

ATTACHMENT XIII

Review of Fischer-Tropsch Work by Statoil

Three patents on Fischer-Tropsch synthesis catalysts assigned Den Norske Stats Olijeselskap A.S., Norway by Norwegian and U.S. investigators are summarized below (XIII.1-XIII.3). These individuals summarize the background for their invention. Anderson's book (XIII.4) is taken as the main background for the inventions and consider this book to indicate that the common Fischer-Tropsch (FT) catalysts are nickel, cobalt and iron. Nickel is considered to be active but it produces mainly methane. Among the Group VIII metals (old U.S. Periodic Table nomenclature), ruthenium is a very active catalyst and produces mainly hydrocarbons. Ruthenium is considered to have higher activity than Fe, Co or Ni at low temperatures. Other metals which possess high activity are considered to produce oxygenates and the patentees cite rhodium as an example (XIII.5). Osmium is considered to have moderate activity and Pt, Pd and Ir to have low activity (XIII.4,XIII.6,XIII.7).

These investigators recognize that others have used various combinations of metals for Fischer-Tropsch Synthesis (FTS). For example, nickel-doped cobalt has a higher productivity of methane than cobalt alone (XIII.8). On the other hand, Kobylinski taught that the addition of small amounts of ruthenium to a cobalt catalyst provided a material with a higher activity and with lower methane production than a similar catalyst comprised of cobalt without the ruthenium (XIII.9). Other work has documented that the activity is higher when ruthenium is added to the catalyst but the lower methane make is not as well documented.

These investigators indicate that, "In general, the catalysts [of combinations of metals] of these [prior] teachings have activities and selectivities which are within the

ranges of the individual components." They also note that the combination of a metal with certain oxide supports may lead to higher productivity of products, presumably due to the increase in surface area of the active metal component. The authors cite the case of using titania to support cobalt or cobalt-thoria (XIII.10) with a resulting increase in activity for the production of hydrocarbons and, by implication, attribute this beneficial effect to strong-metal-support-interactions (SMSI) (XIII.11).

Statoil investigators also indicate that a patent (XIII.12) teaches that combinations of cobalt, rhenium and thoria or cobalt and rhenium supported on titania are useful for hydrocarbon production. The patent indicates that similar improvements in activity can be obtained when using other inorganic oxide supports; however, the inventors indicate that titania is the only support specifically discussed in reference 12. These workers indicate that, "The typical improvement [reported in reference 12] in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2."

The major teaching of the Statoil patent is that the choice of support for Co is critical, "and the addition of a small amount of rhenium to an alumina—supported cobalt catalyst gives a much greater improvement in activity than the addition of rhenium to cobalt supported on any other inorganic oxide. To be effective as a support for cobalt, the alumina should possess low acidity, high surface area and high porosity. The method of adding the active metals to the alumina support is, according to the inventors, not critical.

Included in inventions by the Statoil investigators is the finding that it is beneficial to include a small amount (0.1 - 5%, preferably 0.1 to 2 wt.%) of a metal

oxide promoter in addition to cobalt and rhenium. The inventors conclude that the most preferable metal oxide is La_2O_3 or a mixture of lanthanides rich in La.

After preparation, the catalyst is calcined in a specified manner ultimately to attain a preferred temperature between 250 and 350°C for 2-5 hours. To activate the catalyst, it is reduced in hydrogen, again using a specified heating ramp to attain a preferred temperature of 300-400°C and holding at this temperature for 6-24 hours. Catalyst passivation and rereduction cycles may be carried out.

Catalyst testing was accomplished with a $\text{H}_2/\text{CO} = 2$ synthesis gas. A fixed-bed reactor (0.5 g catalyst) was utilized at atmospheric pressure and temperatures of 185, 195 and 205°C [a standard testing procedure involved 9.82 hr at 195°C, 4.3 hr at 205°C, 4.5 hr at 185°C and 9.5 hr at 195°C]. The flow rate of synthesis gas was 1.68 L/g catalyst/hr. Catalysts were compared using results obtained during the period of 10 and 30 hours-on-stream.

A series of identical catalysts (12 wt.% Co, 1 wt.% rare earth oxide), except for the content of rhenium, were prepared. For the alumina supported catalyst, there was a greater than 3-fold increase in CO conversion as Re content increases to about 1 wt.% and then a gradual decline in CO conversion was noted for further increases in Re content **Figure XIII.1**). The incorporation of these amounts of Re did not substantially increase the production of either methane (10-14%) or CO_2 (0.6-1.3%).

Two series of catalysts were prepared in which the Co loading was increased, one series with and one without rhenium. Re was added so as to keep the wt.% Co/wt.% Re constant at 12 for 3, 6 and 9 wt.% Co; for the 20 and 40 wt.% Co formulations, the ratios were 0, 4, 20 and 0, 8, 20 and 40, respectively. The impact of Re is evident in **Figure XIII.2** (apparently the data for the 20 and 40% Co are for Co/Re

ratio of 20 samples in Table V of reference XIII.1). This patent indicates that the improvement in activity due to the addition of rhenium increases as the cobalt content increases.

The Statoil investigators report that,

"The catalysts in Table VII (Table XIII.1 of this report) were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII (Table XIII.2 of this report) leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity."

Some may question the conclusion that a selectivity that includes 13-18 wt.% methane is a commercially attractive catalyst.

The MgO and Cr₂O₃ supports provide catalysts with very low activity. The zirconia and silica-alumina supported catalysts showed improved but low activity and poor selectivity for C₂⁺. For silica and titania supports, the cobalt only catalysts exhibited activities similar to an alumina supported cobalt catalyst. However, for the addition of rhenium to the alumina, titania and silica cobalt catalysts, a significant improvement was observed **only** for the material employing alumina as a support. The authors report that, "This [latter] result is surprising and would not have been predicted based on teachings in the prior art." [This does not appear to be in complete agreement with some Exxon patents.]

