HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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ABSTRACT This project is focused on the discovery and evaluation of novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. In particular, heterogeneous catalysts will be studied and optimized for the production of: (a) C_1-C_5 alcohols using conventional methanol synthesis conditions, and (b) methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates. An additional aspect of the project is the exploration of novel reactor and process concepts to generate the best combination of chemistry, catalyst, reactor, and total process configuration in converting syngas to liquid fuel products.

Work has concentrated on the development of catalysts for the selective production of methanol and isobutanol. Two general classes of catalysts are known for this reaction: (a) low temperature (300°C) copper metal based "modified methanol" catalysts promoted with cesium and (b) high temperature (400°C) spinel oxide based catalysts also promoted with alkali. The addition of alkali to both systems results in the formation of isobutanol by what is believed to be a base-catalyzed aldol condensation mechanism. Kinetics and thermodynamics favor the formation of higher alcohols at higher temperatures, so we have concentrated our efforts on developing a spinel oxide based catalyst system.

Initial research has discovered catalysts that produce isobutanol at a rate of 38 g/kg-hr with a methanol to isobutanol ratio of 4:1 at 400°C, 1000 psi, GHSV=6000 and syngas ratio = 1:1.

Further work in material preparation, and variations in catalyst composition and in process parameters are expected to produce even better performance in meeting the project goals. A process synthesis study is in progress to determine the most economical process flow sheet for converting coal to fuel alcohols via syngas. The synthesis task will include computer simulation, consideration of design alternatives, heat integration using pinch technology and optimization of design conditions.

INTRODUCTION

In the past ten years, there has been considerable interest in developing processes for the synthesis of higher alcohols (C2 and higher) from syngas for use as additives to gasoline (usually 2-5 wt%) to reduce air pollution and increase the octane number [1]

The push towards pollution control comes from the fact that the single largest source of hydrocarbon emissions in the US are automobiles. Hydrocarbons, in the presence of sunlight and other chemicals, go through a series of complex chemical reactions to produce ground level ozone, the primary ingredient in the smog that affects many of the major US cities, especially in the summer months [2]. Generally, the more hydrocarbons and sunlight, the more ozone and the bigger the smog problem. Other emissions that give cause for concern are CO and NOx. The presence of oxygen in the fuel allows for combustion to proceed to a greater extent, thus lowering one source of hydrocarbon emissions. The need for an octane enhancer stems from the phasing out of lead from the gasoline pool.

Higher alcohols are useful as additives to gasoline or substitute fuels such as methanol. For example, a mixture of C2-C5 alcohols with methanol helps overcome the problem of methanol phase separation with water and lowers the overall vapor pressure of the methanol fuel. An alcohols mixture from syngas could be added to the list of (or be used to synthesize) such established octane improvers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME) or be used directly as are alcohols such as methanol, ethanol and tertiary butyl alcohol (TBA).

Besides their value as a source of acceptable octane enhancers, processes for mixed alcohols from syngas could be of particular interest for the conversion of remote natural gas to easily transportable, high value products [3].

Sponsorship

The present work is being sponsored by the United States Government Department of Energy (DOE) under DOE Contract No. DE-AC22-91PC90046 through the Pittsburgh Energy Technology Center. The principal objectives of the program are to discover and evaluate novel heterogeneous catalysts for the conversion of syngas to oxygenates having use as fuel enhancers, to explore novel reactor and process concepts applicable in this process and to develop the best total process for converting syngas to liquid fuels.

The project is being pursued in two concurrent tasks. Task 1 involves catalyst research and development; this report summarizes the first steps in this effort. Task 2 is largely an engineering activity, and includes process conceptualization, economics and bench-scale process evaluation of systems developed in Task 1.

This project is a successor to DOE Contract No. DE-AC22-86PC90013 which concluded in 1991.

Catalysts for the Production of Alcohols from Syngas

Catalysts for Higher Alcohol Synthesis (HAS) can be divided into the following classes [4], based on the alcohol product distribution.

Modified Fischer-Tropsch (FT) and Group VIII Metal Based Catalysts.

Traditional Fischer-Tropsch catalysts produce appreciable amounts of oxygenates (alcohols, aldehydes, acids, ketones and esters) by addition of alkali. Typical FT metals include Fe, Co, Ni, and Ru.

The products observed follow an Anderson-Schultz-Flory (ASF) distribution, typical of the well-known linear condensation polymerization mechanism. Molybdenum sulfide catalysts promoted with alkali also produce the ASF product distribution. Rh-based catalysts are similar, but produce more C_{2+} oxygenates.

Modified Methanol or Iso-alcohol Catalysts.

HAS catalysts have primarily evolved from modified methanol synthesis catalysts. The original methanol synthesis catalysts were based on a zinc/chromium oxide spinel oxide and operated around 400°C and could tolerate some sulfur impurities in the syngas feed. With the advent of effective desulfurization techniques for the syngas, a second generation methanol synthesis catalyst was developed, based on a more active copper metal based formulation which could operate at substantially lower temperatures (250-300°C). In both cases, the addition of alkali to the system resulted in the formation of higher alcohols, albeit at a substantially lower overall productivity. These consist of Methanol Synthesis catalysts modified with alkali promoters, forming significant quantities of branched primary alcohols.

The reaction is believed to proceed by a combination of hydrogenation and carbon-carbon bond formation via aldol condensation. This should be contrasted with the modified FT catalysts which proceed by a classical CO insertion/hydrogenation mechanism. The result of this is the formation of branched alcohols with a non-ASF product distribution.

The following major reactions take place over the catalyst:

Alcohol Formation

$$n\,CO + 2n\,H_2 = C_nH_{2n+1}OH + (n-1)\,H_2O$$

Hydrocarbon Formation

$$nCO + (2n+1)\,H_2 = C_nH_{2n+2} + n\,H_2O$$

Water-Gas-Shift Reaction Equilibrium

$$CO + H_2O = CO_2 + H_2$$

The research reported here is focused on Modified Methanol or Iso-alcohol Catalysts, with emphasis on discovering a catalyst that has a high selectivity to total alcohols at the expense of hydrocarbons, and a high specific selectivity among the alcohols to isobutanol.

A 50/50 mol% mix of methanol and isobutanol would provide an ideal feed stock for the direct production of methyl isobutyl ether (MIBE) via dehydration or the indirect production of methyl tertiarybutyl ether (MTBE) in two steps by (a) dehydration of the isobutanol to isobutylene, followed by (b) reaction with methanol to produce MTBE. The second route is preferred, as MIBE is not an octane enhancing agent.

The catalysts examined here are high temperature (400°C) materials, consisting of a spinel oxide support (general formula AB_2O_4, where $A = M^{2+}$ and $B = M^{3+}$), promoted with various other elements. HAS requires at least two complementary, yet competing reactions: carbon-carbon bond formation and hydrogenation. In the systems producing linear alcohols with an ASF product distribution, carbon-carbon bond formation is thought to occur via a classical CO insertion mechanism, followed by hydrogenation.

In contrast, the isoalcohol catalysts utilize an aldol condensation mechanism to form the carbon-carbon bonds. Copper metal cannot be used, as it sinters rapidly above 300°C. A fractional factorial design was utilized to determine the importance of each catalyst component.

RESULTS AND DISCUSSION

System Shakedown with a standard Methanol Catalyst

A standard methanol catalyst has been run in the micro reactor system. Reassuringly, it made methanol with adequate selectivities (96%) and activities (>30 lbs/ft3/hr) under the test conditions (285°C, 1050 psi, H2/CO ratio = 1, flow rate =200 cc/min.). The test was repeated twice to ensure reproducibility. The product distribution from the catalyst is displayed in Figure 1.

