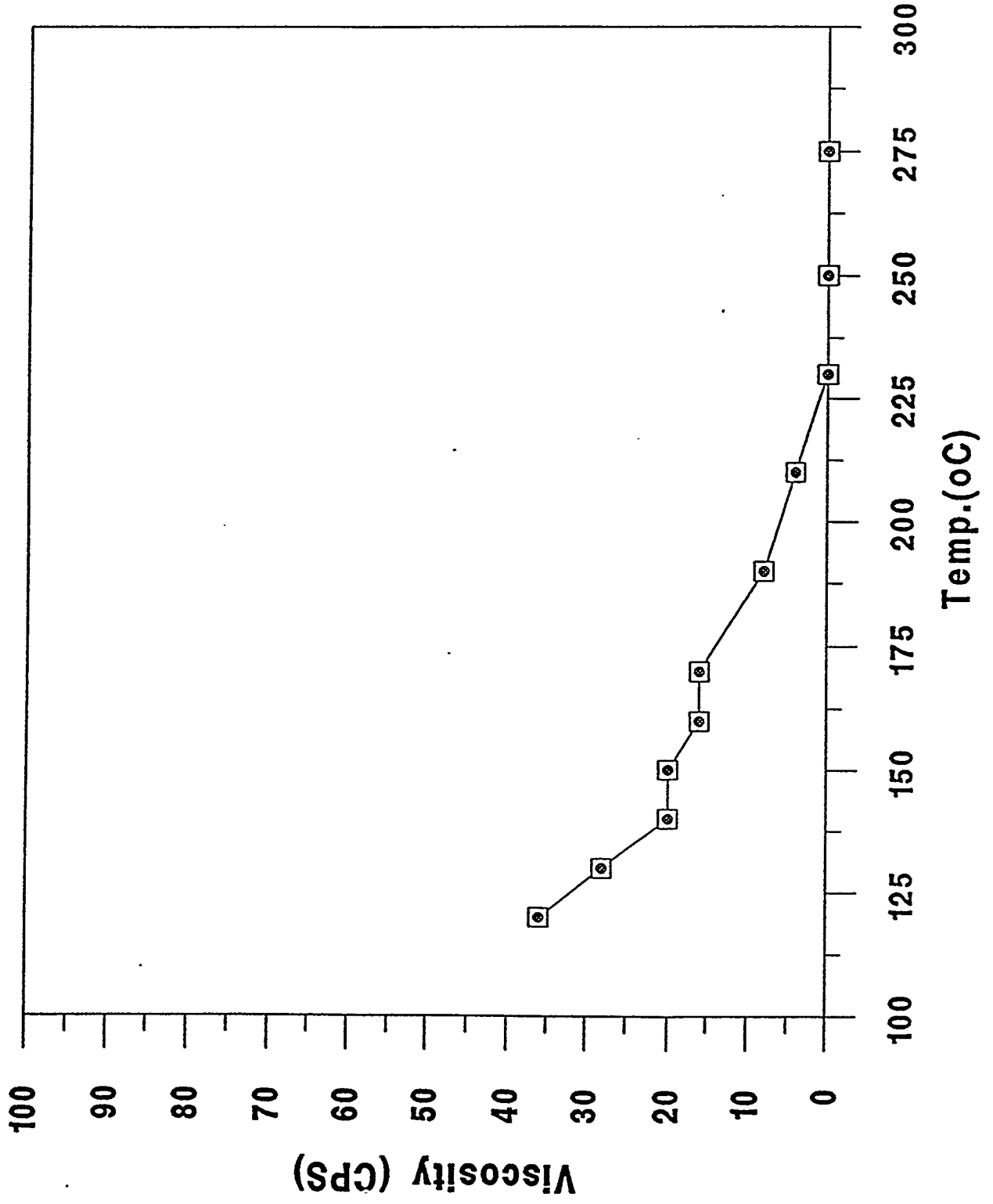


Figure 18. VISCOSITY(LGX149 REWAX & CAT.) VS TIME AT TEMP.130 oC