The "Weisz Window" provides a rule-of-thumb estimation of the productivity needed for commercial operation as $10^{-5} - 10^{-6}$ mole sec^{-1} (cm^3 reactor) $^{-1}$ (XIII.13). In the following we assume: (1) a fixed-bed reactor, (2) the density of the alumina supported catalyst as 2 g/cm^3 , (3) the flow of syngas as 1.88 NL/hr/g and (4) $\text{H}_2/\text{CO} = 2$. From Table XIII.2 for the Re containing catalyst (example 8), the CO conversion is 33%. Thus we calculate that the conversion of CO is 0.209 NL/hr/cm^3 . Using this value, we calculate that the conversion of CO is 0.52×10^{-5} mole/ cm^3/sec ; this is close to the value of the Weisz Window. If the rate increases directly with pressure, then the conversion is in the Weisz Window at 10 atm.

The incorporation of alkali in the cobalt catalyst impacts both the activity and hydrocarbon product distribution. For a catalyst containing Co, Re and rare earth oxide, the incorporation of alkali caused (1) a decrease in CO conversion and (2) an increase in the alpha value of the products (Tables XIII.3 and XIII.4; Figures XIII.3 and XIII.4). However, the conclusion that the alpha value depends upon the K/Co ratio depends entirely upon the two data points obtained for the lowest to K/Co ratios. If these two points are not reliable (or are not considered), the K/Co ratio has no impact upon the value of alpha. The question of promotion changing activity and selectivity is complicated for a cobalt catalyst. Anderson pointed out that selectivity changes can be effected by changing reactor pressure (XIII.14).

van Berge and Everson (XIII.15) point out that the data in reference 1 were obtained at different conversion levels, and thus different reactor partial pressures, and that the chain of chemical promotion by K, Na, Cs and Rb could not be regarded as conclusive. Studies performed at Sastech (XIII.16) are reported to confirm the ineffectiveness of chemical promotion of cobalt Fischer-Tropsch catalysts.

The loss of activity with increasing alkali content allows one to calculate, assuming one K eliminates 1 site, that only 4.5 atomic % of the Co is catalytically active. At first glance, it appears that the data are consistent with each potassium eliminating one catalytic site, or some constant fraction of a site (Figure XIII.4). However, it must be realized that the addition of alkali causes an increase in \bar{R}_n , and a corresponding increase in the average molecular weight of the products. The average number of growing chains, and the average number of catalytic sites, is directly proportional to the average molecular weight of the growing chains (e.g., the average molecular weight of the products). Hence,

$$\overline{\text{No. of Sites}} \propto \overline{M.W.}^{-1/(1+a)}$$

When this is taken into account, the catalytic sites decrease more rapidly than the increase in K, or at least those catalytic sites that initiate chain growth must do so (Figure XIII.5).

During the past few years, Statoil has obtained patents related to a catalytic multi-phase reactor, and specifically to catalyst wax separation (XIII.17-XIII.21). An example of such a reactor is illustrated in Figure XIII.6 (XIII.17). "This is a solid/liquid slurry reaction apparatus which comprises: a reaction vessel (11), a filter member (13) in contact with the slurry (16) defining a filtrate zone which is separated from the slurry and having an outlet (23) for filtrate product (32); means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry (XIII.17)."

One of the claims is for a filter element **(22)** which comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles (XIII.17). The hydrostatic pressure preferably results from the filter member being submerged in the slurry.

The pulsating pressure can be applied directly to the filtrate or to the gas space above the filtrate, preferably by the action of a reciprocating piston in a cylinder. The pressure fluctuation may be of the order of 10 to 200% differential (preferably 2 to 5 mbar).

The filter element material and catalyst are preferably selected so that the maximum hole or pore size of the filter element is of the same order of the catalyst particle size. It might be expected that catalyst would plug the filter but this is found not to be the case. Of course, the particle size of the catalyst may be much larger than the maximum hole or pore size of the filter.

In operation, products pass through the filter element **(12)** to form a product filtrate **(32)** which is free of catalyst. Any gaseous products and unconverted reactants that pass through the filter element can be vented through outlet **(31)** and subsequently through **(17)**. The product filtrate **(32)** leaves through level device **(23)** and outlet **(24)** to collect in **(25)** for regulated continuous or periodic removal.

In an example, a reactor of 4.8 cm x 2 m dimensions was filled with approximately 10 wt.% of a Co on alumina catalyst (30 to 150 Fm). The gas (H₂, CO and N₂) was fed at a superficial gas velocity of 4 cm/s. The temperature was 230°C and pressure was 30 bar.

The filter unit was located in the upper part of the reactor and comprised of Sika stainless steel sintered metal cylinder Type R20 produced by Pressmetall Krebsöge

GmbH. The filter had an outer diameter of 2.5 cm, a height of 25 cm and an average pore diameter of 20 F m.

The slurry was effected using a poly-a-olefin liquid. Fischer-Tropsch product **and a poly-a-olefin that was fed to the reactor** were both withdrawn through the filter unit (ratio of Fischer-Tropsch and poly-a-olefin not specified). Liquid withdrawal rate varied from 2.5 to 320 g/hr, depending on Fischer-Tropsch synthesis rate and feed rate of poly-a-olefin. The experiment lasted for about 400 hrs and approximately 30 liters was withdrawn through the filter unit. Most would therefore conclude that the test was of a short duration compared to the length of time that a commercial unit must operate. Furthermore, the product was diluted with start-up solvent that was added during the run. Thus, it appears that this example is applicable to a limited process scheme, and not for all process schemes.

