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(71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY
P.O.Box 390, 180 Park Avenue
Florham Park, New Jersey 07932 (US)

(72) Inventor: Arcuri, Kym Brian
15346 Schnebelen Drive
Baton Rouge, LA 70817 (US)

(74) Representative: Somers, Harold Arnold et al
ESSO Engineering (Europe) Ltd. Patents & Licences Mailpoint 72 Esso House Ermyn Way
Leatherhead, Surrey KT22 8XE (GB)

(54) Process for hydrocarbon synthesis using slurry Fischer-Tropsch process with Co/TiO2 catalyst.

(57) Cobalt/titania catalyst used in slurry bubble column for the Fischer-Tropsch conversion of CO and H_2 to hydrocarbons gives better results than predicted using engineering principles. Specifically, when operating a slurry bubble column at a Peclet number (N_{pe}) of 3 to 10, productivity is equal to or greater than for plug flow, and the selectivity of fully back-mixed system is obtained.

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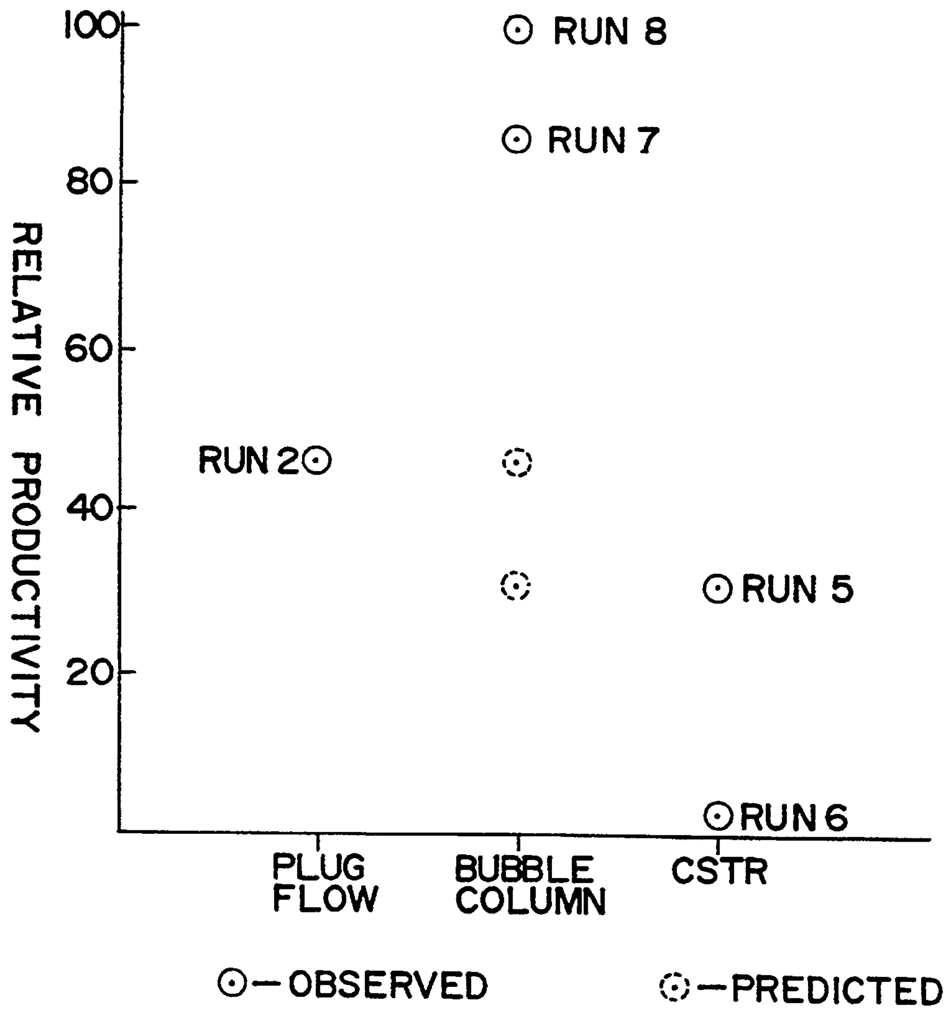


100
80
60
40
20
RELATIVE PRODUCTIVITY
RUN 8
RUN 7
RUN 2
RUN 5
RUN 6
PLUG FLOW
BUBBLE COLUMN
CSTR
—OBSERVED
—PREDICTED

FIG. 1

FIELD OF THE INVENTION

This invention relates to a hydrocarbon synthesis process, particularly the Fischer-Tropsch process, wherein for a particular catalyst system and reaction system, the productivity benefits of a plug flow reaction and the selectivity benefits of back mixed reaction are obtained without their corresponding debits. More particularly, this invention relates to a slurry type hydrocarbon synthesis process employing a catalyst comprising cobalt supported on a titania or titania-containing support in a bubble column type reactor.

BACKGROUND OF THE INVENTION

The hydrocarbon synthesis process involves the catalytic hydrogenation of carbon monoxide with hydrogen to form higher hydrocarbons, preferably C5+ hydrocarbons. Hydrogen and carbon monoxide, synthesis gas, are contacted with a suitable catalyst at appropriate reaction conditions, usually elevated temperatures and pressures, to produce the desired hydrocarbons. Catalytic materials usually include Group VIII metals, particularly iron, cobalt, ruthenium, and nickel supported on a porous inorganic oxide support, such as the oxides of Group IIIA, IV, VA. Promoter materials can be employed, e.g., rhenium, hafnium and other lanthanide metals, zirconium and other Group VIII metals, as well as the metals of Groups IA, IB and IIA.

