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12/19/2001 - 09:34:43

(12) **Patent:**

(11) **CA 646561**

(54) HYDROCARBON SYNTHESIS

(54)

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(45)		Aug. 14, 1962
(22)		
(43)		
(52)		260/678.8
(51)		N/A
	No	
(30)	None	
		N/A Unknown

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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The production of hydrocarbons by the catalytic reduction of carbon monoxide with hydrogen is now a well established process. Most of the previous investigators have developed the process with a view to obtaining a high yield of liquid products boiling in the gasoline range in order to supplement the production of these fuels from petroleum. Others have studies the reaction to establish conditions under which methane is the principal reduction product, and their discoveries have been utilized in increasing the heating value of gaseous fuels.

According to this invention, the problem of hydrocarbon synthesis has been approached to ascertain conditions under which the principal product of the reaction will be a mixture of normally gaseous hydrocarbons containing from two to four carbon atoms (hereinafter termed the C_2-C_4 fraction) and in which the olefin content of this fraction will be high. Hydrocarbon fractions of this nature constitute the raw materials from which the bulk of the industrial aliphatic chemicals are derived, and a synthetic source of these materials to augment the present sources which are primarily natural gas concentrates and refinery gases would be highly desirable.

In the preliminary course of this investigation, principally with iron catalysts in a fixed bed, the usual variables governing catalytic reactions, such as temperature, pressure, reactant ratio, and the like, were explored and found to have no important effect on the amount of the C_2-C_4 fraction formed. For instance, the yield of the C_2-C_4 fraction on a carbon atom basis remained fairly constant over a temperature range of 220°C. to 320°C. at about 25% to 40% of the hydrocarbons formed. It was, however, noted that the concentration of the liquid fraction (C_5 and higher hydrocarbons) did decrease with increasing temperature, but was accompanied by a corresponding increase in methane formation, the amount of the C_2-C_4 fraction

remaining about the same. The percentage distribution of the hydro-
carbons formed on a carbon atom basis, as used in this specification,
is the percentage distribution of carbon atoms among the hydrocarbons.
For example, in a gas mixture whose components are in the ratio of
2 molecules of methane-CH_4 (1 carbon atom per molecule), 1 molecule
of ethane-C_2H_6 (2 carbon atoms per molecule) and 2 molecules of
propane-C_3H_8 (3 carbon atoms per molecule), there will be a total of
ten carbon atoms in five molecules of the mixture, and the percentage
distribution of the hydrocarbons on a carbon atom basis is computed
as follows:

$$CH_4 = \frac{2 \times 1}{10} \times 100 = 20\%$$

$$C_2H_6 = \frac{1 \times 2}{10} \times 100 = 20\%$$

$$C_3H_8 = \frac{2 \times 3}{10} \times 100 = 60\%$$

It has been found that a radical redistribution of the hydro-
carbons formed in the catalytic reduction of carbon monoxide with
hydrogen can be accomplished by selective inhibition of an iron base
catalyst to increase the formation of olefins containing from two to
four carbon atoms and to decrease the formation of carbon dioxide.
Inhibition of the catalyst during synthesis is effected by including
in the reaction system the halogens: chlorine, bromine or iodine or the
corresponding hydrogen halides. The halogens or hydrogen halides may
be introduced themselves, or compounds capable of yielding them under
reaction conditions may be introduced to the reaction system. As
compounds capable of yielding halogens or hydrogen halides, the organic
compounds of chlorine, bromine and iodine may be cited, since such
organic halides decompose under the reaction conditions. When the term
"halogen" or "halide" is hereafter used in this specification the
group of chlorine, bromine or iodine or the corresponding halides will
be intended. Fluorine and the fluorides are excluded because experiments

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have shown that they are not effective inhibitors. When snythesis gas
composed of carbon monoxide and hydrogen is passed over a halide-
inhibited iron-base catalyst at reaction temperatures of 200° to 450°C.
the C_2-C_4 fraction usually constitutes about half of the hydrocarbons
formed, and the olefin content of this C_2-C_4 fraction is approximately
twice the olefin content of C_2-C_4 fractions formed from uninhibited
catalysts after steady operating conditions have been obtained.

The effect of selective inhibition of iron-base catalysts on
the product distribution at reaction temperatures in the range of 220°
to 320°C. can be generalized in the table below:

| Hydrocarbons	Percent Distribution of Hydrocarbons on a Carbon Atom Basis	
	With Untreated Catalysts	With Inhibited Catalysts
CH_4	10 - 30	10 - 25
C_2-C_4 olefins	10 - 20	25 - 45
C_2-C_4 paraffins	10 - 30	10 - 25
C_5 and higher	30 - 60	20 - 50
Total C_2-C_4 fraction	25 - 40	40 - 65

It will be noted from the above table that the olefin content
of the C_2-C_4 fraction produced with inhibited catalysts is markedly
increased. It has also been determined that the olefin content of the
liquid fraction produced with inhibited catalysts is likewise quite
high.

Inhibition of the catalyst also reduces greatly the amount
of carbon dioxide formed in the synthesis reaction. A low concentra-
tion of carbon dioxide in the product gas is an advantage because the
removal of this material from the other products provides an additional
operating expense. Thus, the principal reaction occurring with the
inhibited catalysts may be represented as follows:

$$(1) \quad CO + 2H_2 \longrightarrow (CH_2) + H_2O$$

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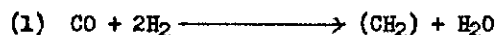
the corresponding reaction (2), below, which yields carbon dioxide, is

decreased.