A solid/liquid slurry reaction apparatus with a filtration section has been submitted for patent coverage (XIII.22) and is illustrated in **figure** XIII.7. The teachings of this patent application is based upon a recent report identified only as "a report issued by the United States Department of Energy." The DOE report addressed the question of catalyst/wax separation in Fischer-Tropsch slurry reactor systems and concludes:

"Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature

termination of the run, and commercial plants are not allowed to take chances."

The patent applicants have discovered that, contrary to the teachings of the DOE report, "...it is possible to provide a continuous reaction system for a Fischer-Tropsch synthesis in which it is not necessary to perform the solid/liquid separation in an external filter unit. Furthermore, a sufficiently high flow rate of filtrate for commercial operation can be achieved."

The description in the patent application indicates that the filter screen and the catalyst are similar, or identical, to those described in the previous patent application (XIII.17). In this instance, however, the filter screen has been made a part of the slurry reactor wall or, as shown in **figures** XIII.8 and XIII.9, it may be incorporated in multiple locations of the slurry reactor wall. In the example shown in **figure** XIII.7, a conical section **(15)** is included as an expansion chamber to prevent the slurry from foaming over and to define a gas space **(16)** above the reaction zone. The cone-shaped portion **(15)** may contain additional means (that are not shown nor specified) for breaking up or reducing foam formation.

The invention was described and was then further illustrated with the following example. Experiments in a laboratory using an apparatus similar to that shown in **figure** XIII.7 were carried out. The length and diameter of the unit were 1250 mm and 55 mm, respectively. The filter member had a mean pore size of 30 F m and a length of 200 mm. A heat transfer oil (diethyl benzene (95%) and minor amounts of other alkyl benzenes) and 20 wt.% alumina were used as the slurry phase. The alumina particles initially had a cut-off at 53 F m. The experimental conditions in the example were: 1 bar pressure, 20-25°C and 6 cm/s superficial gas velocity. After an initial start-up

period, the separation capacity became approximately constant at a level of 750-800 kg/m²h. The calculated pressure differential was approximately 5 mbar. After 40 days of operation, there was only a slight decrease in separation capacity.

The section of the DOE report that was quoted above was concerned with an operating slurry bubble column reactor for Fischer-Tropsch synthesis at a commercial scale operation. The example provided by the patent applicants was for a cold model with only an alumina solid and without Fischer-Tropsch synthesis. It would appear that the patent applicants have not shown by their example anything that would be contrary to the teachings of the DOE report since the patent applicants did not operate at any of the conditions necessary for a commercial Fischer-Tropsch plant that is currently being operated successfully.

Another patent application (XIII.19) relates to a vessel that contains a number of vertical reaction tubes, each suitable for multi-phase catalytic conversions (**figure XIII.10**). In this application, the above DOE report is quoted and the teaching that the applicants have provided a means of accomplishing this. Each reactor tube has essentially the features of the reactor described in the previous reference XIII.ref. 18). In operation, the gas is preferentially fed to each multi-phase catalytic reactor. These reactors are held in place by plates **(18)** and **(14)**; in effect these two plates and the vessel wall **(12)** provide the vessel to hold the heat transfer liquid/vapor.

The filter section of each reactor tube is located above the top plate **(14)**, which serves to hold a level of the wax following separation from the catalyst slurry. In another version, a sieve **(34)** surrounds each filter and is utilized to maintain a minimum wax level for each reactor tube so that the tube does not lose liquid level so

that the reactor tube is depleted of liquid. Thus, the sieve extends above the level of the wax filtrate that is maintained on plate **(14)**.

The heat exchange medium is preferably a liquid at its boiling point; water is the preferred medium since the heat of reaction can be recovered as steam to be used to generate electricity or provide heat for plant operations.

In the only example of the patent application, a slurry bubble column Fischer-Tropsch reactor **is simulated** using a two phase quasihomogeneous one dimensional model. They use typical catalyst performance data contained in US 4,801,573. The simulations are utilized to **calculate** optimum values for the reactor and its operation.

Experimental data of an operating Fischer-Tropsch reactor are not provided in the application. Since the DOE report was for an operating reactor that actually effects a separation of wax and catalyst, it is difficult to understand how the applicants can show that they have provided a solution to the problems enumerated in the DOE report.

A patent application (XIII.20) describes a separation device that has as its main object the prevention of gas from being entrained in the liquid phase in cases where it is desirable to separate gas and liquid or immiscible liquids.

A recent patent application describes a method of regenerating a catalyst in a Fischer-Tropsch synthesis reaction (XIII.21). Examples of regeneration procedures are reviewed and the conclusion is that "These arrangements all suffer the drawback that a separate source of H₂ gas must be provided to achieve regeneration." The present invention (XIII.21) is to overcome this drawback. While the use of hydrogen could be a drawback, it would appear to be so only from an operational viewpoint. For example, Sasol produces a nearly pure hydrogen stream by a pressure swing adsorption

process. It would be a disadvantage to utilize a stream of pure CO since this stream is not available in a normally operating Fischer-Tropsch plant.

Schematic sections through a slurry reactor (figure XIII.12) and a slurry reactor with a separate regeneration vessel (figure XIII.13) are shown. Details of the slurry reactor (figures XIII.12 and XIII.13) are not provided in this patent. To effect regeneration, the feed parameters of the synthesis gas are adjusted to increase the conversion of CO in the synthesis gas until the H₂/CO ratio of the gas leaving the reaction zone exceeds 10:1 and then maintaining this conversion level during the regeneration mode for some period of time to effect regeneration to a desired level. Preferable, the CO conversion is between 95 and 100%, most preferable 100%. Thus, the preferred H₂/CO ratio is 20/1, and most preferably, greater than 30/1. To achieve this high hydrogen/CO ratio, the flow is decreased, preferably slowly, so that the conversion increases to attain the desired level. Alternatively, hydrogen could be increased in the synthesis gas by modification of the generation step of the synthesis gas.