The results obtained with a particular catalyst may vary considerably from results obtained from any other catalyst system. Also, the type of reaction system in which the catalyst is placed can affect the results. The two extremes or poles of reaction system are the plug flow system, exemplified by a fixed catalyst bed where back mixing is either non-existent or considerably minimized, and the well stirred system where complete back mixing is effected, exemplified by fluidized beds and in liquid phase systems by the well stirred or fully back mixed reactor system.

In any hydrocarbon synthesis reaction the rate of CO conversion and product selectivity depends on the partial pressure of the reactants, hydrogen and carbon monoxide, and in some cases the products, e.g., water, olefins, in contact with the catalyst. Thus, the mixing characteristics of the reactor become critical in determining catalyst performance since these characteristics will determine the gas phase composition (and therefore, the partial pressure of the reactants) at any particular point in the reactor.

In the fully back mixed reactor or CSTR, the composition of reactants (gaseous) and products (liquids and gases) and condition of the catalyst at any one point in the reactor is the same as that at any other point in the reactor. Achieving this ideal state of mixing can be accomplished with mechanical stirring devices. The reactant concentration or gas partial pressure of hydrogen and carbon monoxide govern catalyst performance by providing the driving force of the reaction and sets the carbon monoxide conversion occurring in the reactor. Thus, even though pure synthesis gas feed is entering the reactor, catalyst performance is driven by the reactant gas phase concentration corresponding to the reactant gas phase concentration exiting the reactor. This system, fully back mixed, provides maximum selectivity to desired products at the expense of productivity.

The other extreme of reactor mixing occurs in the plug flow reactor where the catalyst is stationary or relatively stationary relative to the flow of reactants (gaseous) and products (liquids and gases). The synthesis gas feed undergoes reaction as it enters the reactor and the reaction continues as the unreacted synthesis gas proceeds through the reactor. Thus, the concentration of, and partial pressure of hydrogen and carbon monoxide, decreases along the path of the reactor and, therefore, the driving force of the reaction also decreases as the concentration of liquid and gaseous hydrocarbon products as well as H_2O by-product increases. Thus, the catalyst at the exit portion of the plug flow reactor never sees fresh feed. The plug flow system provides maximum productivity at the expense of selectivity.

The important difference between the fully backed mixed (CSTR) and plug flow systems is the difference in the gas phase reactant concentration that provides the kinetic driving force for the reaction. In the fully back mixed system the reactant concentration is the same at any point in the reactor; in the plug flow system the reactant concentration steadily decreases along the path of the catalyst bed from inlet to outlet and the reaction rate is obtained by integrating the rate function from inlet to outlet.

Now, because the reactant concentration at any point in a CSTR system always corresponds to outlet conditions the productivity in a fully back mixed system will always be lower than the productivity in a plug flow system particularly in hydrocarbon synthesis where catalysts frequently have a positive rate dependence on hydrogen partial pressure and lesser or negative rate dependent on CO partial pressure. This is axiomatic because the outlet reactant concentration of a plug flow reactor is always the lowest reactant concentration in the reactor. Reactant concentrations at any point upstream of the outlet will be higher than at the outlet and the kinetic driving force will, therefore, be higher upstream of the outlet.

Reactor systems exhibiting plug flow and well stirred characteristics are the extremes of reactor performance. In practice, plug flow reactors may exhibit some back mixed traits and back mixed reactors may exhibit some plug flow traits. Deviations from the ideal systems are due to the dispersion of the reactant gases in the reactor. Insuring complete back mixing is a function of the mechanical energy imparted to the system. Reactor geometry can affect back mixing and low length to diameter ratios, less than about 3, promote back mixing in plug flow reactors. However, with higher energy inputs reactors with greater length to diameter ratios can achieve complete back mixing, too. Conversely, plug flow is favored by high length to diameter ratios. The degree of non-ideal back mixing that can occur in a plug flow reactor can be represented by the Peclet Number, N_{pe} which is equal to LU/Δ, where L is the reactor length (or catalyst size), U is the gas velocity, and Δ is the dispersion coefficient.*

High N_{pe} indicates plug flow while low N_{pe} indicates CSTR. By definition, the dispersion coefficient for an ideal CSTR is infinity and N_{pe} approaches zero.

While plug flow and CSTR represent the ideal extremes of reactor systems, classical chemical engineering principles define a continuous function between plug flow and CSTR. That is, as a system is less and less ideal plug flow it will move in a continuous fashion towards CSTR; similarly, a system exhibiting less and less back mixing will move in a continuous fashion towards plug flow. Therefore, in accordance with classical chemical engineering principles, a given reactor system must follow the continuous function between ideal plug flow and ideal CSTR and cannot fall outside this function. Thus, classical chemical engineering principles teach that productivity reactor with decreasing plug flow characteristics can be no higher than the productivity in the starting point plug flow reactor. Conversely, the selectivity in a reactor with decreasing back mixed characteristics can be no greater than the starting point back mixed reactor.