Reactor Blank Runs

Four experiments were conducted under reaction gas and standard operating conditions with: (a) the empty reactor tube, (b) the reactor tube with an activated carbon filter bed, (c) the reactor tube with the activated carbon and quartz beads and (d) the reactor tube and quartz beads only. The empty tube produced a very small amount of hydrocarbons, probably from some Fischer-Tropsch chemistry catalyzed by the stainless steel reactor walls. The only activity noted for the production of alcohols occurred when the activated carbon was present; this was small (~ 0.5 lbs/ft3/hr). The activated carbon is added to soak up any iron pentacarbonyl impurity in the syngas feed. The iron pentacarbonyl can act as a poison over an extended period of time, but is not likely to be a problem in a short duration (24-48 hr) test. The activated carbon will be removed for screening tests and will be used only outside the catalyst bed for aging studies.

Tests of crushed vs. 12/30 mesh high temperature spinel oxide materials showed some diffusional resistances: Selectivities remain unchanged, but the crushed material can be as much as 60% more active. This difference is not sufficiently large, however, to prevent meaningful catalyst screening.

Bench Marking with Copper Metal Based Formulations

Materials chosen for initial study are higher alcohol catalysts consisting of copper metal promoted with Na, Zn, Ce, and Th on a spinel oxide.. These are low temperature, modified methanol catalysts and operate between 260-300 °C. The results are summarized in Table 1.

The alcohol products follow the classic Anderson-Schultz-Flory distribution, producing primarily linear alcohols with some iso-alcohol formation - see Figure 2 and 3 for a typical distribution. The support itself produces significant quantities of C_3 alcohols (Figure 4), with a mole ratio of propanol to iso-propanol of 1:1. It is likely that the alcohol distribution observed results from a combination of CO insertion/hydrogenation proceeding on the copper metal and some aldol condensation occurring on the support.

We observe selectivities to alcohols as high as 68% and activities as high as 3.2 lbs/ft^3-hr (~50 g/kg-hr) under the test conditions (250-290 °C, 1050 psi, H_2/CO ratio = 1, flow rate = 100 cc/min.).

This type of catalyst is unlikely to meet our goals. For example, the increase in activity required is 3-6 times that required, even for the best catalysts discovered under the prior DOE contract. These catalysts are based on copper metal, which sinters rapidly above 300°C; thus, there is an effective ceiling imposed on using temperature as a lever

to improve reaction rates. Selectivities are closer to target, but will inevitably decline as the catalyst is pushed harder.

Based on these results and examination of catalyst performance in the literature, it was decided to concentrate on higher temperature (~ 400°C) novel spinel oxide materials. The higher operating temperature should allow us to achieve the rates we need. An added advantage is that thermodynamics also favor HAS versus methanol synthesis at higher temperatures.

Catalyst Preparation Design

The variables included in the designed set were metal ratios, calcination temperature, calcination time, promoter levels and reduction temperature. The effect of precipitating pH, calcination temperature and time on surface area, porosity, and powder x-ray diffraction pattern were examined in a preliminary 3x3 designed set.

The design was carried out to determine best values for the precipitating pH and the range for calcination temperature and time to obtain high surface area and porosity. The designed set as well as the analytical results are shown in Table 2.

The analytical data clearly show that the BET surface area is dependent on the calcination temperature, as expected. The pH has a very strong effect on the surface area. and porosity. These two parameters are the main factors influencing the resulting surface area within this design. This is graphically shown in Figure 5.

Statistical analysis of the data yielded a model for the BET surface area, pore volume, and pore diameter in terms of pH and temperature. The optimal pH to achieve the maximum surface area would be around 10.0-10.3. Calcination time is not a factor in these models and therefore could be removed as a variable in future studies.

Catalyst Formulation Design

The design set consisted of a total of 22 separate runs divided into a center point formulation, whose preparation was repeated three times (catalysts 10-DAN-50, 10-DAN-57 and 10-DAN-66), repeat tests of two of these center point preparations (10-DAN-50R and 10-DAN-57R) and sixteen different catalyst formulations. The results are displayed in Table 3.

Center point Catalysts

The center point formulations have all the promoters present in intermediate amounts and show reasonable agreement for two out of the three: 10-DAN-57 and 10-DAN-66. In contrast, 10-DAN-50 is less active and produces a significant amount of C3 products. This C3 split contains significant quantities of both the normal and branched products, n-propanol and isopropanol, suggesting some difference in the preparation. A likely scenario is incomplete incorporation of all of the promoters; 10-DAN-50 was made early in the campaign and may have suffered as a consequence of the learning process.

Alcohol activities for the "good" catalysts are 6-7 lbs/ft^3-hr (96-112 g/kg-hr),with selectivities, on a carbon dioxide free basis, of 57-67%. The amount of isobutanol produced on a wt% basis is 18-20% of the total alcohols (11% on a mol% basis) - see figure 6, giving isobutanol productivities of 17-22 g/kg-hr.

Scope of the Design

The results are summarized in Table 3. A wide range of activities (0.39-10.9 lbs/ft^3-hr (6-174 g/kg-hr). total selectivities to alcohols (26-95%) and specific selectivities to isobutanol (0-34%) are observed. A number of the catalysts tested are highly selective to total alcohols (85-95%) with between 25 - 40 wt% of the alcohols being C_2's or higher. Iso-butanol selectivities between 19-34 wt% are common.

Alcohol Product Distribution

12 of the 22 catalysts make significant quantities of isobutanol (14 wt% or greater). Four catalysts have been selected for illustrative purposes. The alcohol distributions for these catalysts appear in Figures 7-10.

• 3-DAN-90: (see Figure 7). This catalyst is the most active of the set and the least selective for total alcohols, producing hydrocarbons instead.. The formulation gives a unique alcohol distribution, with the major components being the propanols (isopropanol and n-propanol). The ratio of branched to normal product is 1:1.

• 10-DAN-47 and 10-DAN-52: (see Figures 8 and 9). Both exhibit lower activities than the mean, are very selective to alcohols (93-94%) and produce relatively large quantities of methanol as the major alcohol product.

• 10-DAN-54: (see Figure 10). The catalyst is more active than its two counterparts, slightly less selective to total alcohols (but still a very respectable 86%) and the most selective of the whole design for isobutanol (34 wt%).

PROCESS SYNTHESIS A process synthesis study is in progress to determine the most economical process flow sheet for converting coal to fuel alcohols via syngas.

Computer Simulation

The synthesis task will include computer simulation using the ADVENT™ System, implemented from a desktop computer . The focus is on the total process and not on individual unit operations. A process is a complex system in which the selection and arrangement of unit operations is critical to process performance - in both product quality and cost. The optimal design of a unit operation in a process is different from that of one standing alone.

Measures of process performance such as energy consumption and capital cost are established before design. This process is known as "targeting". After targets are set, the process is designed to meet the targets. This represents a major departure from the normal approach of developing an initial design by experience and then evolving that design towards an optimum using detailed analysis and case studies.

Pinch Technology

Heat integration using pinch technology provides a clear picture of the energy flows. Once again, the process is viewed as a total system and not just as a set of unit operations. The hot and cold streams in the process are summed and plotted on a temperature-energy diagram. The area of closest approach of the two composite curves is called the pinch (see Figure 11) and divides the process into two parts. Above the pinch, there is insufficient energy in the hot composite curve to provide energy needed to heat the cold composite. The deficiency is made up by a hot utility. This amount is the "hot utility target". The process above the pinch is deficient in energy and can be thought of as a heat sink. Below the pinch, there is more energy available in the hot composite than is needed by the cold composite. This excess heat must be discharged into a cold utility. The amount is the "cold utility target". The process below the pinch has excess heat and can be thought of as a heat source. This leads to some simple, yet powerful rules:

- Don't transfer heat across the pinch.
- Don't cool with utilities above the pinch.
- Don't heat with utilities below the pinch.

Heat recovery can be viewed as a tradeoff between energy and the area of the exchanger (hence capital cost) required to transfer the energy. Pinch technology provides a way of optimizing the design to provide the optimal use of energy and capital.

CONCLUSIONS

System Shakedown and Bench Marking

- The micro reactor system is up and running.

- A standard methanol synthesis catalyst and several reactor blank runs have been used to shakedown the system.

- Some copper-based catalysts have been tested as a bench mark.

- We observe selectivities to alcohols as high as 68% and activities as high as 3.2 lbs/ft3-hr (~50 g/kg-hr) under the test conditions (250-290 °C, 1050 psi, H2/CO ratio = 1, flow rate = 100 cc/min.).