At the high conversion level, the reaction changes from synthesis to a regeneration mode. The regeneration mode is characterized by: high H₂/CO ratio, low C₅₊ selectivity and high CO₂ selectivity. This is taken to indicate a high water gas shift rate due to the high hydrogen partial pressure. Experimentally, it has been found that a few hours of regeneration is normally sufficient; however, it may take longer for more severely deactivated catalysts.

When a separate regeneration vessel is used, "normal" conditions for synthesis are maintained on the synthesis side and the high hydrogen (100% CO conversion)

condition is maintained on the regeneration side. Preferably, there is a flow of deactivated and regenerated catalyst between the two sides.

Two examples are given for the regeneration. In the first example, a catalyst containing 12% Co and 0.5% Re on alumina are used at 220°C and 20 bar (2 MPa) total pressure in a continuous slurry stirred tank reactor (CSTR). The reactor volume is 2 L and is half-filled with slurry. The H₂/CO inlet synthesis gas ratio was 2; the exit gas was also close to this value. The initial stable hydrocarbon activity is set relative to 1; note that this is based on hydrocarbon production. The CO conversion was 63% at this hydrocarbon production level of 1.

After the catalyst had operated for a few days, the catalytic activity had declined so that the relative hydrocarbon productivity activity number had declined to 0.69. At the relative activity number of 0.69, the CO conversion was 68% at a flow rate of 2100 NL/kg cat./hr. It is not clear whether this flow rate is for synthesis gas or for CO only; in the following we shall **assume that the flow is for CO only**. The C₅₊ selectivity was 89.4%. At this stage of catalyst deactivation, a decrease of the flow rate to 1050 NL/kg cat/hr resulted in an increase in CO conversion to 88% with a C₅₊ selectivity of 89.9%.

To establish a regeneration mode at this point (0.69 relative activity), the flow rate was reduced to 750 NL/kg cat/hr and the CO conversion was 99%. The exit H₂/CO ratio was 14/1. This regeneration mode was maintained for 10 hours and was then brought back to the Fischer-Tropsch mode by increasing the flow rate to 2100 NL/kg cat/hr. The reaction continued to produce a C₅₊ selectivity of over 88%. The relative activity at these final Fischer-Tropsch conditions was 0.77. This value is above the value of 0.69 for the deactivated catalyst but still considerably below the value of 1.0 for the fresh catalyst.

Example 2 is for a catalyst that contains 20% Co and 1% Re on alumina; however, the data are less extensive than for example 1. They report that the 20 wt.% Co catalyst was brought back to the initial level following 24 hours of the regeneration mode whereas 10 hours for the 12 wt.% Co catalyst only restored the activity to 77% of the initial activity.

The hydrocarbon production of the deactivated catalyst (relative activity of 0.69) in Example 1 corresponds to 0.983 g hydrocarbon/g cat/hr. For the fresh catalyst (relative activity of 1.0) the hydrocarbon productivity is calculated by us to be 1.29 g hydrocarbon/g cat/hr. For the reactivated catalyst (relative activity 0.77) the productivity is 1.16 g hydrocarbon/g cat/hr.

If it is assume that the catalyst productivity is linear in Co content, the productivity of the deactivated 20 wt% Co catalyst would be 1.49 g hydrocarbon/g cat/hr and that of the fresh and regenerated catalyst would be 2.15 g hydrocarbon/g cat/hr.

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Table XIII.1 (from ref. XIII.1)						
Example No.	Support	Weight of Support, g	Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, Wt.%	
			Co(NO ₃) ₂	HReO ₄ *	Co	Re
28	Silica	20	13.47	---	12	---
29	Silica	20	13.62	0.38	12	1.0
30	Titania**	25	16.84	---	12	---
31	Titania**	24.64	16.78	0.46	12	1.0
32	Titania***	25	16.84	---	12	---
33	Titania***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	---	12	---
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	---	12	---
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica-alumina	20	13.47	---	12	---
39	Silica-alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	---	12	---
41	Zirconia	20	13.62	0.38	12	1.0

* Weight of 82.5% perrhenic acid solution.
** Calcined at 500°C.
*** Calcined at 600°C.

Table XIII.2 (from ref. XIII.1)

Example No.	Co %	Re %	Support	CO Conversion %	C ₂ ⁺ Selectivity %	CH ₄ Selectivity %	CO ₂ Selectivity %
1	12	---	Al ₂ O ₃	12	90.0	8.9	1.1
8	12	1	Al ₂ O ₃	33	87.7	11.4	0.9
28	12	---	SiO ₂	11	90.1	8.7	1.2
29	12	1	SiO ₂	12	88.1	10.7	1.2
30	12	---	TiO ₂ *	11	87.6	11.8	0.6
31	12	1	TiO ₂ *	17	86.5	12.8	0.7
32	12	---	TiO ₂ **	11	87.6	11.7	0.7
33	12	1	TiO ₂ **	17	85.8	13.5	0.7
34	12	---	Cr ₂ O ₃	1	83.5	15.5	1.0
35	12	1	Cr ₂ O ₃	2	80.8	12.3	6.9
36	12	---	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	---	SiO ₂ /Al ₂ O ₃	5	76.3	22.2	1.5
39	12	1	SiO ₂ /Al ₂ O ₃	6	78.6	19.8	1.6
40	12	---	ZrO ₂	4	80.9	16.3	2.8
41	12	1	ZrO ₂	7	78.8	18.7	2.5

* Support calcined at 500°C.