A number of review articles and patents have been published in which both slurry and fixed bed hydrocarbon synthesis reactions with various catalysts have been prepared. Among the articles are: Carrol, E.E. et al, Quarterly Tech. Prog. Report for Period 4/1-6/30/86, DDE Report #DE87 006115, Contract No. DE-AC22-84 PC 70030; Hall, C.C. et al J. Inst. Pet. <u>38</u> 845 (1952); Results from the Rheinpreussen-Koppers Demonstration Plant, presented by Kolbel, N. and Ralek, M., Catalyst Rev. Sci. Eng. 21 (2) 225 (1980); European Patent Application 0-194-552; U.S. Patent #4,619,910; Fujimoto, Faud Kajaka, M, Bull. Chem. Soc. Jpn. <u>60</u> 2237 (1987); Satterfield, C.N. et al Ind. Eng. Chem. Fund. <u>1985</u>, 24, 450-454; Dry, M.E. Catalysis Sci & Tech., Vol 1, ed. J.R. Anderson & M. Boudart, Springer Verlag (1981); Van Vuuren, Council for Scientific & Ind. Res. Rep; LENG 432 (1982).

This invention provides a process wherein catalyst stability is virtually constant (i.e., there is little if any catalyst deactivation with time), CH_4 selectivity is quite low, while at the same time CO productivity is quite high, and CO_2 selectivity is low.

For purpose of this invention, the following definitions apply:

CO productivity is the moles CO converted per gram of catalyst - hour;

CO_2 selectivity is the moles CO_2 produced per 100 moles CO converted;

CH_4 selectivity is the moles CH_4 produced per 100 moles CO converted;

C_5+ selectivity is the moles C_5+ produced per 100 moles CO converted; and

Catalyst stability is the percent loss in CO productivity per day.

The objective of this invention is providing a hydrocarbon synthesis system that allows the productivity of fixed bed reactors and the selectivity of back mixed reactors. This objective can be satisfied by using a cobalt/titania catalyst system in a bubble column reactor. A bubble column reactor is a slurry system: it operates in the liquid phase, but it is not a well stirred reactor. Therefore, the results, according to engineering principles should show lower productivity than a fixed bed and selectivity approaching that of a well stirred reactor. In fact, the bubble column with a cobalt/titania reactor system shows essentially at least the productivity of fixed bed reactors <u>and</u> the selectivity of well stirred reactors.

SUMMARY OF THE INVENTION

This invention comprises the reaction of hydrogen and carbon dioxide at hydrocarbon synthesis conditions over a non-shifting catalyst* comprising cobalt and a titania or titania-containing support, the catalyst being slurried in a liquid medium, preferably the indigenous hydrocarbon wax produced by the hydrocarbon synthesis process, and the reaction taking place in a bubble column that is not a well stirred reactor, that is, N_{pe} is greater than about 3 but less than about 10. In a preferred embodiment, the catalyst is promoted with rhenium. In another preferred embodiment the slurry liquid comprises hydrocarbon synthesis waxes boiling, at atmospheric pressure, above about 700°F, more preferably between about 700°F and about 1025°F. Following this invention

* Dispersion coefficient is described by Kobel and Ralek in "The Fischer-Tropsch Synthesis in the Liquid Phase", Catal.Rev.Sci.Eng., 21(2), 225-274 (1980).

* i.e., a catalyst which does not substantially promote the water gas shift reaction.

allows obtaining a relative productivity in a slurry bubble column at least as great as that obtained in a plug flow system, and ideally, a selectivity to C_5+ hydrocarbons at least as great as that obtained in a fully back mixed system.

DESCRIPTION OF THE DRAWINGS

Figure 1 shows the relationship between relative CO productivity and increasing degree of back mixing, that is from 0% back mixing in a plug flow reactor to 100% back mixing in a fully back mixed reactor. Bubble column results with a cobaltrhenium/titania catalyst are far in excess of predicted results.

Figure 2 shows the same relationship for a cobalt-rhenium/titania-alumina binder catalyst.

Reaction conditions for hydrocarbon synthesis processes are generally well known. However, for this invention temperatures may range from about 160°C to about 360°C, preferably about 190°C to about 230°C, and more preferably about 190°C to about 220°C. Pressures are normally above about 80 psig, preferably 80-600 psig, more preferably about 150 psig to about 350 psig. Increasing temperature generally increases CO productivity, all other things being equal, however, methane selectivity also tends to increase and catalyst stability diminishes. Thus, while CO conversion increases, the yield of desirable liquid products, e.g., C_5+, C_{10}+, may not be as great.

Hydrogen to carbon monoxide ratios may vary widely, also. Although the stoichiometric H_2:CO ratio for Fischer-Tropsch reactions approaches 2.1:1, most slurry phase processes use relatively low H_2:CO ratios. For example, U.S. 4,681,867 discloses preferred hydrogen:carbon monoxide operating ratios of 1:2 to 1:1.4. Slurry-type processes generally employ H_2:CO ratios of 1.0 or less and is evidence of either a less active catalyst or mass transfer limitations on CO entering the liquid phase. This invention is not limited to low ratios of H_2:CO and, in fact, H_2:CO ratios at or near the stoichiometric ratio are preferred. Thus, H_2:CO ratios may range from about 1.5:1.0 to about 2.5:1, more preferably about 1.2:1 to about 2.2:1.

The operation of bubble columns has been described generally in several prior art references, e.g., the Van Vuuren and Kolbel and Ralek references mentioned above, South African patent application 85/5317, U.S. patent 4,681,867, and European patent application 0313375. However, as previously mentioned, and in accordance with this invention, the bubble column is operated within a particular Peclet number range, i.e., greater than about 3 and less than about 10.