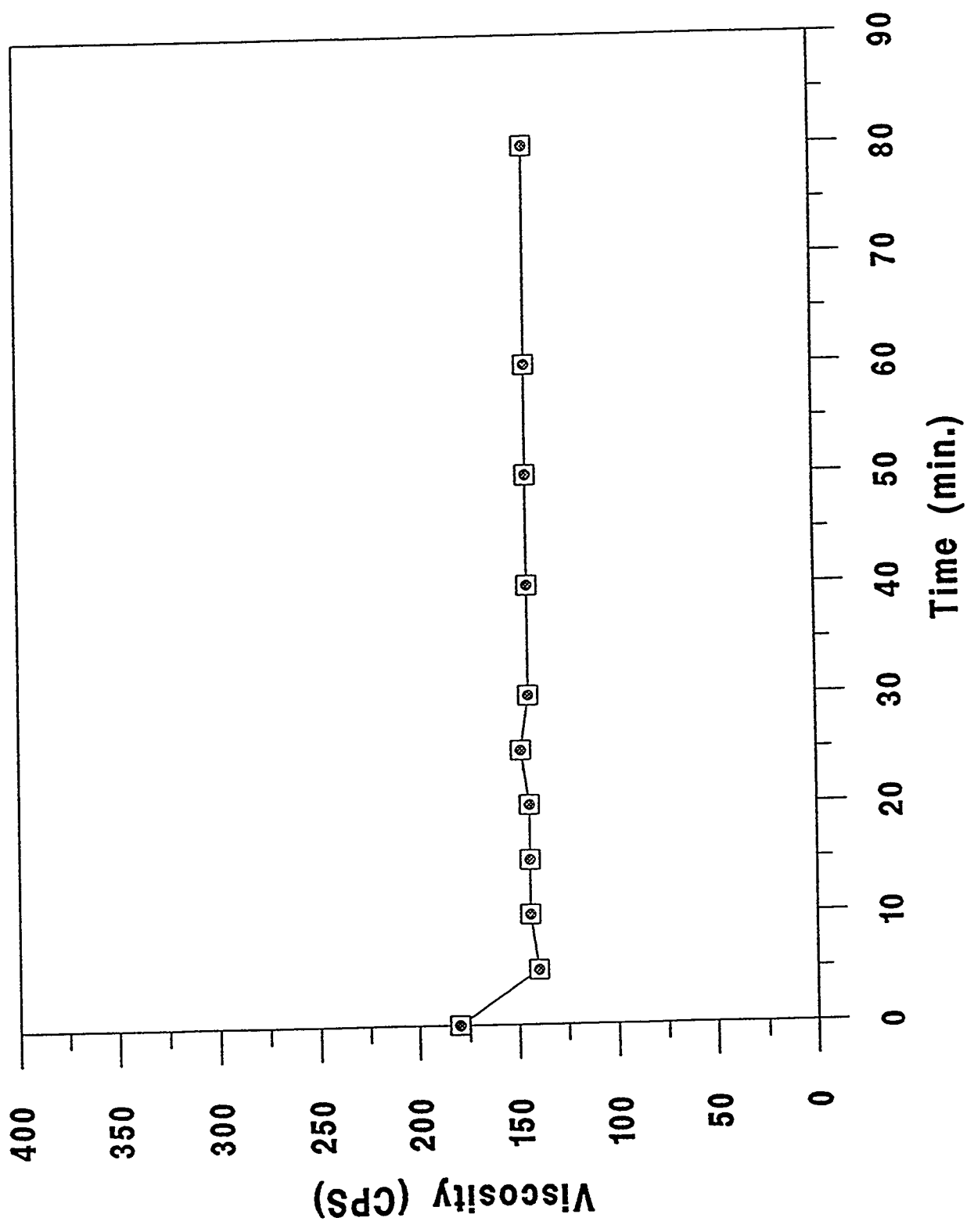


Figure 19. VISCOSITY(LGX149 REWAX & CAT.) vs TIME AT TEMP.190 oC