** Support calcined at 600°C.

Table XIII.3 (from ref. XIII.1)										
Example No.	Wt. of Al ₂ O ₃ , g	Type of Alkali	Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst, Wt.%			
			(a)	(b)	(c)	(d)	Co	Re	RE	Alkali
42	300.0	---	1039.6 5	17.2 1	13.9 9	---	40	2.0	1.0	0.0
43	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
44	75.0	K	256.36	4.25	---	0.67	40	2.0	---	0.2
45	175.0	K	609.03	10.0 8	8.20	1.59	40	2.0	1.0	0.2
46	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
47	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
48	60.0	Na	205.49	3.40	---	0.93	40	2.0	---	0.24
49	60.0	Cs	209.55	3.47	---	2.12	40	2.0	---	1.36
50	65.0	Rb	225.38	4.23	---	1.71	40	2.0	---	0.87
51	20.0	---	13.78	0.38	0.62	---	12	1.0	1.0	---
52	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
53	20.0	Li	13.64	0.38	---	0.11	12	1.0	---	0.05
54	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
55	20.0	Cs	13.67	0.38	---	0.10	12	1.0	---	0.3
56	20.0	Cs	13.83	0.38	0.62	0.10	12	1.0	1.0	0.3

(a) Co(NO₃)₂·6H₂O
(b) 82.5% HReO₄ solution, except for example 50 which was 72.9% HReO₄
(c) Rare earth nitrates (RE) (see example 1)
(d) LiNO₃, NaNO₃, KNO₃, RbNO₃ or CsNO₃

Table XIII.4 (from ref. XIII.1)					
Example No.	Alkali		CO Conversion %	CH ₄ Selectivity %	Product Alpha*
	Type	Content Wt.%			
42	---	---	52.5**	14.2**	0.75**
43	K	0.1	52	8.6	0.86
			50	11.1	0.79
44	K	0.2	43	9.3	0.83
45	K	0.2	51	9.5	0.84
			44	11.6	0.84
			41	9.4	0.81
46	K	0.4	30	7.3	0.87
			35	7.8	0.85
47	K	1.0	12	7.0	0.88
			9	7.9	0.85
			6	6.2	0.87
48	Na	0.24	21	8.3	0.82
49	Cs	1.36	14	8.5	0.86
50	Rb	0.87	11	7.3	0.86
51	---	---	31.7***	10.9***	0.77***
52	K	0.1	19	7.6	0.78
			22	9.8	0.84
53	Li	0.05	31	11.7	0.78
54	Li	0.05	27	12.0	0.78
55	Cs	0.3	21	11.1	0.83
56	Cs	0.3	21	10.3	0.84

* Calculated by plotting $\ln(W_n/n)$ vs. n , where n is carbon number and W_n is the weight fraction of the product having a carbon number n , and determining the slope of the line.

** Average of 21 tests.

*** Average of 6 tests.

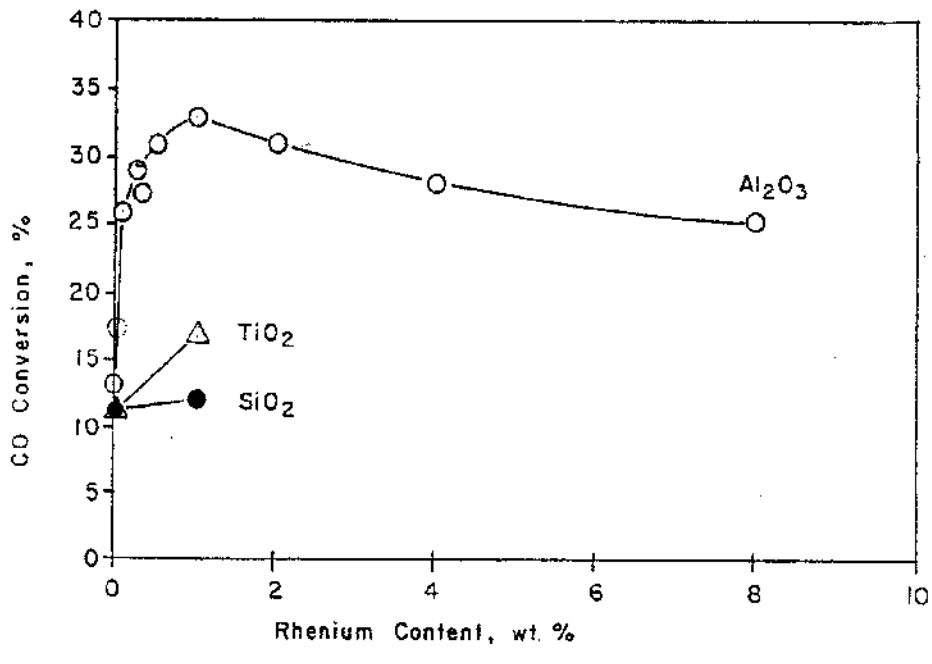


Figure XIII.1. Effect of rhenium on CO conversion catalysts containing 12% cobalt (from ref. XIII.1).

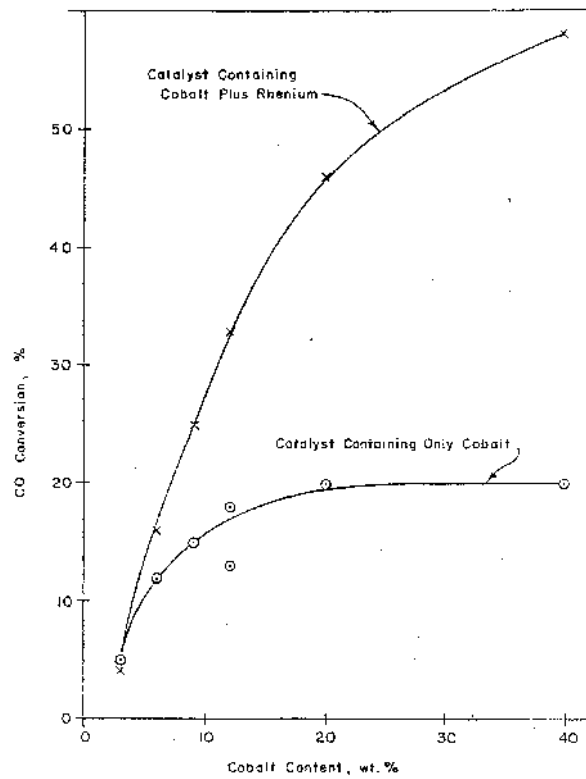


Figure XIII.2. Effect on conversion of adding rhenium to cobalt on alumina catalyst (from ref. XIII.1).

