Design - Development of Fischer - Tropsch Synthesis Reactor & Catalysts and their Interrelationship

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Abstract

The Fischer-Tropsch (F-T) Synthesis process is an unique example of catalyst and catalytic reactor interrelationship, as a dozen type of reactors have been investigated during the development of the process since 1923. From these investigations it is seen that different types of catalysts are needed for different types of F-T reactors. Relevant fundamental design aspect of various type of F-T reactors have been examined from the view point of catalyst - reactor interrelationship. Analysis have shown the role of active site and its concentration, pore size, effect of liquid hydrocarbons presence during synthesis in the pores on pore diffusion and ultimate effective utilization of total volume of catalyst and reactor. Different physical properties of catalyst have been found to be associated with different reactor configuration while dealing with heat transfer system design.

Introduction

Though F-T synthesis process is being exploited commercially on limited scale for more than half a century, the development work is continuing for the last eighty years. Industrial and academic interest in F-T synthesis is evident from various publications [1,2J that are appearing continuously. The objectives of the present paper are to examine the design correlations used in the design-development of F-T reactors and reactor specific catalysts and interrelation between them. Nearly a dozen type of reactors have been studied and keeping with the variation of the reactor design, changes in the Physico-chemical properties, selectively etc. of the catalysts have been made. 1 Such characteristic of the F-T synthesis has provided scope to study the interrelationship aspect.

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Catalyst and Catalytic Reactors Interrelationship

For heterogeneous gas-solid catalytic vapour phase reaction, development of the full scale process like F-T synthesis involve proper design of both the catalyst and catalytic reactor. That the two are interdependent can be found from the following points:

- different type of reactors can be employed for a particular process as in F-T synthesis and' according to changes in the preparation methods of the catalysis viz. precipitated, fused, sintered lathe turnings, mill scale, Steel shot, steel wool etc., various types of reactors like fixed bed, fixed fluidized bed, entrained flu1dzed system, slurry phase are employed. For different type of reactors, changes in the composition, shape, strength and pre-treatment method of the catalysts are made.

- the volume of the catalyst required for specific production depends on the rate of reaction and the same in turn determines the initial 8ize of the reactor. The disposition of the catalyst determine the reactor configuration e.g. tubular/multistage if fixed bed reactor is considered, and fixed fluidized bed/antrained fluidized system if fluidized bed is considered which determines the final size of t he reactor

- Catalyst selectivity may influence type of reactor to be employed in a multi product reaction system like F-T synthesis e.g. fluidized bed reactor is selected for lower boiling range hydrocarbons production as main products and when formation of wax is absolutely undesirable.

- for same volume of catalyst higher productivity can be achieved by proper combination of improved reactor design, use of different type of reactors, catalyst layout arrangement and corresponding changes in the shape and size of the catalyst e.g. difference between old and improved fixed bed F-T reactors or between fixed bed, fixed fluidized bed and slurry phase reactors.

- The approximate productivity in term of space-time-yield of f-T process increases in the order of old fixed bed, slurry phase, improved fixed bed and fixed fluidized bed reactors as 250,900, 14.00 and 3500 Kg/N.3 catalyst/day respectively.

- Catalyst deactivation period also decides the. type of reactor to be employed. Catalyst which deactivates quickly requires reactors which allow on-stream discharging and recharging facilities e.g. F-T fluidized bed and slurry phase reactors.

- Selection of reactor construction material may also depend on the catalyst, considering methanol and hydrocarbon synthesis from. CO and H2 the use of carbon steel reactor at high pressure leads to poisoning of typical Cu - Zn – Al203 catalyst for methanol synthesis due to the formation of iron carbonyl while no such poisoning occurs at the operating conditions during F-T synthesis with typical Fe - Cu - K_2O / Co - MgO catalyst.

Elaboration on these points has been made under the heading “Design-Development of F-T Catalysts and reactors”. Before discussing design-development aspect the evolution of F-T synthesis reactors is described very briefly for better understanding.

Evolution of F-T synthesis Reactors:

Evolution of F-T synthesis reactors is a classic example of catalyst-catalytic reactor interrelationship and design of various type of heterogeneous gas-solid catalytic vapour phase reactors for such a multi product reaction system. The reactors with their main features have been listed in Table 1. Like any other heterogeneous gas-solid catalytic vapour phase reaction process fixed bed reactor was used in the beginning for the development of F-T technology. Four types of fixed bed reactors are shown in fig. 1. Amongst these two shell and tube type fixed bed reactors (fig.1a, fig.1b), the second one i.e. Arge reactor (fig.1b) is more efficient in respect of removal of exothermic heat of reaction and product output. These fixed bed reactors are usually employed for the production of heavier hydrocarbons viz. Diesel Oil, WaX etc