Peclet numbers were calculated, where possible and making reasonable assumptions where appropriate, from several prior art references regarding bubble column operation as shown below:

Deckwer et al, Chem. Eng. Sci., 29 2177 (1974)	N_{pe} - 0.39
Kato et al, J. Chem. Eng. Japan, 5 112 (1972)	N_{pe} - 0.35
Joshi, Chem. Eng. J., 24 213 (1982)	N_{pe} - 20
Field et al, Trans. Inst. Chem. Engrs., 58 228 (1980)	N_{pe} - 32
Mangartz et al, Verfahreustechnik, 14 40 (1980)	N_{pe} - 20.7
European Patent Application 0 313 375	N_{pe} - 94

In a bubble column reactor the catalyst is suspended and mixed by the motion induced by the rising gas bubbles. Feed gas is introduced into the bottom of the reactor and rises through the suspended catalyst as individual bubbles, thereby creating mixing by displacing both liquid and solids.

Hydrocarbon synthesis is a positive order reaction for hydrogen and at best zero order for carbon monoxide. Kinetics of the reaction and product selectivity then depend on the partial pressure of the reactants, hydrogen and carbon monoxide. The table below depicts a qualitative assessment of experimental facts, predictions based on engineering kinetics, and actual observance. P' denotes productivity, S denotes selectivity to C_5+ hydrocarbons, Δ is dispersion, and 1 is back mixed, 2 is fixed bed, and 3 is bubble column, PP is partial pressure, and P is total pressure.

	Experimental Assumptions		Predictions	Actual
	Back Mixed	Fixed Bed	Bubble Column	Bubble Column
P'	low	high	$P'_2 > P'_3 > P'_1$	$P'_3 \geq P'_1$
S	high	low	$S_2 < S_3 < S_1$	$S_3 \geq S_2$
Δ	∞ (1)	0	intermediate	intermediate towards fixed bed
PP_{CO}, PP_{H_2}	low	high	$PP_{CO_1} < PP_{CO_3} < PP_{CO_2}$	$PP_{CO_3} \sim PP_2$
P_{CO+H_2} (i.e., total pressure of $CO + H_2$)	high	low	intermediate	intermediate

(1) dispersion at full back mixing approaches infinity

Operation of bubble columns requires controlling variables other than temperature, pressure, and synthesis gas ratio. Thus, the liquid medium used for slurrying the catalyst can be generally any material that will be liquid at operating temperatures and pressures, maintain the catalyst in suspension, relatively or largely inert at reaction conditions, and a good solvent for carbon monoxide and hydrogen. Suitable materials can be saturated paraffins or olefinic polymers boiling above about 300°F, preferably at least about 550°F. Additionally, suitable slurry media can be Fischer-Tropsch waxes produced by any Fischer-Tropsch catalyst but particularly hydrocarbon materials produced using a cobalt on titania supported catalyst, and most preferably those liquids that boil above between about 700°F, still more preferably at about 700°F-1025°F. As the reaction proceeds, the indigenous wax, that is, the wax produced by the process of this invention will replace the material used for startup purposes, and eventually the slurry medium is most preferably substantially completely, e.g., at least 90%, indigenous wax.

Oxygenates tend to promote foaming and the slurry medium should contain no more than about 2 wt% oxygenates. Catalysts such as cobalt or cobalt-rhenium on titania or a titania containing support produce very low levels of oxygenates and are ideally suited for operation in this process.

The solids loading, that is, volume of catalyst per volume of slurry or diluent is up to about 50% and preferably ranges from about 10% to about 40%. The solids may range from powders to discreet particles, for example, from about 5 microns to about 1 mm, preferably about 10 microns to about 200 microns, more preferably from about 20 to 100 microns. (Sizes are expressed as mean particle size, e.g., because particles usually have a size distribution.)

Feed gas, which may be diluted with some inert gas, i.e., less than about 30 vol%, preferably less than about 20 vol%, such as nitrogen or CO_2, is usually introduced into the bottom of the reactor and bubbles,through to the top of the reactor. Use of higher levels of diluent gas will not only limit the maximum amount of product formed per total volume of gas fed to the reactor, but also require costly separation steps to remove the diluent from valuable H_2 and CO reactants. Feed gas velocity is usually as high as possible while avoiding foaming which results when gas bubbles do not disengage from the liquid. Thus, stable operation occurs when the gas contained in the slurry does not increase with time or increases only slightly. Foaming occurs when gas holdup time increases with time. Gas holdup can be defined as the fraction of gas in the three phase slurry mixture.

Suitable gas velocities are those that result in suspending the particles in the liquid medium and are usually greater than about 2 cm/sec.

Generally, a disengagement zone is provided where catalyst and product are separated. Separation may be effected in a quiescent zone where catalyst settles out of the slurry and product. Filtration can also be used and may be external or internal. With external filtration, the catalyst and slurry medium are recovered and recycled to the reaction zone. With internal filtration, liquid is removed as quickly as it is formed maintaining the liquid level at a somewhat constant volume in the reactor. Magnetic separation of catalyst from liquid may also be used.