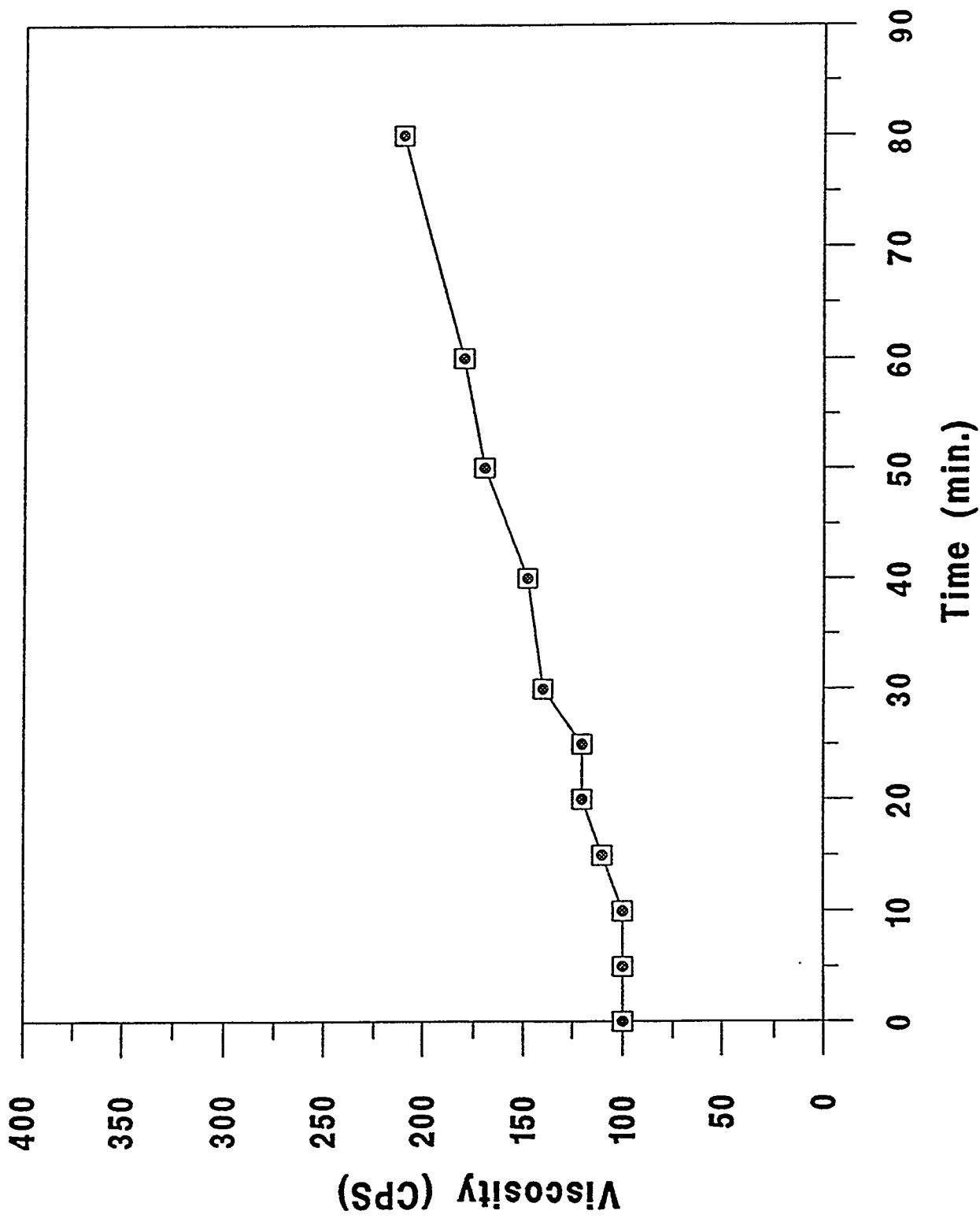
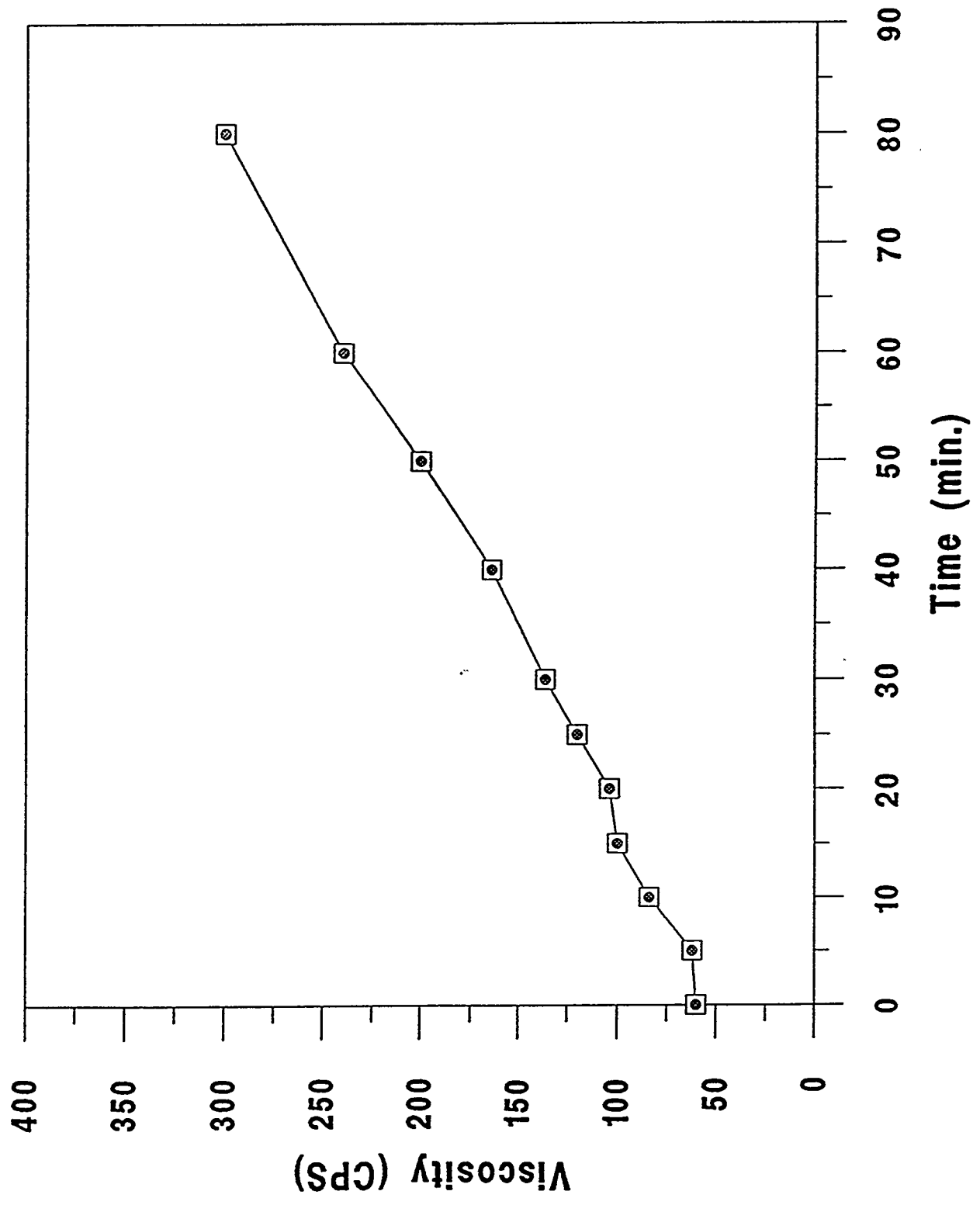


Figure 20. VISCOSITY(LGX149 REWAX & CAT.) vs