(2) $2CO + H \longrightarrow (CH_2) + CO_2$
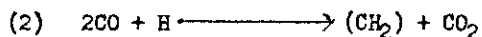
As a rule, inhibited catalysts are less active than the

catalysts before inhibition, and, as a result, the conversion of

synthesis gas to total hydrocarbons will be less per pass using the

inhibited catalysts, other conditions being equal. However, the per-

cent conversion per pass of synthesis gas to hydrocarbons can be

increased by raising the reactor temperature up to an appropriate

operating level for the catalyst used. The percent conversion as used

in this specification is given by the equation:

$$\% \text{ Conversion} = \frac{V_1}{V_2} \times 100; \text{ where}$$

V_1 = Volumes of CO+H_2 reacted.

V_2 = Total volumes of fresh feed gas.

For example, where the total volume of feed gas contained 50 mols of

carbon monoxide and 50 mols of hydrogen, and exit gas produced from

that feed gas contained 30 mols of carbon monoxide and 20 mols of

hydrogen, the percent conversion was 50.

Two methods of calculating the conversion as so defined are

(1) from the measured inlet and outlet gas flow and the outlet gas

analysis and (2) from the outlet gas flow, the outlet gas analysis and

the measured amount of product water, by a simple stoichiometric

relation well known to the art. Generally the latter method was found

more accurate and convenient, and most conversions were calculated by

this method.

Inhibition of catalysts has been successfully accomplished in

either the fixed or fluid bed type reactors. There are no fundamental

differences in the results obtained by the two procedures. Addition

of inhibitor can be either intermittent or continuous in order to make

up for its loss from the system by reason of equilibrium considerations.

However, with fixed beds there is some tendency to produce different degrees of inhibition along the bed, so that in practice it is somewhat easier to operate with a fluidized bed where the continuous mixing of the catalyst gives a more homogeneous distribution of inhibitor.

Several methods of inducing initial inhibition of a fixed bed catalyst are available. According to one method, the catalyst is first activated in a known manner as by reduction with hydrogen or by reaction with carbon monoxide or a mixture of hydrogen and carbon monoxide (when carbon monoxide is used either by itself or in admixture with hydrogen, the process is known in the art as "forming"). After activation of the catalyst, a suitable carrier gas, such as hydrogen, carbon monoxide or mixtures of the two known as synthesis gas, to which may be added an organic halogen compound in an amount which for convenience may be determined by its saturated vapor pressure, is passed over the catalyst at an elevated temperature sufficient to decompose the halogen compound. When the inhibitor used is a gas, such as chlorine, it may be metered conveniently into a side-stream of the feed gas. The temperature of the catalyst bed during inhibition will vary depending on the halogen compound used, temperatures of 75° - 100° C. being sufficient when the halide is an easily decomposed iodine compound, and temperatures of 200° - 300° C. or higher being required for the more stable bromides and chlorides. The amount of the halide used to treat the catalyst may be varied widely depending on the degree of inhibition desired. Under different conditions of treatment, the amounts could vary from 1 to 300 grams of halogen per kilogram of catalyst. As a specific example, iron or an iron-silica catalyst can be inhibited to obtain the benefits of this invention, such as an increase in the olefin content of the product and a decrease in carbon dioxide formation during synthesis, by treating it for 2.5 hours at

400 space velocity and at 240° to 300° C. with an equimolar mixture of hydrogen and carbon monoxide feed gas which has been saturated at room temperature and 250 psig. with ethylene dichloride.

In practice, the inhibitor may be added to the feed gas after the catalyst has been on stream and steady operation obtained. To avoid danger of complete deactivation of the catalyst, it may be desirable to start with a small amount of the inhibitor in the feed gas and gradually increase the concentration while closely following the changes in the composition of the reaction products. The percent carbon dioxide in the effluent gases can be measured with an automatic recorder, and a significant drop in the carbon dioxide content of the product gases would indicate that inhibition was being effected.

After a catalyst has been brought to an appropriate state of inhibition, the effects, although persisting for prolonged periods, gradually decrease. At the same time it is observed that halogen is lost from the catalyst. Hence, to maintain a constant degree of inhibition it is necessary to compensate for this loss, usually by a continuous addition of inhibitor with the feed gas. The persistence of inhibition after the removal of inhibitor from the feed stream is no doubt caused by temporary retention of halide by the catalyst. Such retention of halide is illustrated in the specific example above where after four days operation following the introduction of inhibitor, chloride analysis of the catalyst showed: at the top and entrance to the bed, 6.0%, in the middle, 3.3%, and at the exit, 2.3% (percent Cl by weight).

Another method for the initial introduction of inhibitor to a fixed bed catalyst is by passing a carrier gas saturated with the inhibitor at room temperature over a formed catalyst at a temperature slightly above that of the carrier gas until a sufficient amount of inhibitor has been adsorbed on the catalyst. Then the catalyst,

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containing the adsorbed inhibitor is heated, generally above 200° C.

to decompose the organic halogen compound.

As previously stated, the effects of inhibition disappear slow-

ly, because of the progressive loss of halogen by the inhibited

catalyst during the synthesis operation. For the most part the halogen

lost appears as hydrogen halide in the liquid water product from the

reactor. Thus, after the initial addition of 1 to 300 grams of halogen

per kilogram of catalyst to the catalyst, it is necessary to add

inhibitor in small regulated amounts with the feed gas during operation

in order that production of olefins may be kept high and carbon

dioxide formation kept low. As a specific example, an unpromoted iron

catalyst in the fluidized state required from 5 to 15 grams of chlorine

per kilogram of catalyst to effect initial inhibition of the catalyst,

the chlorine being introduced as ethylene dichloride with the feed

gas. Thereafter the catalyst was maintained in the inhibited state by

adding ethylene dichloride to the feed gas at a rate equivalent to 0.5

grams of chlorine per kilogram of catalyst per hour (0.7 grams of

$C_2H_4Cl_2$ per kilogram of catalyst per hour).