- Based on these results and examination of catalyst performance in the literature. it was decided to concentrate on higher temperature (~ 400°C) novel spinel oxide materials.

Results from the catalyst preparation design set show that:

- The optimal pH to achieve the maximum surface area is around 10.0-10.3.

- In general, surface areas decline with higher calcination temperatures, as expected.

- Calcination time is not a factor in these models and therefore could be removed as a variable in future studies.

Results from the Iso-alcohol design set show that:

- A number of the catalysts tested are highly selective to total alcohols (85-95%) with between 25 - 40 wt% of the alcohols being C_2's or higher.

- Iso-butanol selectivities between 19-34 wt% are common.

- The activities range from < 1 lbs/ft^3-hr to as high as 10.9 lbs/ft^3-hr (6-174 g/kg-hr)with values of 5-7 lbs/ft^3-hr (80-112 g/kg-hr) being common.

- The alcohols produced are almost exclusively methanol and iso-butanol. The iso-butanol is believed to be formed because the HAS proceeds predominately via an aldol condensation mechanism over the promoted spinel oxide catalysts.

• Process conversion is estimated to be around 12% for the catalysts most selective to isobutanol.

Process Synthesis

• A process synthesis study is in progress to determine the most economical process flow sheet for converting coal to fuel alcohols via syngas.

• The synthesis task includes computer simulation, consideration of design alternatives, heat integration using pinch technology and optimization of design conditions.

FUTURE PLANS

- Investigation of new material preparation techniques.
- Systematic variation in catalyst composition based on statistical designs.
- A process parameter design in temperature, pressure, GHSV and syngas ratio.
- The process synthesis study will continue to optimize the overall design.

EXPERIMENTAL

Reactor System

The Syn-Gas Micro reactor system is designed to screen heterogeneous catalysts for the conversion of synthesis gas to methanol and higher alcohols over a pressure range of 15-1500 psi, a temperature range of 25-450°C, and feed gas flow rate range of 50-500 sccm. Two fixed bed reactor tubes may be independently (except for reaction temperature) operated at any one time. The unit consists of three sections: the feed section, the reaction section, and the analytical section.

1. Feed Section

The feed section is designed to allow the operator to select any one of three premixed feed gases independently for any reaction tube. In addition, a nitrogen purge and pressure testing stream is available for selection. After stream selection, the feed gas for a reaction tube is passed through a activated carbon trap to remove metal carbonyl contaminants. The purified gas then passes through a mass flow meter and into the reaction tube inlet.

2. Reaction Section

Each reaction tube is manufactured from stainless steel and can hold up to ten milliliters of catalyst. The reaction tubes are heated using an air fluidized sand bath which is operated by a PID controller that senses the process temperature via a thermocouple positioned directly in the sand bath. The reaction tube offgas passes into a spring loaded back pressure regulator (used to elevate reaction pressure) equipped with a bypass valve.

3. Analytical Section

From the back pressure regulator, the product gas stream enters into the analytical section of the unit. The analytical section consists of automated, air actuated, gas sampling valves (GSVs) to provide on-line offgas sampling, followed by knock-out drums to collect liquid product for future analyses.

Product Analysis

Each reaction line in the micro reactor system passes through an independent six port, two position, gas sampling valve . These valves alternatingly provide 0.6 ml reactor offgas samples to a Varian 3700 gas chromatograph. All valves are pneumatically actuated using a collection of solenoid valves controlled via the UCC computer automated laboratory system (CALS).

Once a sample enters the Argon carrier gas stream (see Figure 3), it is transported outside of the fume hood to a four port, two position, air actuated, switching valve (GSV-4) located at the GC. This valve directs the sample to either the organics separation (Tenax column) and detection leg of the analysis scheme or to the inorganics separation (Carbosieve S-2 column) and detection section. While GSV-4 is directing samples to the Tenax column, GSV-5, a six port, two position, gas sampling valve, back-flushes the Carbosieve column of accumulated organic compounds from previous analyses. GSV-4 and GSV-5 are bridged so that they actuate at the same moment. The analytical section is designed to have GSV-1or 2 send two samples to the GC two minutes apart. The first sample goes to the organics analysis section. On the second sampling, GSV-4 and 5 are actuated to divert the second gas sample to the inorganics analysis section.

GC Analysis

A single Varian 3700 gas chromatograph equipped with two detectors is used for offgas analysis. Inorganics (H_2, N_2, CO, and CO_2) are separated on a 10', 1/8", 80/100 Carbosieve S-2 column purchased from Supelco and detected by thermal conductivity. All organic products are resolved on a 12', 1/8", 80/100 Tenax column obtained from Alltech and detected using flame ionization. The Tenax column has been calibrated on an absolute weight basis using quantified mixtures of C_1-C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Argon is used as the carrier gas for both columns.

Data Analysis

Upon collecting the dual channel GC chromatogram for a reactor tube, CALS determines the identity and area of all components eluted and passes the results to a VAX mainframe computer. The operator accesses the VAX using a terminal in the laboratory and enters a FORTRAN program that has been written to provide further data analysis. The operator inputs the feed and offgas flow rates, reaction conditions, and catalyst reference numbers. The program calculates the catalyst activity and selectivity as well as performing carbon, hydrogen, and oxygen mass balances. In general, the oxygen and hydrogen mass balance is not 100% because the analytical system is unable to quantitate the H_2O concentration in the offgas.

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TABLE 1

Cu/Spinel Catalyst Formulation Results

CATALYST SAMPLE	ACTIVITY [1]	SELECTIVITY TO ALCOHOLS [2]	C1 (wt%)	C2 (wt%)	C3 (wt%)	C4 (wt%)
7GRS24-3	0.1	68.0	0.0	1.6	66.4	0.0
7GRS24-4	2.4	37.6	8.7	-	-	0.0
7GRS24-7	1.3	47.3	21.1	13.7	12.5	0.0
7GRS24-8	3.2	35.8	15.1	11.2	9.7	0.0

[1] ACTIVITY= lbs/ft3/hr

[2] SELECTVITY= wt%

TABLE 2

Designed Set and Analytical Results for the Catalyst Preparation Design

Sample Reference	pH	Temp (°C)	Time (hr)	BET S.A. (m2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
3DAN79	7.5	300.0	4.0	36.6	0.19	20.9
3DAN79	7.5	400.0	11.0	16.1	0.10	25.1
3DAN79	7.5	500.0	18.0	20.2	0.13	26.1
3DAN69	9.5	300.0	18.0	98.2	0.41	16.6
3DAN69	9.5	400.0	4.0	74.7	0.39	20.9
3DAN69	9.5	500.0	11.0	46.0	0.36	31.1
3DAN75	11.0	300.0	11.0	97.9	0.49	20.0
3DAN75	11.0	400.0	18.0	63.0	0.45	28.5
3DAN75	11.0	500.0	4.0	47.8	0.41	34.5

TABLE 3

CATALYST FORMULATION DESIGN SET RESULTS

CATALYST SAMPLE	ACTIVITY [1]	SELECTIVITY TO ALCOHOLS [2]	C1 (wt%)	C2 (wt%)	C3 (wt%) [3]	C4 (wt%)[4]
10DAN50	4 79	87 88	55.32	0 00	16 34	16 22
10DAN50R	3 63	70 11	52 14	0 00	11.60	6 37
10DAN57	6 77	93 53	67.32	0 00	3 72	20 09
10DAN57R	6 74	83 99	65 74	0 00	1 76	16 09
3DAN90	10 86	26 00	4 64	3 50	13.50	4 37
11DAN45	5 93	91 44	64 43	0 53	2.65	23.83
11DAN44	0 85	65 00	47.86	0.00	9 09	8.05
10DAN47	3 69	94 78	81 32	1 62	6 55	5 29
10DAN54	6 89	85 59	41 87	1 51	5 08	34 38
10DAN49	0 39	69 78	57 79	0 00	11 99	0 00
10DAN55	7 96	89 93	55 34	1 65	9 32	23 61
10DAN52	3 05	93 62	81 92	0 00	1 97	9 72
10DAN53	4 87	79 28	70.01	0 00	0 00	9 26
10DAN48	4 20	80 80	54.07	0 00	9 22	17 52
10DAN51	6 33	80 51	57 77	0.00	1 85	19.01
10DAN56	5 72	96 31	71 17	0.00	3.46	19 25
10DAN24	3 81	92 61	63.31	0.00	4 43	24.88
10DAN66	6 66	78 43	57 69	0 00	2.00	18 20
10DAN65	4 45	74.61	64.53	0.00	1 82	8 26
10DAN58	2 79	49.67	32 32	0 00	6.46	10.89
10DAN59	5 90	65 06	49.11	0 00	1 73	14 22
10DAN67	3 23	85 95	72 94	0.00	8 23	4 78