TIME AT TEMP. 230 oC



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Figure 21. VISCOSITY(LGX148 REWAX & CAT.) vs TEMPERATURE

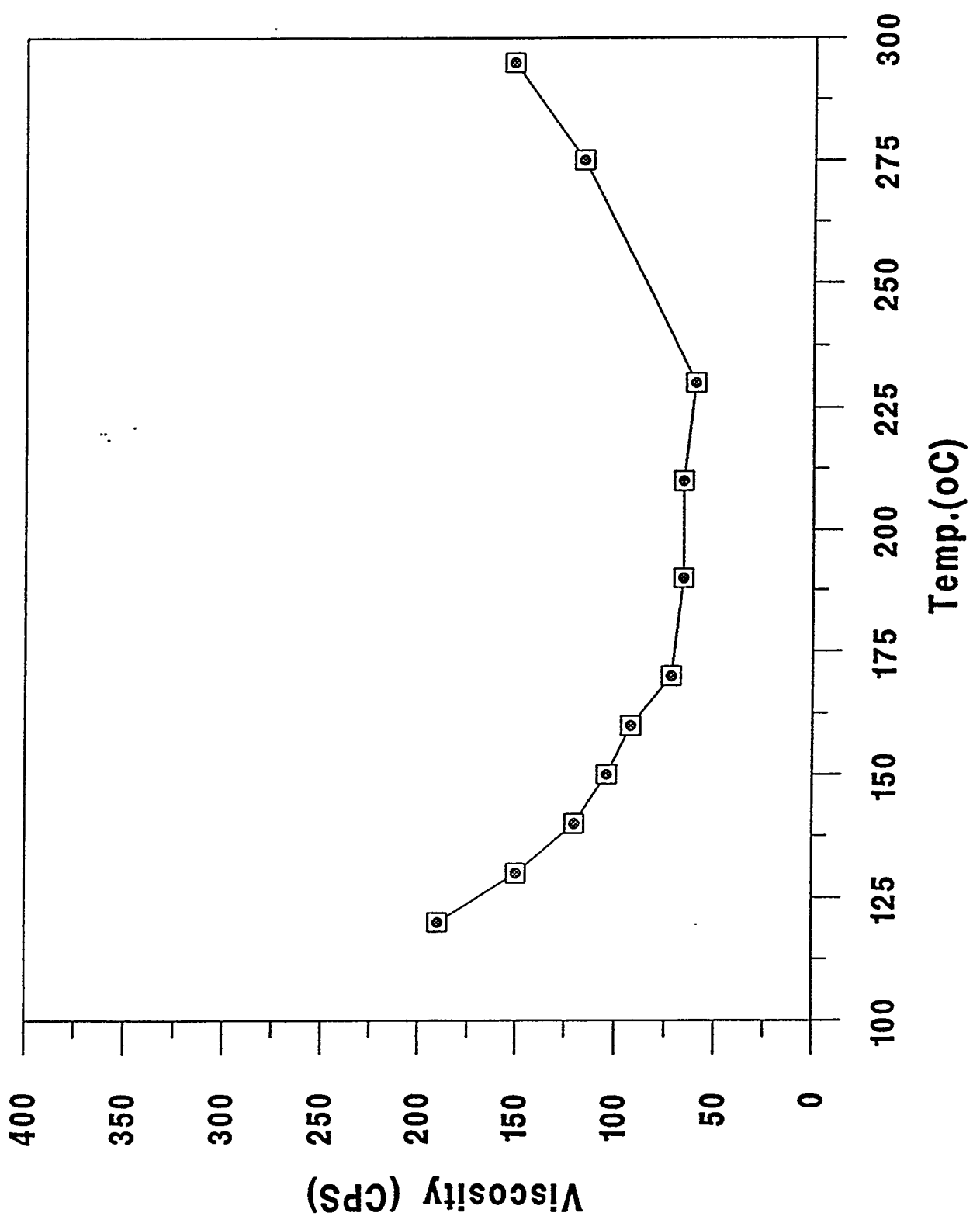


Figure 22. VISCOSITY(LGX149 REWAX & CAT.) vs TEMPERATURE