It is believed that the loss of chlorine (or other halogen)

from an inhibited catalyst is related to an equilibrium which exists

between iron halides and hydrogen. In the case of the iron chlorides,

this equilibrium may be represented as:

$$FeCl_2 + H_2 \rightleftharpoons Fe + 2HCl$$
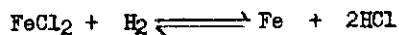
Thus, unless chlorine in some useful form were added with the feed

gas, the chlorine content of the catalyst would be depleted, as the

hydrogen chloride is swept from the reaction zone with the product

gases. In operation, the amount of chlorine which need be added to

maintain the catalyst in an inhibited state at various temperatures may

be estimated from the approximate equation -
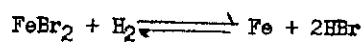
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$$\log_{10} K = \frac{-7620}{T(^\circ K)} + 6.75$$

K = Equilibrium Const. $= \frac{(P_{HCl})^2}{P_{H2}}$ (atm. abs.)
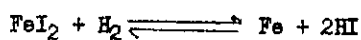
$T(^\circ K)$ = Absolute temp.

P_{HCl} = Partial pressure of HCl, atm. abs.

P_{H2} = Partial pressure of H_2, atm. abs.

For other halogens, the equilibrium and equilibrium constants are given by the relations:

$$FeBr_2 + H_2 \rightleftharpoons Fe + 2HBr$$

$$\log_{10} K = \frac{-8390}{T(^\circ K)} + 6.66. \qquad K = \frac{(P_{HBr})^2}{P_{H2}} \quad \text{(atm. abs.)}$$

$$FeI_2 + H_2 \rightleftharpoons Fe + 2HI$$

$$\log_{10} K = \frac{-7930}{T(^\circ K)} + 6.66. \qquad K = \frac{(P_{HI})^2}{P_{H2}} \quad \text{(atm. abs.)}$$

For example, using these relations, in the temperature range of 250° to 450° C. for operation at 18 atmospheres absolute (250 psig.), exit hydrogen partial pressure of 6 atmospheres and an exit flow of 1500 liters of gas per hour, converted to standard conditions, the ranges for the amount of combined or free halogen in the inhibitor to be added to the feed gas to maintain inhibition are approximately as follows; the lowest values corresponding to the lowest temperature and vice versa.

Halogen	Amount (grams per hour)
Chlorine	0.04 – 4
Bromine	0.015 – 2.5
Iodine	0.07 – 8

Thus, it is seen that the concentration of inhibitor in the feed gas is important, and that the amount to be added to maintain inhibition will increase with the temperature and will vary with the other conditions which affect the equilibrium.

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The curves in the drawing show the effects of varying the rate
of addition of inhibitor during limited periods of time. The rate of
addition is plotted as the abscissa in the form of a ratio: the pres-
sure of hydrogen chloride calculated on the assumption that all the
ethylene dichloride inhibitor added had decomposed to gaseous hydrogen
chloride, divided by the pressure of HCl calculated to be in equili-
brium with $FeCl_2$ and H_2 according to the equation above. The expres-
sion p_{HCl} is the partial pressure of hydrogen chloride in the wet exit
gas from the reactor calculated by assuming that all of the inhibitor
(ethylene dichloride) added decomposed to form hydrochloric acid and
that none of this was lost in the reactor. The expression p°_{HCl} is
the equilibrium partial pressure of hydrogen chloride computed from
the equation given above. The ratio of p_{HCl} to p°_{HCl} then gives the
theoretical excess or deficiency of the amount of inhibitor. The data
shown in the curves were obtained in an experiment with a fluidized
iron catalyst prepared from magnetite. Synthesis gas ($2.2H_2:1CO$) was
used at 60 psig., and a 1:1 ratio of recycle to fresh synthesis gas
was employed. It is to be expected that the effects with various modes
of operation and of catalyst preparation will vary somewhat in degree
from the specific results shown in the graph.

The curves illustrate that the ethylene content of the C_2
fraction increases with the degree of inhibition, while the propylene
content of the C_3 fraction is very high even for slightly inhibited
catalysts. The methane formed decreases with the degree of inhibition,
an important effect. By increasing the amount of inhibitor, the
formation of carbon dioxide can be completely suppressed but the
conversion is reduced to low levels. It is probably significant that
the slopes of the conversion, methane and carbon dioxide curves are
very steep in the region where p_{HCl}/p°_{HCl} is approximately one,
indicating the sharp change in the results obtained with uninhibited

catalysts and with fully inhibited catalysts. Operation at ratios of P_{HCl}/P°_{HCl} much greater than one for prolonged periods may result in an excessive chlorination on the catalyst. Should this occur, the catalyst may be regenerated, either continuously or intermittently, by a number of methods such as by a high temperature treatment with hydrogen, or by a temporary decrease in the amount of inhibitor in the feed stream.

A representative number of organic halogen compounds have been tested as inhibitors and found to be operative, and the invention is directed broadly to the use of any organic halogen compound which is capable of being vaporized at the reaction temperatures. The halogen compounds which have been evaluated include the following: n-butyl chloride, t-butyl chloride, ethylene dichloride, 1,4-dichlorobutane, 1,2,3-trichloropropane, dichloroethyl ether, glycerol-dichlorohydrin, m-dichlorobenzene, p-dichlorobenzene, carbon tetrachloride, ethylene dibromide, trimethylene chlorobromide, ethyl iodide and n-butyl iodide.