As mentioned earlier, length to diameter ratios have an effect on determining the Peclet number, and greater length/diameter ratios tend toward plug flow as smaller length/diameter ratios tend toward increased back mixing. One skilled in the art can design suitable bubble columns by using the Peclet Number equation:

$$\frac{\Delta}{uL} \quad \frac{d^2X_{CO}}{dZ^2} - \frac{d\ C_A}{dZ} - \frac{(-r)}{V/Q} = 0$$

wherein Δ/uL is the reciprocal of the Peclet Number and L is the length of the reactor.

u is the feed gas velocity

Δ is the dispersion coefficient

X_{co} is the mol fraction CO or CO partial pressure

C_A is

Z is

-r is the molar rate of CO consumption

Q is gas flow rate, i.e., H_2 + CO + diluent per unit time

V is reactor volume

and the dispersion coefficient Δ is obtained from experimentation or texts and will be easily available to one skilled in the art.

We have found that only the catalyst of this invention provides results which have the attributes of plug flow productivity and fully back mixed selectivity.

The catalyst comprises cobalt on a primarily titania support. Cobalt is present in amounts sufficient to be catalytically active for Fischer-Tropsch synthesis. Usually cobalt concentrations may be at least about 5 wt%, preferably about 5 to 45 wt%, more preferably about 10-30 wt%. The cobalt or cobalt and promoter is dispersed on titania or a primarily titania support. Preferably the titania is in the rutile phase, that is the rutile/anatase ratio is at least about 2:3, preferably 3:2, more preferably at least 4:1 to completely rutile. The ratio is determined in accordance with ASTM D 3720-78: Standard Test Method for Ratio of Amatase to Rutile in Titanium Dioxide Pigments By Use of X-Ray Diffraction. The support is at least about 50% titania, preferably about 80% titania and may contain other inorganic oxides suitable as catalyst supports. Materials such as alumina, silica, and zirconia may be employed in amounts ranging from about 0.5 to 10 wt% as a binder material. Alumina and silica are preferred, alumina is most preferred.

The catalyst may also contain another metal that is either active as a Fischer-Tropsch catalyst, e.g., Group VIII non-nobel metals, such as ruthenium, or a promoter metal, such as, rhenium, hafnium, zirconium, cerium, thorium or thoria, and uranium. Promoter metals are usually present in amount of at least about 0.05:1 relative to cobalt, preferably at least 0.1:1, and most preferably about 0.1:1 to 1:1. Rhenium is a preferred promoter.

The catalytically active metal, or metals, preferably cobalt or cobalt promoted or modified with an additional metal, or metals, can be dispersed upon a calcined titania or titania-binder support in a manner which will distribute the metal, or metals, essentially uniformly throughout the support particles from the center outwardly, or essentially upon the peripheral surface of the particle. Catalysts can be prepared by the several techniques known in the art for the preparation of catalysts, generally. In distributing the metal, or metals, uniformly throughout the support, the metal, or metals, can be deposited on the support from solution in preselected amounts to provide the desired absolute amounts, and weight ratio of the respective metal, or metals. Suitably, e.g., cobalt, or cobalt and ruthenium or cobalt and rhenium, are composited with support by contacting the support with a solution of a cobalt-containing compound, or salt, or a rhenium-containing compound, or salt, followed by impregnation of the other component. Optionally, the cobalt, or cobalt and rhenium can be co-impregnated upon the support. The cobalt used in the impregnation can be any organometallic or inorganic compound which decomposes to give cobalt oxides upon calcination, or can be reduced directly to cobalt with hydrogen, such as cobalt nitrate, acetate, acetylacetonate, naphthente, carbonyl, or the like. Likewise the rhenium compound used in the impregnation can be any organometallic or inorganic compound which similarly decomposes, e.g., perrhenic acid, ammonium perrhenate and the like. The amount of impregnation solution used should be sufficient to completely immerse the carrier, usually within the range from about 1 to 20 times of the carrier by volume, depending on the metal, or metals, concentration in the impregnation solution. The impregnation treatment can be carried out under a wide range of conditions including ambient or elevated temperatures. On the other hand, the catalytically active cobalt component is most preferably dispersed and supported upon the peripheral or outer surface of calcined titania-binder particles as a thin catalytically active surface layer ranging in average thickness from about 20 microns to about 200 microns when employing particles of about 1 mm or above. However, slurry catalysts are usually powders as discribed above (even though larger particles can be slurried) and in that case the active surface layer may be about 2 to 20 microns, preferably 2-10 microns. The feature of a high cobalt metal loading in a thin catalytically active layer located at the surface of the particles can optimize the activity, selectivity and productivity of the catalyst in producing liquid hydrocarbons from synthesis gas, while minimizing methane formation in fixed bed or plug flow reactors.