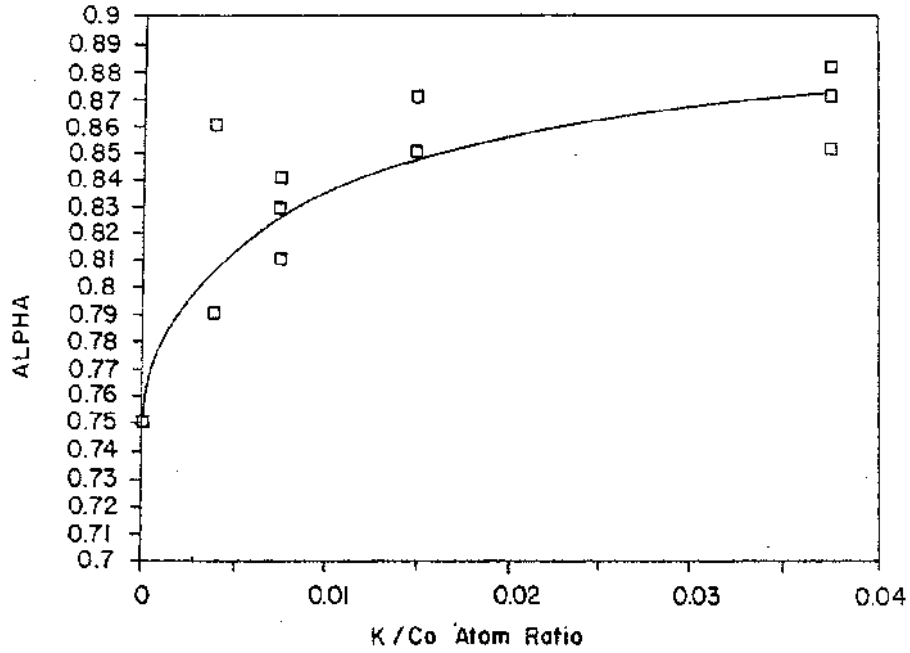


Figure XIII.3. Alpha versus K/Co (from ref. XIII.1).

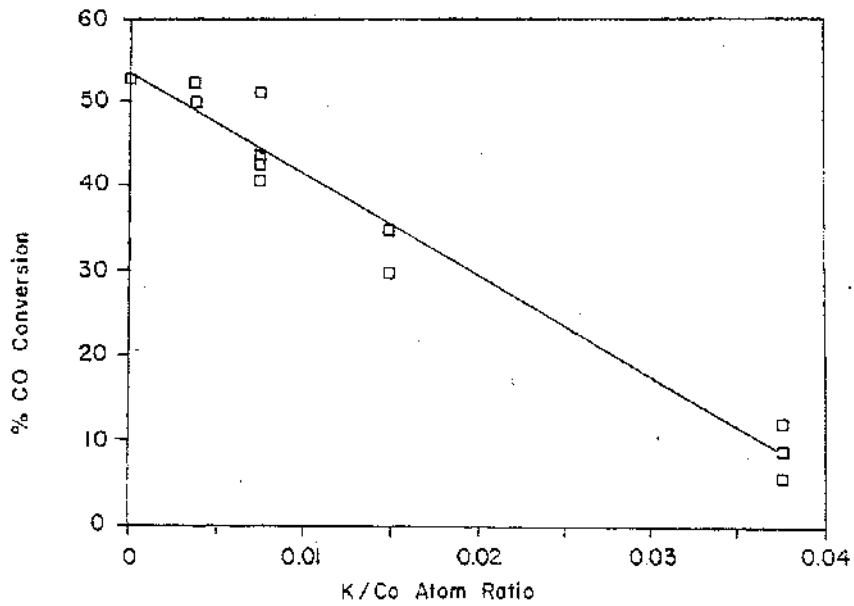


Figure XIII.4. Percent CO conversion versus K/Co (from ref. XIII.1).

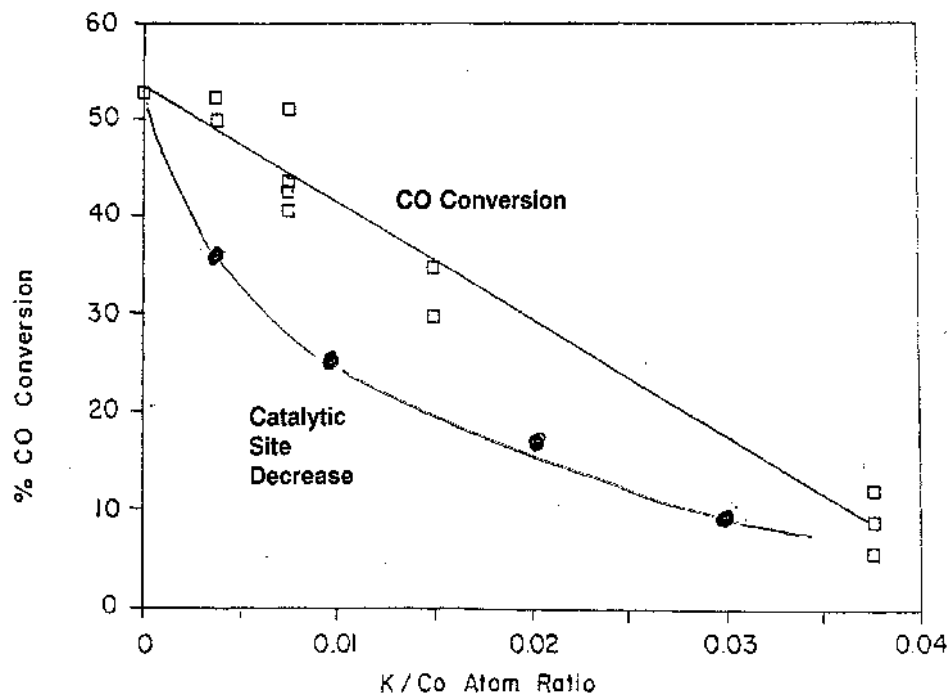


Figure XIII.5. Percent CO conversion versus K/Co (from ref. XIII.1) and our decrease calculated assuming a is related directly to the site density.