Since the experimental evidence indicates that organic inhibitors function by releasing halogens or hydrogen halides in the reactor, useful inhibition can also be obtained by treating the catalysts with the halogens themselves, i.e. chlorine, bromine and iodine, the halogen halides, or inorganic compounds capable of yielding hydrogen halides or halogens, such as carbonyl chloride. Thus, it is evident that there are many ways by which the iron catalysts can be subjected to the action of halogens or hydrogen halides during the synthesis operation.

The catalysts which are useful in our process of hydrocarbon synthesis include any of the typical iron-base catalysts which are known in the art. Iron catalysts containing promoters may be inhibited and the following promoters and supports, taken as typical of the additives which may be used with iron catalysts, have been

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present in significant amounts in inhibited iron-base catalysts: SiO_2, TiO_2, Cu, Al_2O_3, Cd, Ni, and K_2CO_3. In preparing an iron-base catalyst, either iron or an oxide of iron may be used, although after reduction or "forming" of the catalyst, as by reduction with hydrogen, carbon monoxide or a mixture of the two, iron oxide catalysts may exist in a reduced state or in a carbided state. Fluid catalysts must, of course, be prepared with a suitable particle size distribution, as is known in the art, so that they exhibit the typical qualities of a fluid catalyst bed.

Control of the usual process variables of the hydrocarbon synthesis can be effected with the inhibited catalysts, and the phenomenon of inhibition is exhibited over a wide range of these process variables. The significant process controls are temperature, pressure, space velocity, ratio of hydrogen to carbon monoxide, and in cyclic operations, the ratio of product gas which is recycled through the converter to the fresh synthesis gas introduced. In general, any temperature, pressure, space velocity, hydrogen to carbon ratio, and recycle ratio otherwise suitable for hydrocarbon synthesis may be used, and the following ranges may be listed as illustrative:

Temperature	250° – 420° C.
Pressure	60 to 600 psi.
Space velocity	100 to 5,000 (Vols./Vol.Cat./hr.)
H_2:CO ratio	1:2 to 5:1
Recycle ratio	None to 10:1

The reaction temperature is probably the most significant process variable. Although the present conversion increases with temperature for both inhibited and untreated catalysts, the conversion per pass with an inhibited catalyst will be less for the same reaction temperature than with untreated catalyst, other conditions being equal. There is evidence that the temperature sensitivity (i.e. change in activity with temperature) as well as the activity of the catalyst is

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reduced by inhibition, so that inhibition of the catalyst simplifies

temperature control of the highly exothermic synthesis. Operation at

temperatures of 320° to 400° C. is feasible with inhibited catalysts.

In fact, the higher temperatures are not disadvantageous since highly

olefinic products are made without increase in the production of

methane. With uninhibited catalysts, methane formation is pronounced

at high temperatures. Operation over a wide temperature range has also

shown that wax formation and carbon deposition on the catalyst are

significantly reduced as a result of inhibition. The reduction in

wax formation and carbon deposition obtained by the present process is

of considerable importance as the life of the catalyst before regenera-

tion is required is thereby increased.

Of the examples to follow, the first six are concerned with

fixed bed catalysts, and Examples 7 to 9 relate to fluid bed catalysts.

FIXED BED CATALYSTS

Apparatus and Procedure

The reactor consisted of a 1/4 inch I.D. steel tube which

contained the catalyst and extended through an insulated steel shell

filled with Dowtherm. The steel shell was wrapped with resistance

wire for electrical heating. The catalyst tube was sealed into the

jacket at both ends with compression fittings, which made its installa-

tion and removal simple. The charge of catalyst was 20 cc., as measur-

ed in a graduate before charging and extended over about 25 inches of

the tube. The catalyst was held in place with copper gauze packing

at both ends.

In operation, the catalyst chosen was loaded into a piece of

steel tubing of appropriate length. This was installed in the empty

jacket by means of the compression fittings. Both ends of the tube

were soldered into the copper tubing connecting to the rest of the

unit. The system was tested for leaks with carbon dioxide or nitrogen

at 250 - 300 psig. The gas used for reduction or forming (hydrogen,
carbon monoxide or their mixtures) was then introduced to the system
and the reactor temperature raised to the level appropriate for that
gas (usually 300° to 350° C.). Forming in general was done at atmos-
pheric pressure and space velocities of 1000 - 3000 (20-60 L/hr.).
After forming, the temperature of the reactor usually was lowered to a
level suitable for synthesis. This was done with the forming gas still
flowing. On reaching the proper reactor temperature, synthesis gas
was admitted at the selected pressure, in most cases 250 psig.

EXAMPLE 1 - Ethylene Dichloride Inhibitor

The catalyst, Fe_2O_3:CuO:SiO_2 (100:2.5:100 parts by weight), was
prepared by precipitation from a solution of copper and iron nitrates
by sodium carbonate to an end point pH of 7.8. Silica (Filtercel) was
added and the mixture boiled. It was then filtered and the precipitate
washed. The bulk density of the final catalyst preparation was about
0.9 grams per cubic centimeter. The catalyst was charged to the
reactor and treated with carbon monoxide at 310° - 335° C. for two
hours with a space velocity of 3000.