[1] ACTIVITY= lbs/ft3-hr

[2] SELECTIVITY= wt%

[3] product is almost exclusively n-propanol

[4] product is almost exclusively iso-butanol

FIGURE 1

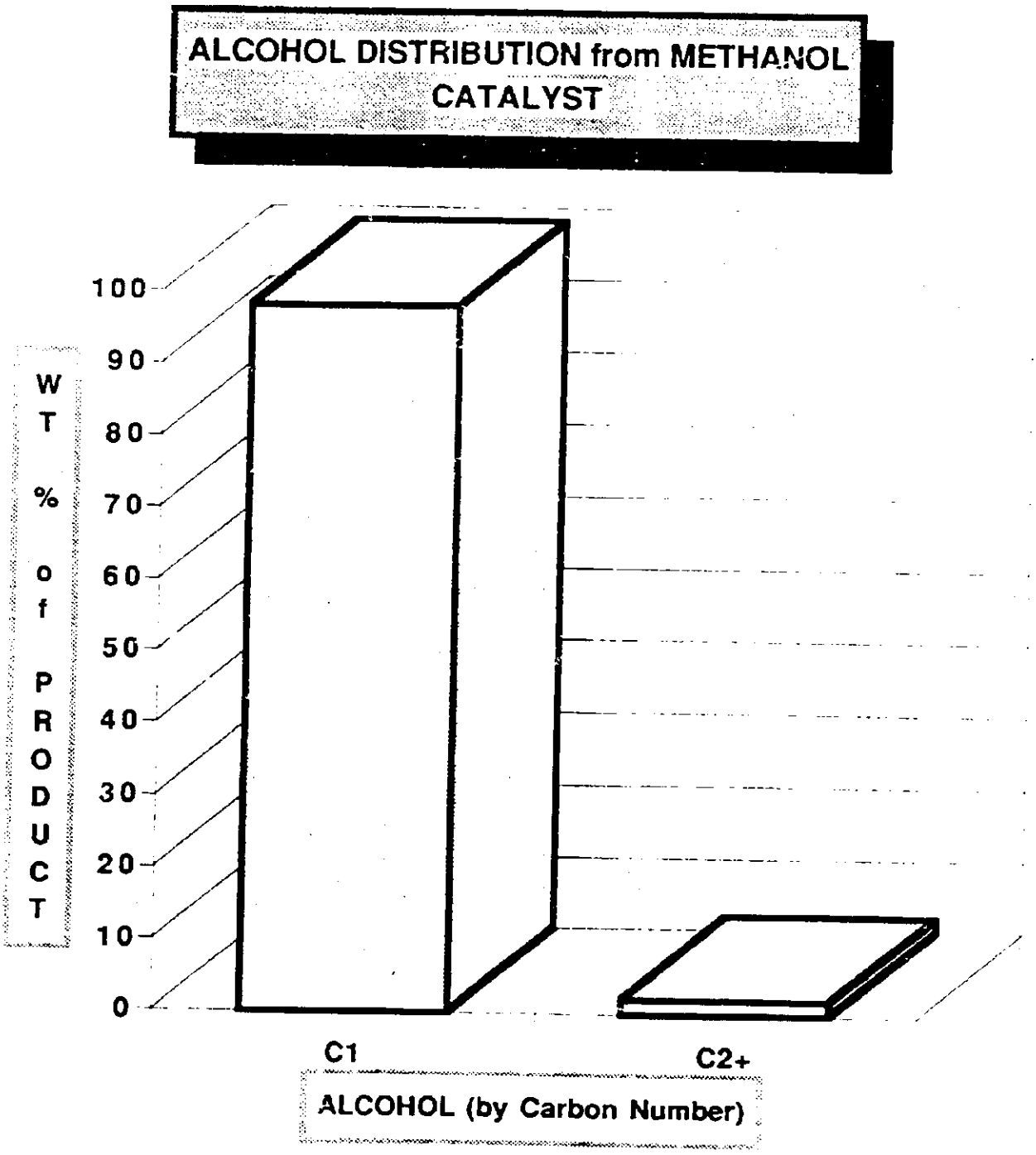
ALCOHOL DISTRIBUTION from METHANOL CATALYST
WT % of PRODUCT
100
90
80
70
60
50
40
30
20
10
0
C1
C2+
ALCOHOL (by Carbon Number)

FIGURE 2

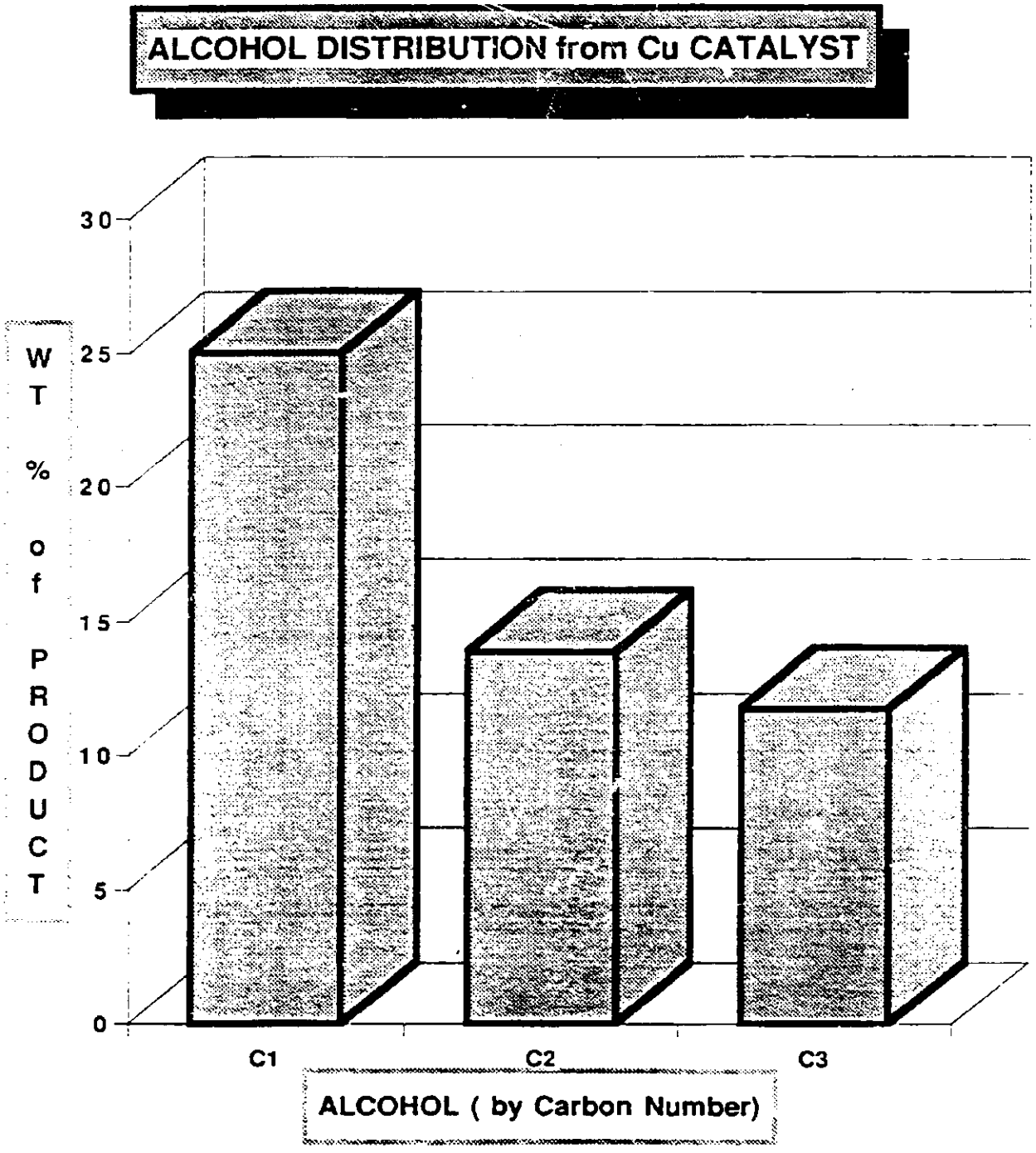
ALCOHOL DISTRIBUTION from Cu CATALYST
30
25
20
15
10
5
0
W T % o f P R O D U C T
C1
C2
C3
ALCOHOL (by Carbon Number)