The surface impregnated catalysts can be prepared by spray techniques where a dilute solution of a cobalt compound, alone or in admixture with a promoter metal compound, or compounds, as a spray is repetitively contacted with hot support particles. The support particles are maintained at temperatures equal to or above about 140°C when contacted with the spray, and suitably the temperature of the support particles ranges from about 140°C up to the decomposition temperature of the cobalt compound, or compounds in admixture therewith; preferably from about 140°C to about 190°C. The cobalt compound employed in the solution can be any organometallic or inorganic compound which decomposes to give cobalt oxide upon initial contact or upon calcination, such as cobalt nitrate, cobalt acetate, cobalt acetylacetonate, cobalt naphthenate, cobalt carbonyl, or the like. Cobalt nitrate is especially preferred while cobalt halide and sulfate salts should generally be avoided. The cobalt salts may be dissolved in a suitable solvent, e.g., water, organic or hydrocarbon solvent such as acetone, methanol, pentane or the like. The total amount of solution used should be sufficient to supply the proper catalyst loading, with the film being built up by repetitive contacts between the support and the solvent. The preferred catalyst is one which consists essentially of cobalt, or cobalt and promoter, dispersed upon the support, especially a support the titania portion of which is comprised of rutile. Suitably, the hot support particles are contacted with a spray which contains from about 0.05 g/ml to about 0.25 g/ml, preferably from about 0.10 g/ml to about 0.20 g/ml, of the cobalt compound or cobalt compound plus the compound containing the promoter metal, generally from at least about 3 to about 12 contacts, preferably from about 5 to about 8 contacts, with intervening drying and calcination steps being required 'to form surface films of the required thicknesses. The drying step is generally conducted at temperatures ranging above about 20°C, preferably from about 20°C to about 125°C, and the calcination steps at temperatures ranging above about 150°C to about 500°C.

For practical operations, bubble column operation should have CO conversions of at least about 40%, preferably at least 50%, and C_5+ selectivities of at least 70%, preferably at least 85%.

Accepted chemical engineering principles teach that a bubble column reactor must lie between the mixing regimes defined by plug flow and full back mixing. However, the cobalt or cobalt promoted, particularly with rhenium/titania, catalyst exhibits the productivity of a plug flow system without the selectivity debits that these principles predict.

EXAMPLES 1-8

Several experiments were conducted in plug flow (fixed bed), bubble column, and fully back mixed reactors (CSTR).

The results are shown in Table I below.

TABLE I

Reactor	Exp #	T, avg °C	P, psig	H_2/CO Feed Ratio	(1) Feed Gas Rate	% CO Conv	CO_2	Product Selectivities C_1	C_2-C_4	C_5+	Productivity	Wt% Co	Wt% Re
Fixed	1	214	280	2.07	0.909	89.6	0.2	7.03	~4	89	0.0110 (2)	12	0.5
Fixed	2	218	280	2.07	0.909	92.2	0.5	7.57	~4.3	88.1	0.0110 (2)	12	0.5
Fixed	3	222	280	2.08	0.909	91.0	0.67	10.9	~5.4	83.7	0.0110 (2)	12	0.5
Fixed	4	216	280	2.1	3.00	49	<.1	8.1	6.4	85.5	0.0430	12	1
CSTR	5	210	280	2.1	1.360	47.9	<0.05	4	4.1	91.9	0.0090	12	0.5
CSTR	6	215	280	2.1	0.909	65.8	<0.05	3	4	93	0.0081	12	0.5
Bubble	7	214	280	2.02	2.0	81.2	0.19	3.2	2.7	93.9	0.0420	12	1
Bubble	8	190	280	2.08	1.40	41.5	<0.05	2.3	3.3	94.4	0.0510	12	1
Bubble	9	230	280	2.07	2.2	91	1.0	6.9	3.9	88.2	0.051	12	1

Notes:

(1) liters syn gas @ 60°F/1 atm/gm cat-hour

(2) used catalyst

The Peclet Number of the fixed bed runs were all well above 10 and usually above about 30. The back. mixed reactor runs had Peclet Numbers approaching 0. The bubble column runs all had Peclet Numbers ranging between 3 and 10.

In hydrocarbon synthesis, the goal is avoiding methane formation, methane being virtually useless, other than a fuel, and having the lowest product value. In the plug flow (fixed bed) reactors, methane selectivity was relatively high, 7-10 wt%, while in the fully back mixed reactors (CSTR) which favor product selectivity, methane was relatively low, 3-4 wt%. However, the bubble column reactor exhibited methane selectivities in the same order as the CSTR, when accepted principles would have predicted methane selectivites somewhere between CSTR and plug flow.

Run 4 shows the best productivity for a fixed bed reactor but methane selectivity remains relatively high. Runs 5 and 6 represent a fully back mixed reactor system and productivities are relatively low. In fact, the productivity for Runs 1-3 even with a used catalyst, is higher than that for a back mixed reactor with fresh catalyst, thereby highlighting the effect of classical engineering principles.

Now, bubble column Runs 7, 8, and 9 all exhibit a productivity at least as high as that for the fixed bed Runs 1-4. However, contrary to what would have been predicted C_5+ selectivities are higher than for plug flow/fixed bed systems and methane selectivities are in the range of the back mixed systems.

Run 9 shows high productivity with equivalent C5+ relative to runs 1-4. However, the methane selectivity is relatively high as well. This can be readily accounted for by the temperature of Run 9 which was 230°C. While higher temperatures generally favor increased productivity, the selectivity is generally more to gases, e.g., methane, than to higher hydrocarbons.

Thus, the productivity of the bubble column reactors was much higher than the productivity of the CSTR runs. Thus, the bubble column exhibited fully back mixed selectivity with increased productivity.

The plug flow (fixed bed) reactor productivity of Run 2 is shown on Figure 1 above the fixed bed point.* The fully back mixed points are Runs 5 and 6. Because slurry phase hydrocarbon synthesis reactions are negative order with respect to CO, or at best, zero order, the best possible result in a bubble column would be equivalent productivity or a horizontal line from point 2 (zero order reaction). For negative order reactions, chemical engineering principles predict a line of negative slope from fixed bed (point 2) to fully back mixed (point 4 or point 5) with bubble column productivity falling on the lines of negative slope. The dotted circle represents the predicted point for bubble column operation for averaging Runs 5 and 6. However, actual bubble column results are shown by points 7 and 8, both of which have methane selectivities of the same order as back mixed Runs 5 and 6.