Synthesis gas in the ratio of one mol of hydrogen to one mol
of carbon monoxide was passed over the catalyst at a pressure of 250
psig. and a space velocity of 300 and analysis of the products under
steady conditions was made. After some time, the feed gas at reaction
pressure was passed through ethylene dichloride at 25° C. to saturate
the gas and introduce inhibitor to the catalyst for a total of 3-1/2
hours at a space velocity of 300 to 400 and a catalyst temperature of
280° C. The amount of inhibitor introduced was about 140 cc. of vapor
measured at standard conditions. (The amount of ethylene dichloride
added was equivalent to about 25 grams of chlorine per kg. of catalyst).
A comparison of the reaction conditions and results with inhibited and
uninhibited catalysts is given below:

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	Before Inhibition	After Inhibition		Av.
Age of catalyst, hours	31	194	197	
Temperature, ° C.	270	290	297	
Conversion, %	80	68	56	

Carbon atom distribution in hydrocarbons formed, % to

	Before Inhibition	After Inhibition		Av.
CH_4	18	14	15	15
C_2H_4)	3)	9	12)	
C_3H_6) C_2-C_4 olefins	13) 25	20	22)	44
C_4H_8)	9)	12	13)	
C_2H_6)	11)	21	13)	
C_3H_8) C_2-C_4 paraffins	3) 16	-	-)	21
C_2H_{10})	2)	2	6)	
C_5+	41	22	19	20
CO_2/CO_2+H_2O (molar ratio)	0.75	0.32	0.24	0.28

It will be noted that inhibition resulted in a decided increase in olefin formation, and a radical change in the molar ratio of carbon dioxide to water formed in the reaction, the carbon dioxide decreasing and the water increasing. The inhibited catalyst was also less active as shown by a decreased conversion at a higher reaction temperature.

EXAMPLE 2 - Ethylene Dichloride Inhibitor

The catalyst was a taconite iron ore and the synthesis was conducted in a manner similar to that of Example 1. The catalyst was reduced with hydrogen at 450° C. for 20 hours. Inhibition was effected by passing over the catalyst at 325° C. for 3 minutes 0.1 cf. of hydrogen saturated at room temperature and one atmosphere with ethylene dichloride. The amount of inhibitor added was equivalent to 0.9 grams of chlorine and equaled about 30 grams of chlorine per kilogram of catalyst (the catalyst used having a volume of 20 cc. and a bulk density of 1.6 grams per cubic centimeter). The reaction conditions and results, before and after inhibition, are tabulated below:

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Conditions	Before Inhibition	After Inhibition
Ratio, H_2:CO	1:1	1:1
Pressure, psi.	250	250
Age of catalyst, days	2	9
Temperature, ° C.	288	336
Space velocity	420	420

Results

	Before Inhibition	After Inhibition
Over-all conversion, %	40	37
$CO_2/CO_2 + H_2O$ (molar ratio)	0.31	0.06

Carbon atom distribution
in hydrocarbons formed, % to

	Before Inhibition	After Inhibition
CH_4	22.5	20.7
C_2H_4)	2.1)	12.5)
C_3H_6) C_2-C_4 olefins	12) 23.1	18.5) 42.5
C_4H_8)	9)	11.5)
C_2H_6)	7.9)	3.7)
C_3H_8) C_2-C_4 paraffins	3.8) 16.7	1.5) 6.9
C_4H_{10})	5)	1.7)
C_5+	38	30

This example illustrates that under conditions whereby the yield of the C_2-C_4 fraction is fairly high with an uninhibited catalyst, the principal effects of inhibition on the product distribution are a marked increase in the olefins formed, a sharp reduction in carbon dioxide formed, and a decrease in methane formation despite the higher temperature of the inhibited catalyst.

EXAMPLE 3 - Various Amounts of Ethylene Dibromide Inhibitor

The catalyst was similar to that described in Example 1. The method of introducing inhibitor was the same except that the temperature of the catalyst during inhibition was 240° - 260° C. The synthesis gas ratio was $1H_2$:1CO. Other conditions and results are given below:

Amount of $C_2H_4Br_2$ cc. of Vapor at Standard Conditions	g/kg. Cat.	Synthesis Temp. °C.	Conversion %	$\frac{CO_2}{CO_2+H_2O}$	Carbon Atom Distribution of Hydrocarbons Formed, % to			
					CH_4	C_2-C_4 Olefins	C_2-C_4 Paraffins	C_5+
80	32	293	47	0.39	11	38	23	28
250	100	295	39	0.10	15	38	16	31

EXAMPLE 4 - Ethyl Iodide Inhibitor

The catalyst was Fe_2O_3-SiO_2 in equal parts by weight and had a bulk density of around 0.9. The carrier gas containing the volatilized ethyl iodide inhibitor in the amount of 1500 cc. of vapor at standard conditions (about 950 g. iodine per kg. catalyst) was passed over the reduced catalyst at 75-86° C., a large amount of inhibitor being required because of the low temperature of treatment. The synthesis gas ratio was $1H_2$:1CO. Other conditions and results are given below:

Reaction temperature ° C.   299

Conversion, %   35

CO_2/CO_2+H_2O (molar ratio)   0.20

Carbon atom distribution
of hydrocarbons formed, % to

CH_4 20

C_2-C_4 olefins   41

C_2-C_4 paraffins   10

C_5+ 29

EXAMPLE 5 - Various Organic Chloride Inhibitors

Several organic chlorides were passed over reduced Fe_2O_3-SiO_2 (equal parts by weight) catalysts by means of the carrier gas procedure described in Example 1. The synthesis gas ratio was $1H_2$:1CO. Other conditions and results are given below:

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Amount of inhibitor	1,4-Dichloro-butane	1,3-Dichloro-benzene	1,2,3-Tri-chloro-propane
cc. of vapor at standard conditions	200	1500	300
g./kg catalyst	36	270	54
Inhibition temperature, °C.	220-260	220-260	225-240
Reaction temperature, °C.	302	269	253
Conversion, %	54	44	42
CO_2/CO_2+H_2O (molar ratio)	0.36	0.15	0.12
Carbon atom distribution of hydrocarbons formed, % to			
CH_4	20	14	15
C_2-C_4 olefins	35	36	30
C_2-C_4 paraffins	22	13	20
C_5+	23	39	35

The specific effect of the inhibitor on the olefin concentration is to be noted in each instance.