FIGURE 3

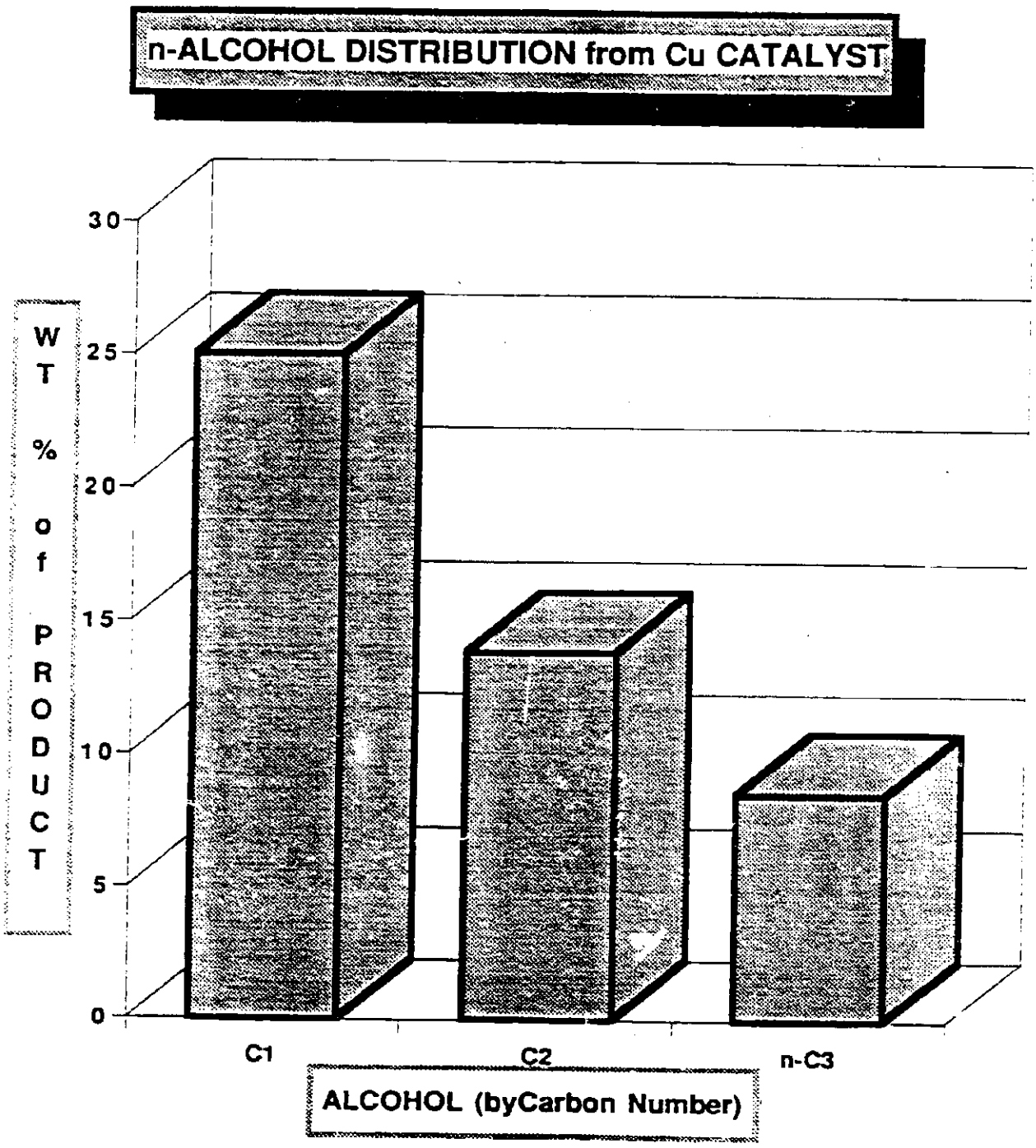
n-ALCOHOL DISTRIBUTION from Cu CATALYST
WT % of PRODUCT
30
25
20
15
10
5
0
C1
C2
n-C3
ALCOHOL (byCarbon Number)

FIGURE 4

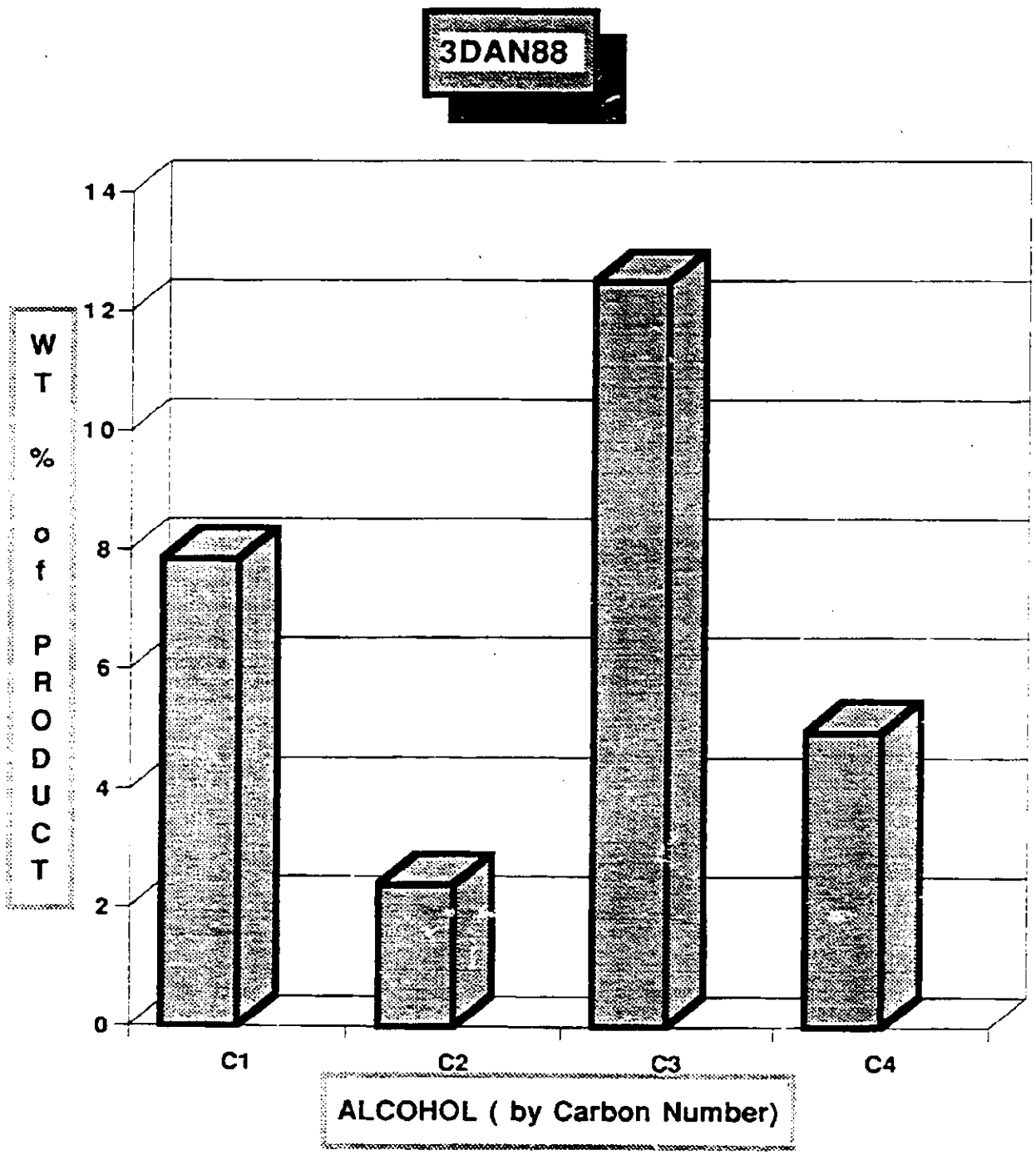
3DAN88
14
12
10
8
6
4
2
0
WT % of PRODUCT
C1
C2
C3
C4
ALCOHOL (by Carbon Number)

FIGURE 5

Surface Area of the Spinel Oxide Catalysts as a Function of Precipitation pH and Calcination Temperature.