Figure 2 shows actual results for a plug flow (fixed bed) reactor at 215°C using 12 wt% CO, 1 wt% rhenium on a titania-3 wt% alumina binder support. The negative or zero order reaction rate for a fully back mixed system suggests a predicted value shown by the dotted circle above "CSTR", and therefore, bubble column results should be no greater than that shown by the dotted circles above "Bubble Column". However, the actual result showed a higher productivity than for plug flow with a methane selectivity of only 2.9 wt% versus a methane selectivity of 9.2 wt% for the plug flow reactor.

EXAMPLE 9

Experiments were conducted using different liquids as the slurry medium. Results are shown in Table II below.

The results were obtained using a stirred autoclave reactor in a semi-batch mode wherein liquid product was periodically removed through an internal filter element. When the start-up liquid was light (700°F-), volumetric activity was good but methane selectivity was relatively high. At the other end of the range, with 1025°F+ material, the methane selectivity was low but activity was relatively poor. The intermediate liquid, 700-1025°F, gave both relatively low methane selectivity and relatively high volumetric activity.

The six hour period was selected to allow the gas phase composition to reach steady state; after 48 hours the initial liquid was diluted with about 25 wt% of liquids produced by hydrocarbon synthesis.

* The graphs of the drawings show relative productivity values (productivity normalized to weight of catalyst), since productivity-comparisons with different processes cannot easily be made.

TABLE II

INITIAL SOLVENT CUT (°F)	500°F (C-16)	300-700°F	700-1025°F	700°F+	1025°F+
6 Hours On Syngas					
% CO CONVERSION	40	62	62	62	43
CH_4 SELECTIVITY	3.5	2.2	1.5	1.5	3.4
RELATIVE VOLUMETRIC ACTIVITY	64.5	100	100	100	69.3
48 Hours On Syngas					
% CO CONVERSION	48	50	58	58	48
CH_4 SELECTIVITY	2.8	2.2	1.3	1.6	1.6
RELATIVE VOLUMETRIC ACTIVITY	82.7	86.2	100	100	82.7

Process Conditions: 280 PSIG, 1000 GHSV, 195°C, H_2/CO ~2/1
Catalyst: 12% C_o - 1% Re/T_iO_2

Claims

1. A hydrocarbon synthesis process which comprises reacting hydrogen and carbon monoxide at reaction conditions in a slurry bubble column in the presence of catalyst containing cobalt on a titania support or a titania-containing support, and obtaining a relative productivity at least as great as obtained in a plug flow reactor.

2. The process of claim 1 wherein the catalyst contains rhenium in a weight ratio relative to cobalt of at least 0.05/1 (e.g., 0.1:1 to 1:1).

3. The process of claim 1 or claim 2 wherein the Peclet number is at least about 3 but not greater than about 10.

4. The process of any one of claims 1 to 3 wherein the catalyst is slurried in a wax having a boiling point above about 700°F (i.e., above about 371.1°C).

5. The process of claim 4 wherein the wax boils in the range of from about 700-1025°F (371.1 to 551.7°C).

6. The process of claim 4 or claim 5 wherein the wax is produced by a hydrocarbon synthesis process employing a cobalt or cobalt/rhenium on a titania or titania containing support.

7. The process of any one of claims 1 to 6 wherein cobalt is present in an amount of at least 5 wt%.

8. The process of any one of claims 1 to 7 wherein the reaction conditions include temperatures of from about 160-360°C, pressures of about 80-600 psig (0.5516 to 4.137 MPa), and hydrogen to carbon monoxide ratios of from about 1.5/1 to about 2.5/1.

9. The process of any one of claims 1 to 8 wherein the reaction conditions include temperatures of about 190-230°C, and pressures of from about 150-350 psig (1.034 to 2.413 MPa).