EXAMPLE 6 - Hydrogen Chloride Inhibitor

Inhibition of an iron-silica-copper catalyst, $Fe_2O_3(100)$, $SiO_2(100)$, $Cu(2.5)$, in parts by weight was accomplished by adding hydrogen chloride to the synthesis gas ($1H_2:1CO$) and passing the gas over the catalyst at a temperature of about 70° C.; the amount of hydrogen chloride added in this manner being about 1.5 grams. The results are tabulated below:

Age of catalyst, hours	168
Reaction temp. ° C.	271
Conversion, %	49
CO_2/CO_2+H_2O (molar ratio)	0.30
Carbon atom distribution in hydrocarbons formed, % to	
CH_4	15
C_2-C_4 olefins	30
C_2-C_4 paraffins	13
C_5+	33

The typical effects of increased olefin formation are to be

noted.

FLUID BED CATALYST

Apparatus and Procedure

The reactor was constructed of a three inch I.D. steel pipe having a jacket filled with a circulating liquid. The jacket was heated electrically. The catalyst was charged to the reactor and kept in a fluid condition by the passage of the synthesis gas through the bed. The exit gases passed through a ten inch I.D. header containing ceramic or sintered metal filters to recover suspended catalyst, the recovered catalyst being periodically blown back to the catalyst bed. The exit gas passed through a water-cooled condenser at the reaction pressure to remove liquid. The inlet flow to the reactor was measured by calibrated orifices and the exit flow by dry gas meters. Means for recycling part of the product gas, when desired, were provided.

EXAMPLE 7 - Ethylene Dichloride Continuous Inhibition

Pigment grade iron oxide (Fe_2O_3) was made into a thick paste with water. The paste was dried in an oven and then sintered at 1200° C. for two hours. The catalyst was crushed and ground to a fineness so that all particles passed through a standard 270 mesh screen and the catalyst fines having a particle size less than 20 microns were removed by gas elutriation. The catalyst was reduced with hydrogen and charged to the reactor. The catalyst volume was 4920 ml.

As previously stated, catalysts when given a single treatment with inhibitor gradually cease to be inhibited due to halide loss. For instance, the above catalyst, when initially treated with about 17 grams of chlorine from ethylene dichloride yielded a C_2-C_4 fraction at 48% conversion and one to one recycle ratio which contained on a carbon atom basis 67% olefins. After continued operation for a period of time, the hydrocarbons produced with the same catalyst contained 36% olefins in the C_2-C_4 fraction and the conversion increased to 63%, indicating

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that the effects of inhibition had been largely lost. Loss of

chloride from the catalyst bed was confirmed by the fact that the water

product of the reaction contained hydrochloric acid.

Upon adding ethylene dichloride to the feed gas at the rate of

7 grams per hour (1 gram of chlorine per kilogram of catalyst) for 14

hours the conversion dropped to 43% and the olefin content of the

C_2-C_4 fraction rose to 72%. Thereafter, ethylene dichloride was added

continuously at an average amount equivalent to 0.3 grams Cl/kg

catalyst per hour for 25 additional hours, the rate of addition being

sufficient to prevent any increase in activity of the catalyst, under

the particular operating conditions, as measured by the present

conversion.

The conditions and results before and after the foregoing

continuous inhibition period are tabulated below:

	Before Continuous Inhibition	After Continuous Inhibition
Pressure, psig.	250	250
Linear velocity, ft./sec.	0.4-0.5	0.4-0.5
Make-up synthesis gas, H_2:CO	2.2:1	2.2:1
Recycle ratio	1:1	1:1
Age of catalyst, hours	579	618
Temperature, ° C.	312	318
Over-all conversion, %	63	46
Carbon atom distribution in hydrocarbons formed, % to		
CH_4	26	14
C_2H_4)	1)	9)
C_3H_6) C_2-C_4 olefins	13) 21	20) 42
C_4H_8)	7)	13)
C_2H_6)	19)	7)
C_3H_8) C_2-C_4 paraffins	10) 36	4) 17
C_4H_{10})	7)	6)
C_5+	17	27
Olefins in C_2-C_4 fraction, %	36	72
Propylene in C_2-C_4 fraction, %	23	34
$CO_2/CO_2+ H_2O$ (molar ratio)	.28	0.034

The effect of the continuous addition of inhibitor is shown

by the significant increase in the olefins formed, by the sharp

decrease in carbon dioxide formation, and by the fact that these

results were maintained over an extended period of operation.

EXAMPLE 8 - Ethylene Dichloride Continuous Inhibition

The run started in Example 7 was continued at a recycle ratio

of product gas to feed gas of three to one and at various temperatures.

During the 69 hour period of the run for which representative samples

of the analytical data are given below, ethylene dichloride was added

continuously at an average rate of 0.8 gram Cl/kg catalyst per hour.

The conditions and results are tabulated below:

Pressure, psig.	250	250
Linear velocity, ft./sec.	0.4-0.5	0.4-0.5
Make-up synthesis gas, H_2:CO	2.2:1	2.2:1
Recycle ratio	3:1	3:1
Age of catalyst, hours	708	751
Temperature, ° C.	319	330
Over-all conversion, %	71	80.5
Carbon atom distribution in hydrocarbons formed, % to		
$\quad CH_4$	17	18.0
$\quad \left.\begin{array}{l} C_2H_4 \\ C_3H_6 \\ C_4H_8 \end{array}\right\}$ C_2-C_4 olefins	$\left.\begin{array}{r} 3.6 \\ 17.5 \\ 10.0 \end{array}\right\}$ 31.1	$\left.\begin{array}{r} 2.4 \\ 16.9 \\ 10.2 \end{array}\right\}$ 29.5
$\quad \left.\begin{array}{l} C_2H_6 \\ C_3H_8 \\ C_4H_{10} \end{array}\right\}$ C_2-C_4 paraffins	$\left.\begin{array}{r} 12.5 \\ 4.5 \\ 3.2 \end{array}\right\}$ 20.2	$\left.\begin{array}{r} 12.2 \\ 5.0 \\ 3.3 \end{array}\right\}$ 20.5
$\quad C_5+$	32	32
Olefins in C_2-C_4 fraction, %	60	59
Propylene in C_2-C_4 fraction, %	34	34
CO_2/CO_2+H_2O (molar ratio)	0.047	0.046