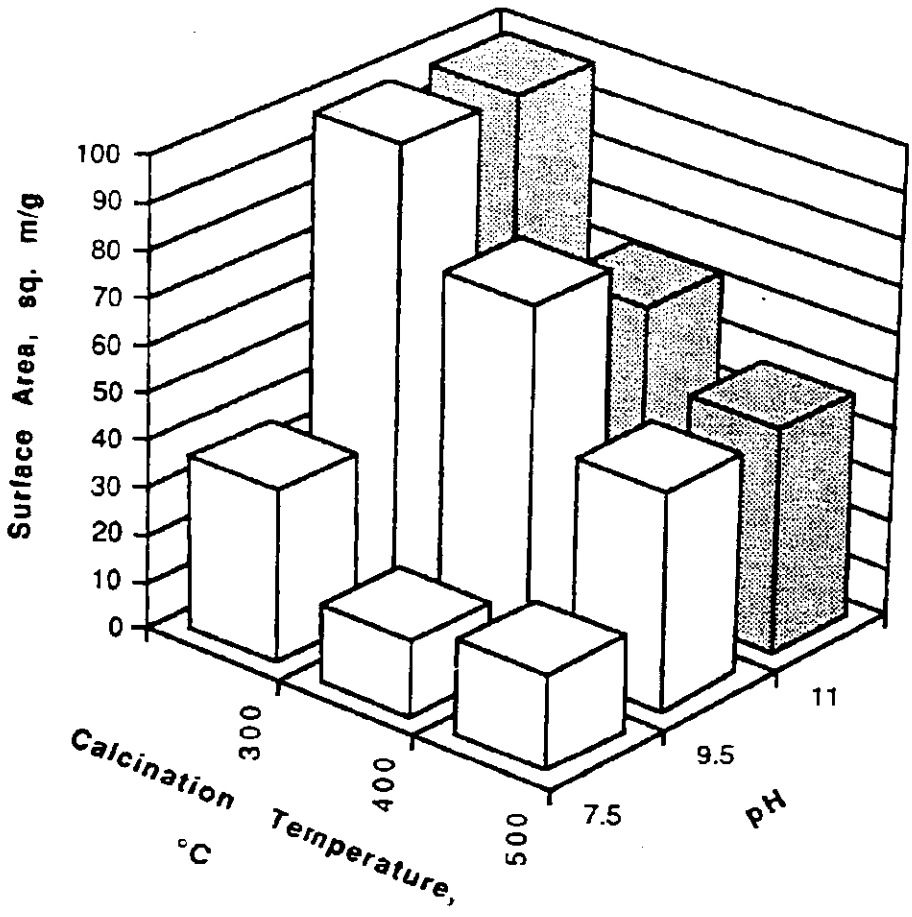

FIGURE 6

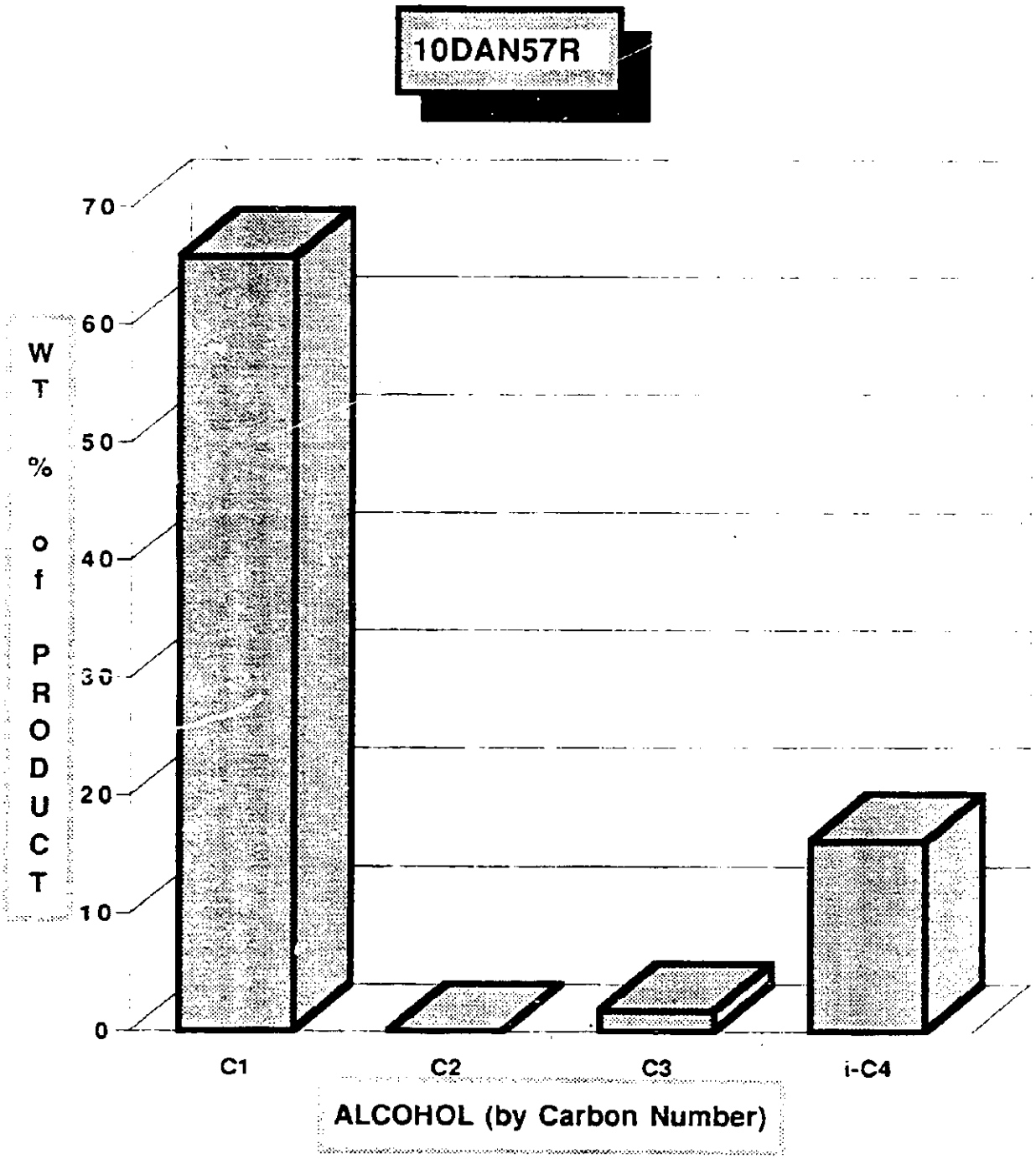
10DAN57R
70
60
50
40
30
20
10
0
WT % of PRODUCT
C1
C2
C3
i-C4
ALCOHOL (by Carbon Number)