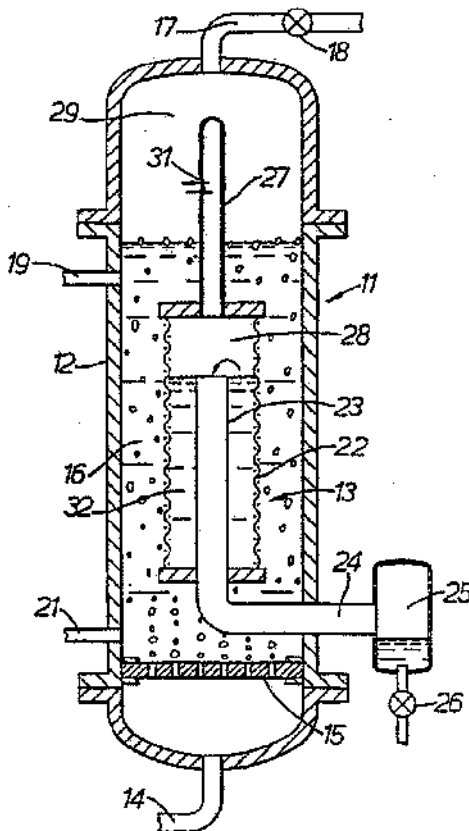


Figure XIII.6. Slurry reactor with internal filter for wax/solids separation from ref. XIII.17).

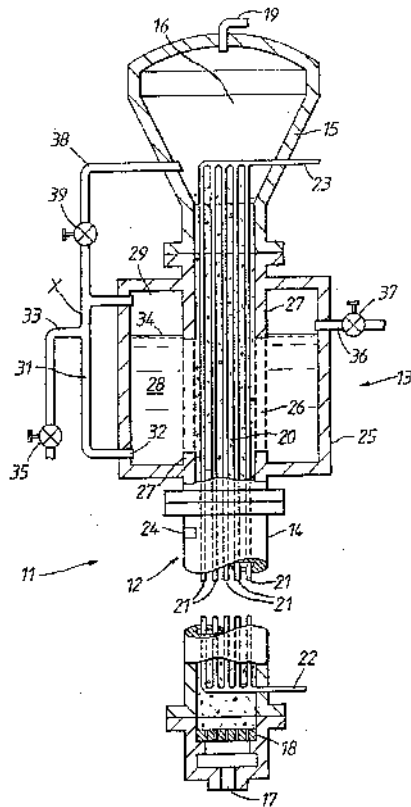


Figure XIII.7. Slurry reactor incorporating a filtration system into the reactor wall (from ref. XIII.22).