Operation at high recycle ratios and increased temperature

resulted in greater over-all conversions. The effect of the inhibitor

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on maintaining the olefin content of the C_2-C_4 fraction at a high
level is also evident, despite the fact that at the higher recycle
ratios conditions for hydrogenating olefins to paraffins are much
more favorable.because of the longer average residence time of olefin
molecules in the reactor.

EXAMPLE 9 - Chlorine Gas Inhibition

An iron oxide catalyst was operated with the continuous
addition of ethylene dichloride for a prolonged period. Then the
introduction of the inhibitor into the feed gas was stopped and
synthesis continued for nine hours. During this period, chlorine was
removed from the catalyst bed as hydrogen chloride and the carbon
dioxide formation and percent conversion increased. Then chlorine
gas was added in small regulated amounts for 10 hours to the synthesis
gas to re-inhibit the catalyst. The conditions and results, during
inhibition with ethylene dichloride, nine hours after stopping the
flow of inhibitor, and after re-inhibition with chlorine gas, are
tabulated below:

CONDITIONS

Temperature, ° C.	338 - 340
Pressure, psig.	60
Recycle ratio	1:1
Space velocity	400
Feed gas	(2.2 H_2 + 1 CO)
Catalyst charge	12 kg.

RESULTS

Carbon atom distribution % to	During Inhibition with $C_2H_4Cl_2$	Inhibition Stopped	After Inhibition with Chlorine Gas
CH_4	17	30	17
C_2-C_4 (total)	64	58	65
C_5+	19	12	18
% olefins in C_2-C_4 fraction	79	60	77
CO_2/H_2O+CO_2 (molar ratio)	0.05	.16	0.04

Thus, it is shown that re-inhibition with chlorine gas is
equivalent to the original inhibition with ethylene dichloride. The
increase in methane formation when the inhibitor was discontinued at

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the high temperature involved, as well as the control of the methane

formation by re-inhibition, are noteworthy.

Modifications of the invention other than as specifically

disclosed in the examples will be apparent to those skilled in the

art, and are included within the scope of the invention as defined

in the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a process for producing liquid and gaseous
hydrocarbons wherein an iron-containing hydrocarbon
synthesis catalyst is contacted with a gaseous mixture
of H_2 and CO at synthesis conditions of temperature and
pressure, the improvement comprising contacting said
iron-containing catalyst during the synthesis reaction
with a mixture comprising H_2 and CO and one member selected
from the group consisting of (a) chlorine, (b) bromine,
(c) iodine, (d) hydrogen chloride, (e) hydrogen bromide,
(f) hydrogen iodide, (g) volatile organic chlorides, (h)
volatile organic bromides, and (i) volatile organic
iodides.

2. In a process for producing liquid and gaseous
hydrocarbons wherein a fluidized promoted iron-containing
hydrocarbon synthesis catalyst is contacted with a gaseous
mixture of H_2 and CO at synthesis conditions of temperature
and pressure, the improvement comprising contacting said
iron-containing catalyst during the synthesis reaction
with a mixture comprising H_2 and CO and one member selected
from the group consisting of (a) chlorine, (b) bromine,
(c) iodine, (d) hydrogen chloride, (e) hydrogen bromide,
(f) hydrogen iodide, (g) volatile organic chlorides, (h)
volatile organic bromides, and (i) volatile organic
iodides.

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3. In the synthesis of hydrocarbons by the reaction of carbon monoxide and hydrogen in the presence of an iron-base catalyst, the improvement which resides in subjecting the catalyst to intimate contact with regulated amounts of a chlorine-containing material capable of releasing hydrochloric acid in contact with the catalyst, the amount of such chlorine-containing material being regulated with the reaction conditions so as to maintain hydrogen chloride in the reaction system in an amount at least approximately equal to that determined by the equilibrium: $FeCl_2 + H_2 \rightleftarrows Fe + 2HCl$.

4. In the process for producing liquid and gaseous hydrocarbons wherein an iron-containing hydrocarbon synthesis catalyst is contacted with a gaseous mixture of H_2 and CO at synthesis conditions of temperature and pressure, the improvement comprising contacting said iron-containing catalyst during the synthesis reaction with a mixture comprising H_2, CO and hydrogen chloride.

5. In the process for producing liquid and gaseous hydrocarbons wherein an iron-containing hydrocarbon synthesis catalyst is contacted with a gaseous mixture of H_2 and CO at synthesis conditions of temperature and pressure, the improvement comprising contacting said iron-containing catalyst during the synthesis reaction with a mixture comprising H_2, CO and a volatile organic chloride.

6. In the process for producing liquid and gaseous hydrocarbons wherein an iron-containing hydrocarbon synthesis catalyst is contacted with a gaseous mixture of H_2 and CO at synthesis conditions of temperature and pressure, the improvement comprising contacting said iron-containing catalyst during the synthesis reaction with a mixture comprising H_2, CO and ethylene dichloride.

7. In the process for producing liquid and gaseous hydrocarbons wherein an iron-containing hydrocarbon synthesis catalyst is contacted with a gaseous mixture of H_2 and CO at synthesis conditions of temperature and pressure, the improvement comprising contacting said iron-containing catalyst during the synthesis reaction with a mixture comprising H_2, CO and chlorine.