FIGURE 7

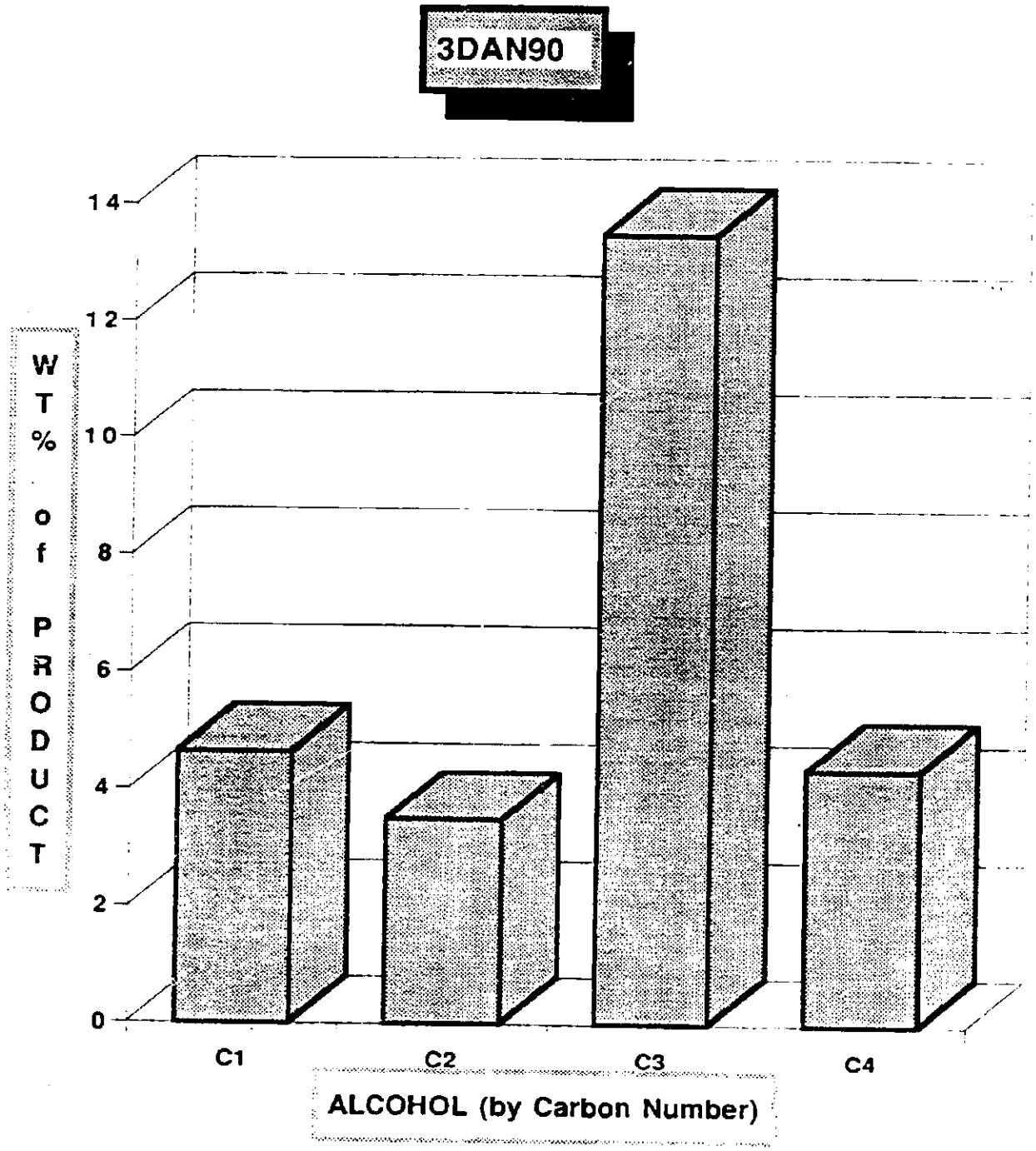
3DAN90
14
12
10
8
6
4
2
0
WT % of PRODUCT
C1
C2
C3
C4
ALCOHOL (by Carbon Number)

FIGURE 8

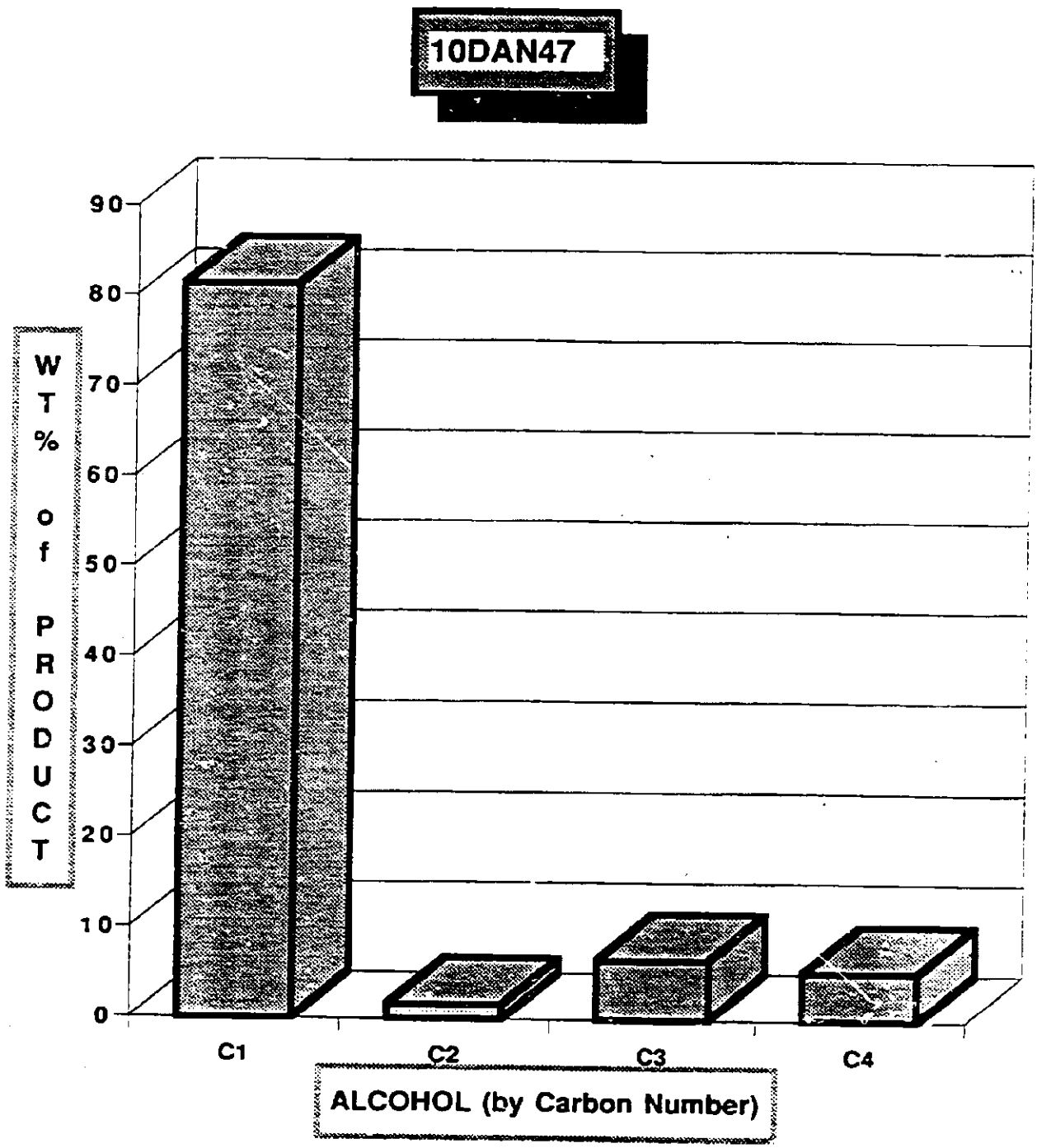
10DAN47
90
80
70
60
50
40
30
20
10
0
WT% of PRODUCT
C1
C2
C3
C4
ALCOHOL (by Carbon Number)