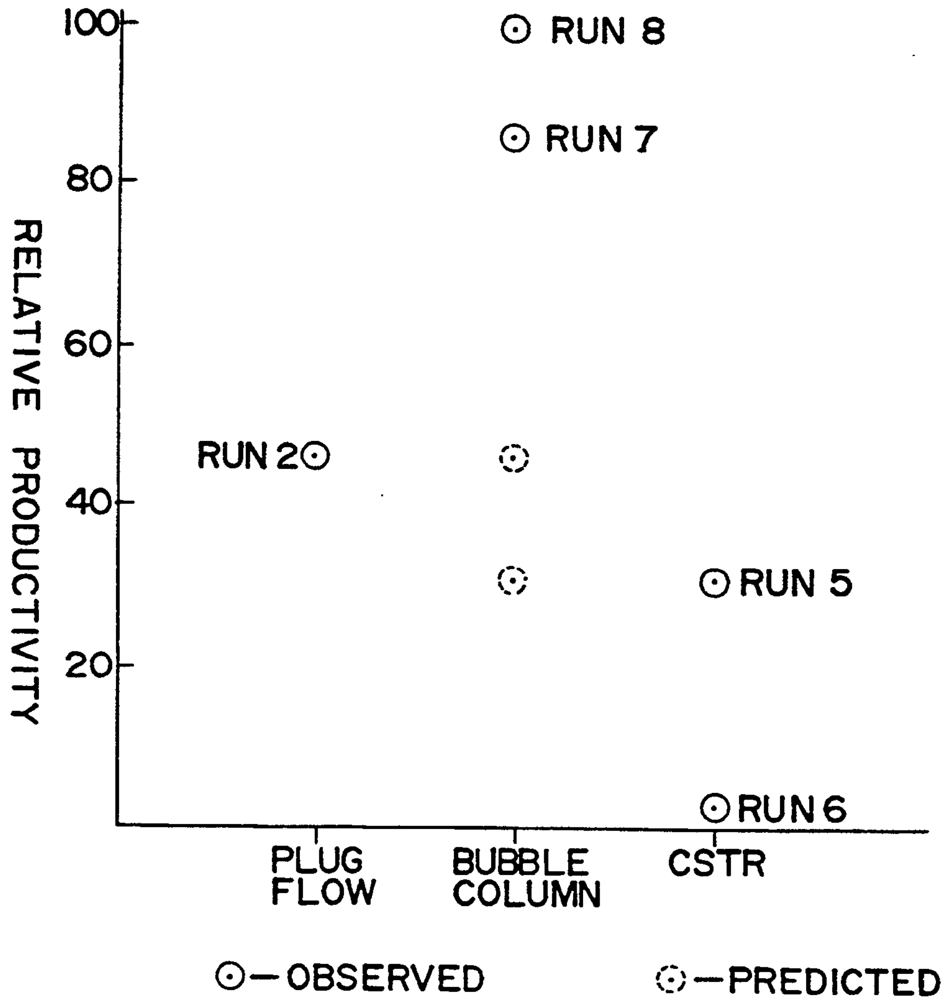
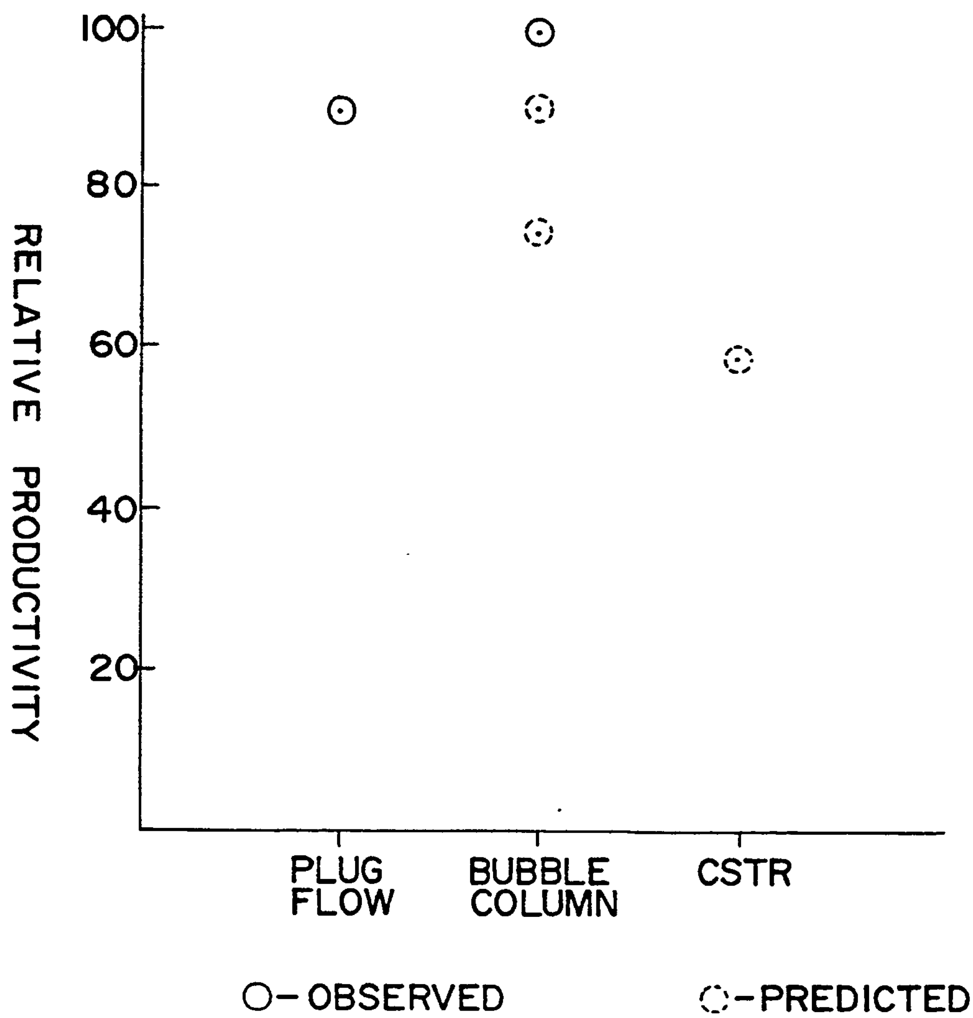

100
80
60
40
20
RELATIVE PRODUCTIVITY
RUN 8
RUN 7
RUN 2
RUN 5
RUN 6
PLUG FLOW
BUBBLE COLUMN
CSTR
—OBSERVED
—PREDICTED

FIG. I



100
80
60
40
20
RELATIVE PRODUCTIVITY
PLUG FLOW
BUBBLE COLUMN
CSTR
O- OBSERVED
-PREDICTED

FIG. 2