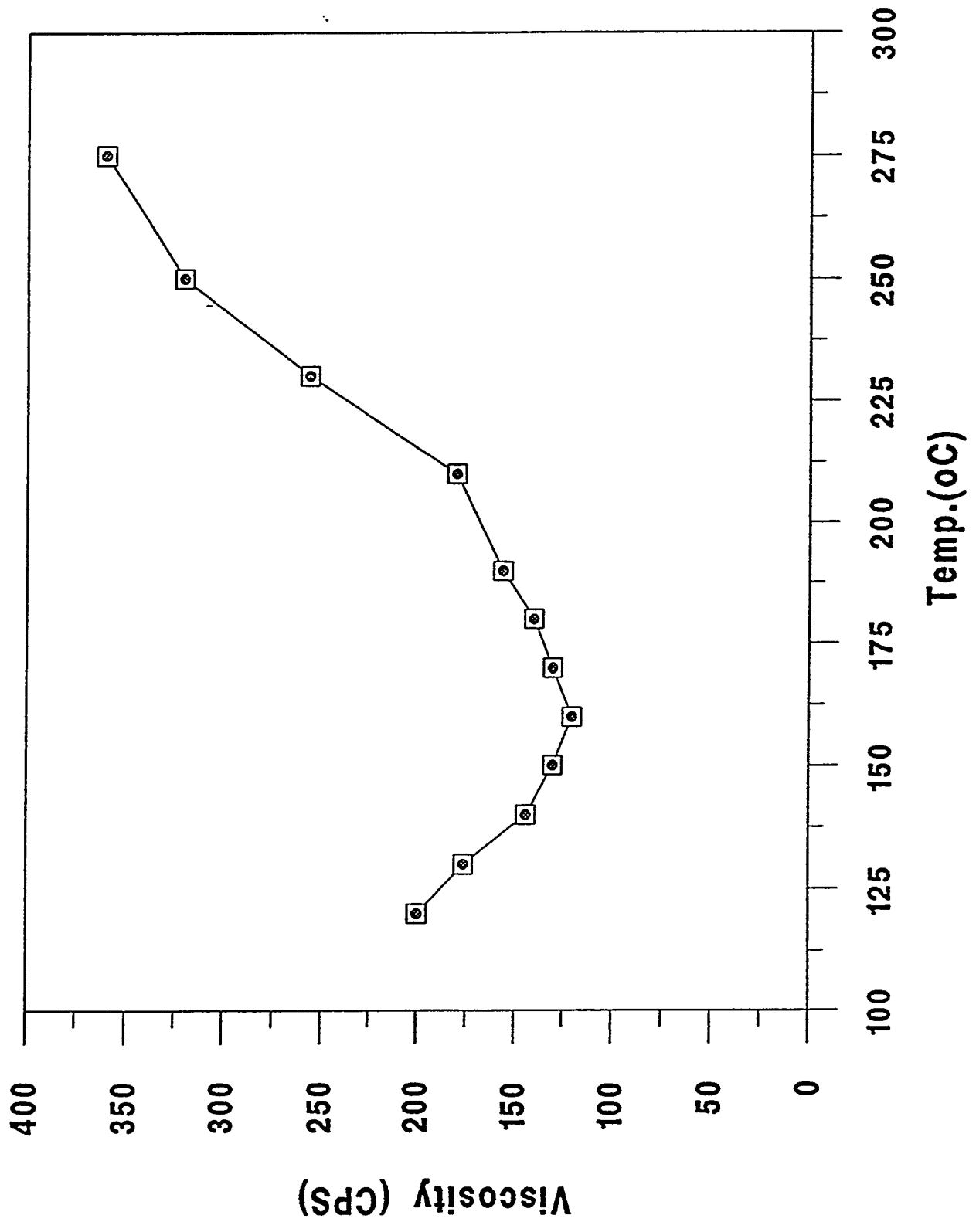


Figure 23. VISCOSITY(LGX150 REWAX & CAT.) vs TEMPERATURE