FIGURE 9

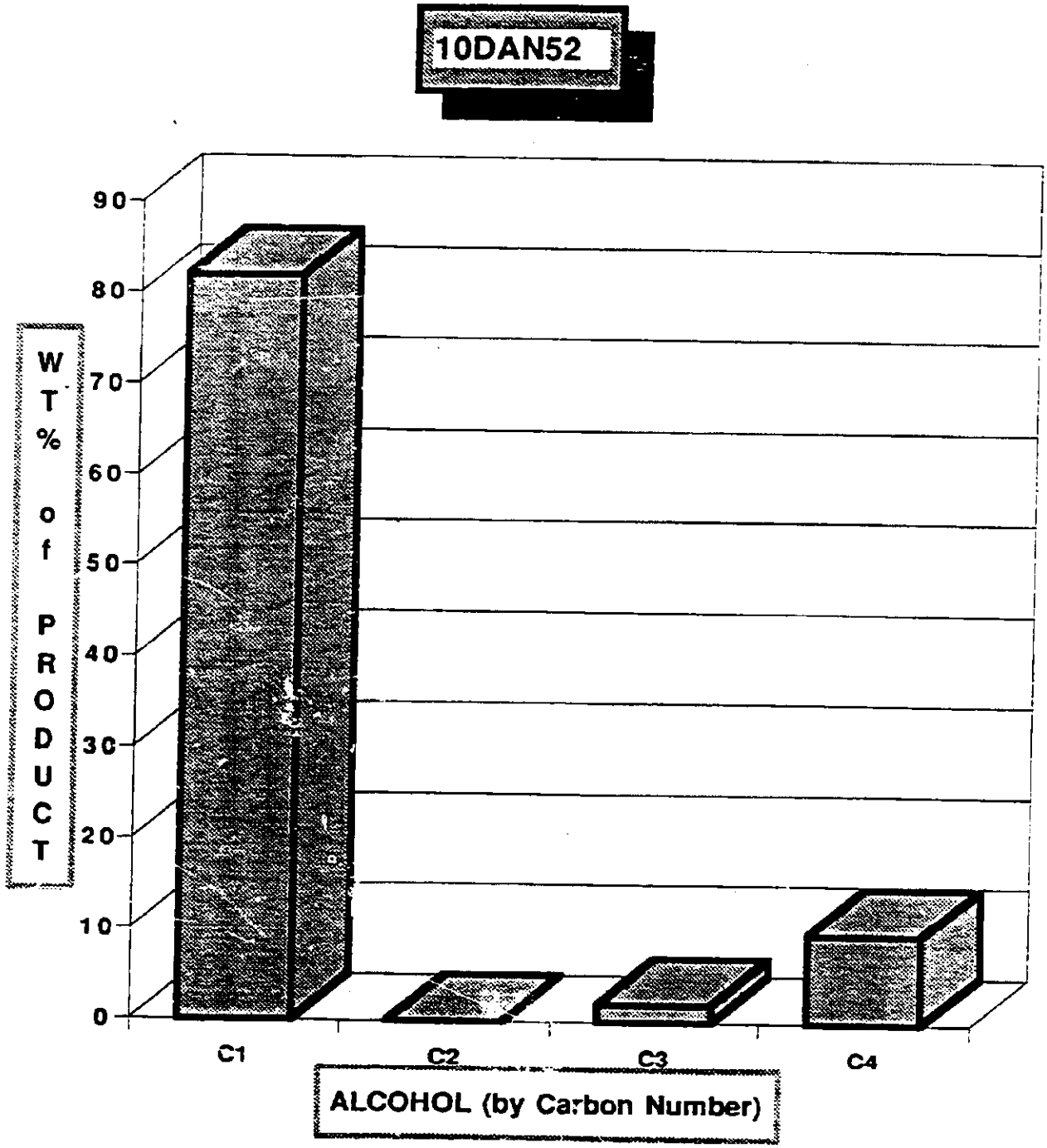
10DAN52
WT % of PRODUCT
90
80
70
60
50
40
30
20
10
0
C1
C2
C3
C4
ALCOHOL (by Carbon Number)

FIGURE 10

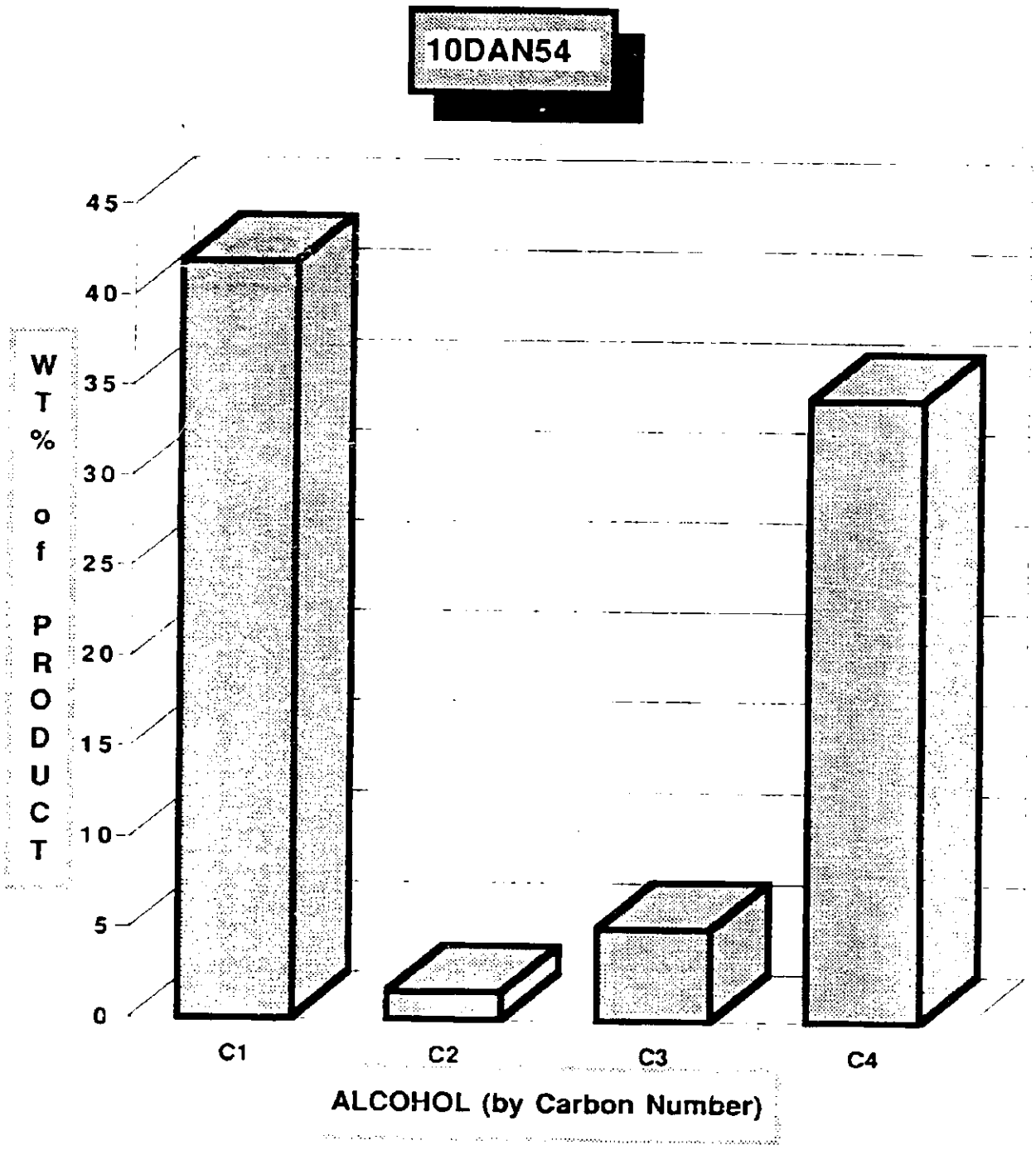
10DAN54
45
40
35
30
25
20
15
10
5
0
WT % of PRODUCT
C1
C2
C3
C4
ALCOHOL (by Carbon Number)

FIGURE 11

TEMPERATURE-ENERGY DIAGRAM ILLUSTRATING THE PROCESS PINCH