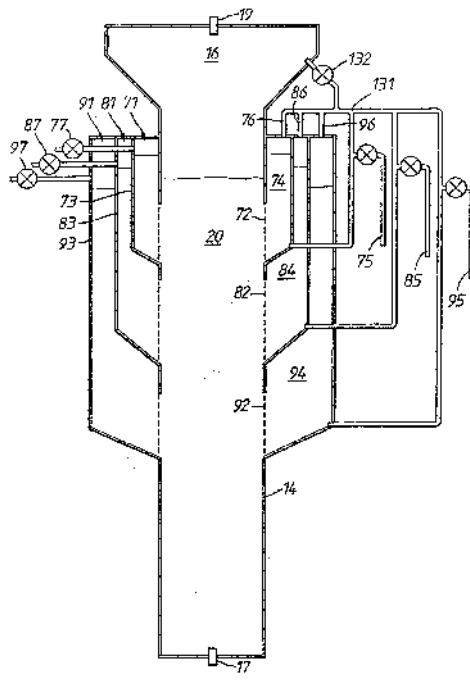


Figure XIII.8. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

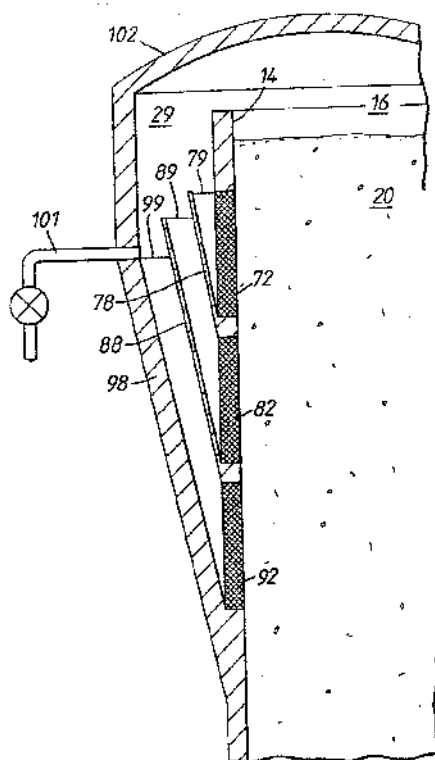


Figure XIII.9. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

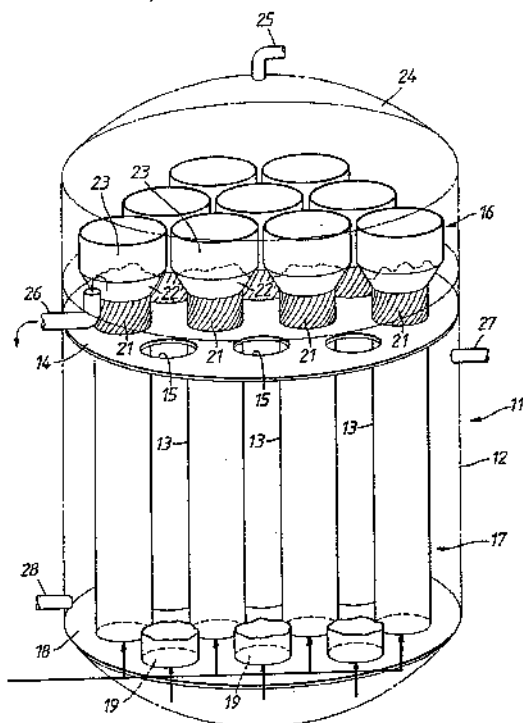


Figure XIII.10. A multi-phase catalytic reactor with multiple tubes for slurry phase reactor systems (from ref. XIII.19).

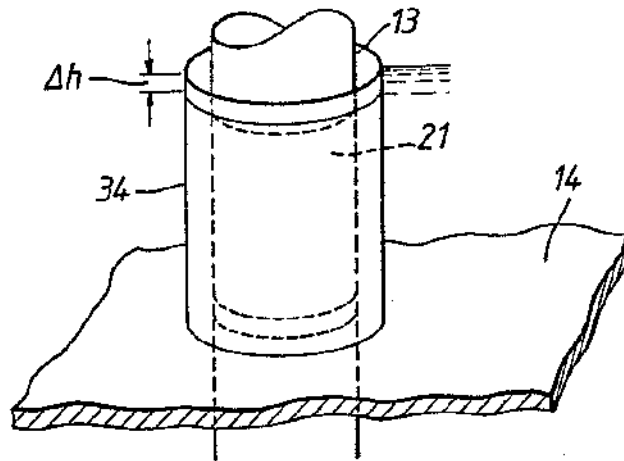


Figure XIII.11. Schematic of sleeve on reactor tube in Figure 10 to maintain slurry level in each reactor tube (from ref. XIII.19).

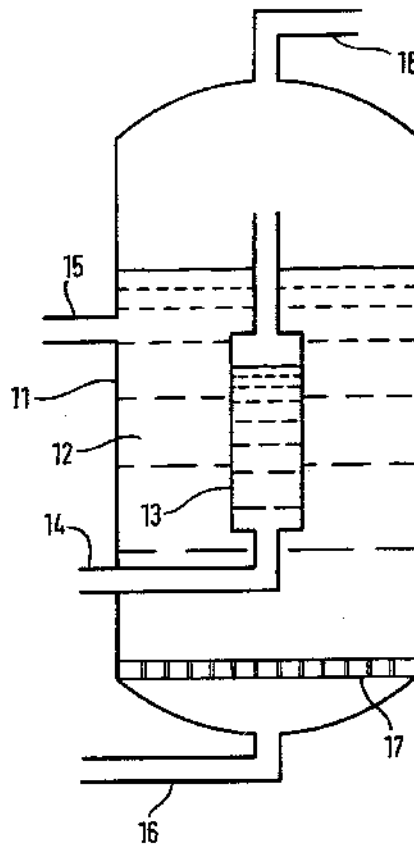


Figure XIII.12. Schematic of slurry phase reactor with internal wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

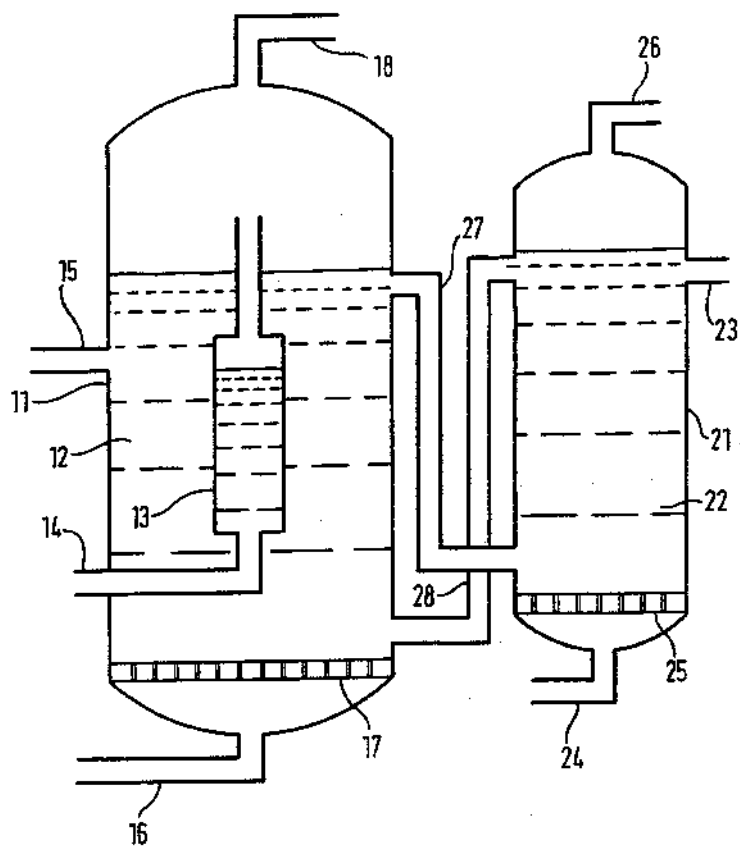


Figure XIII.13. Schematic of slurry phase reactor with external wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).