8. In the synthesis of hydrocarbons by the reaction of carbon monoxide and hydrogen in the presence of an iron-base catalyst, the improvement which resides in subjecting the catalyst to intimate contact with regulated amounts of a bromine-containing material capable of releasing hydrobromic acid in contact with the catalyst, the amount of such bromine-containing material being regulated with the reaction conditions so as to maintain hydrogen bromide in the reaction system in an amount at least approximately equal to that determined by the equilibrium: $FeBr_2 + H_2 \rightleftarrows Fe + 2HBr$.

9. In the process for producing liquid and
gaseous hydrocarbons wherein an iron-containing hydro-
carbon synthesis catalyst is contacted with a gaseous
mixture of H_2 and CO at synthesis conditions of temperature
and pressure, the improvement comprising contacting said
iron-containing catalyst during the synthesis reaction
with a mixture comprising H_2, CO and hydrogen bromide.

10. In the process for producing liquid and
gaseous hydrocarbons wherein an iron-containing hydro-
carbon synthesis catalyst is contacted with a gaseous
mixture of H_2 and CO at synthesis conditions of temperature
and pressure, the improvement comprising contacting said
iron-containing catalyst during the synthesis reaction
with a mixture comprising H_2, CO and a volatile organic
bromide.

11. In the process of making hydrocarbons wherein
a mixture containing carbon monoxide and hydrogen is
passed under superatmospheric pressure over an iron-base
catalyst at a temperature of about 250°C. to about 450°C.,
the improvement which comprises subjecting the catalyst
during reaction to intimate contact with regulated amounts
of a member selected from the group consisting of (a)
chlorine, (b) bromine, (c) iodine, (d) hydrogen chloride,
(e) hydrogen bromide, (f) hydrogen iodide, (g) volatile
organic chlorides, (h) volatile organic bromides, and

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1   (i) volatile organic iodides, and thereby increasing the

formation of olefins containing from two to four carbon

atoms.

12.   Process as claimed in claim 11 in which the

catalyst is maintained in a fluid state.

13.   Process as claimed in claim 11 in which the
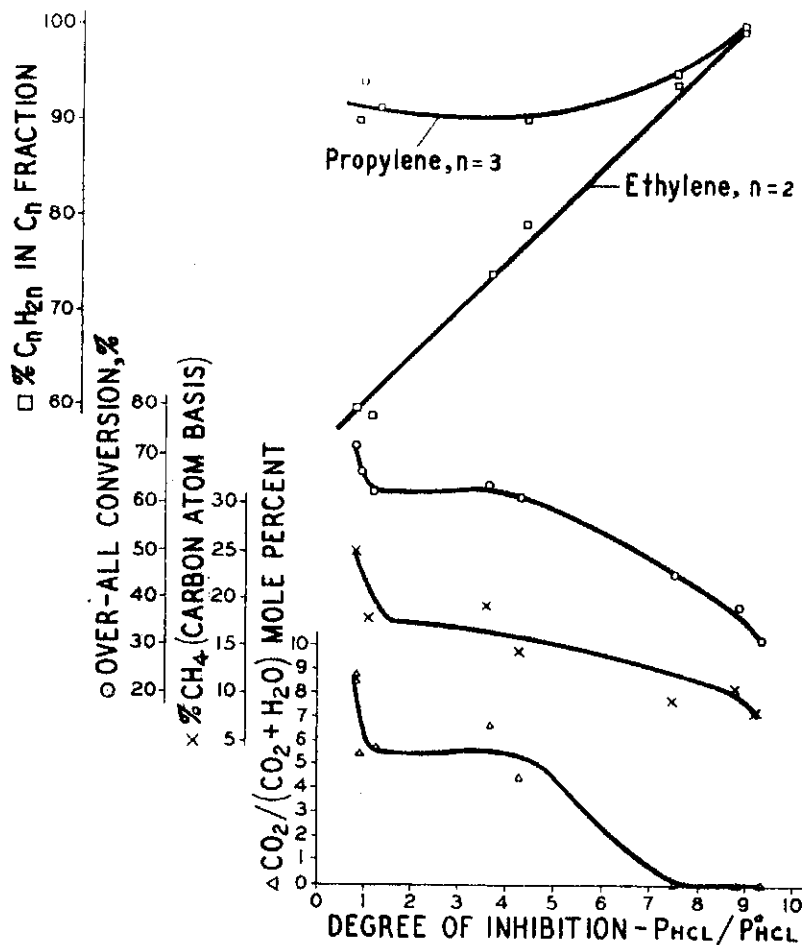
member selected is ethylene dichloride.

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14.   Process as claimed in claim 11 in which the

temperature is about 320°C. to about 400°C.

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EFFECT OF DEGREE OF INHIBITION ON OLEFIN, METHANE
AND CO_2 FORMATION AND CONVERSION OF $(CO+H_2)$ TO HYDROCARBONS
USING A FLUIDIZED IRON CATALYST AND $C_2H_4Cl_2$ INHIBITOR

□ % C_nH_{2n} IN C_n FRACTION

○ OVER-ALL CONVERSION, %

× % CH_4 (CARBON ATOM BASIS)

△ $CO_2/(CO_2+H_2O)$ MOLE PERCENT

Propylene, n = 3

Ethylene, n = 2

DEGREE OF INHIBITION — P_{HCL}/P^o_{HCL}

P_{HCL} = CALC. PARTIAL PRESSURE OF HCl IN WET EXIT GASES
P^o_{HCL} = EQUILIBRIUM PARTIAL PRESSURE OF HCL
AT REACTION TEMP.
PRESSURE = 60 P.S.I. G.
TEMPERATURE = 339°- 375°C.

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