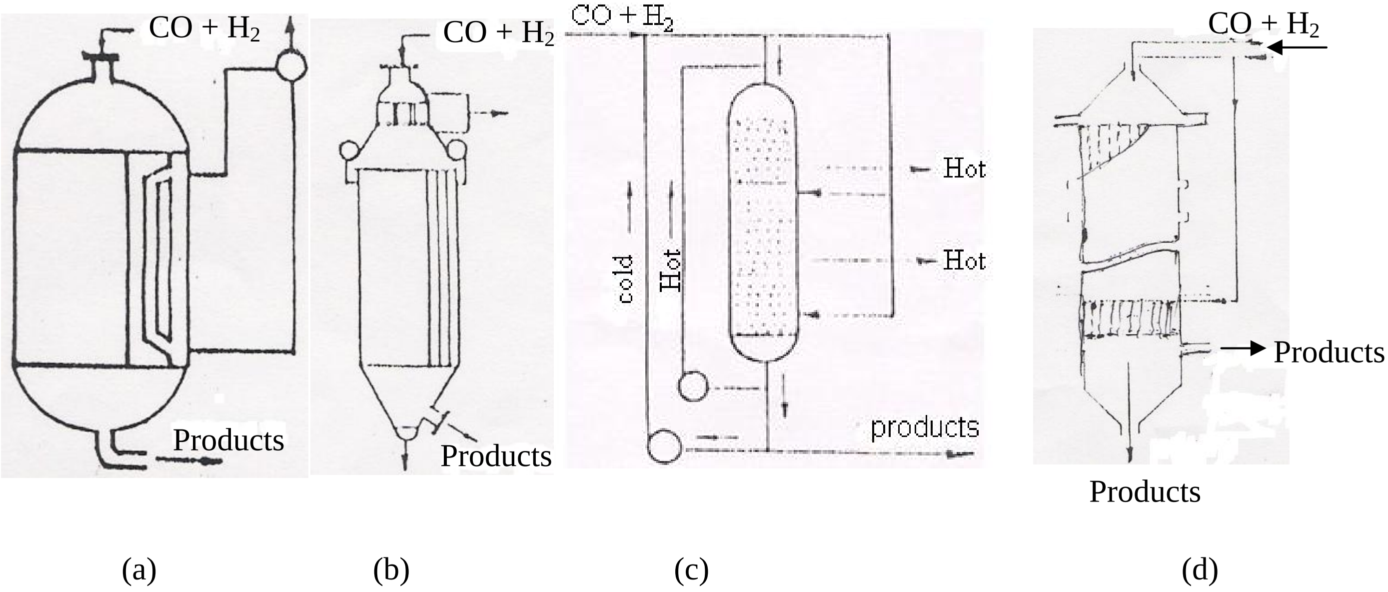
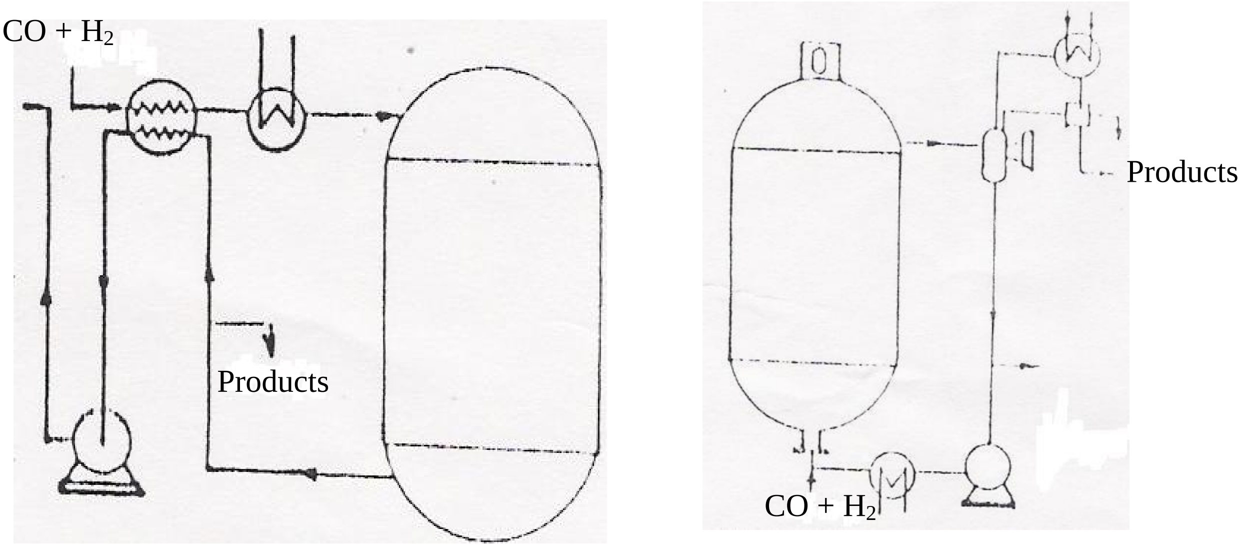


Fig 1 (a) old fixed bed reactor (b) improved fixed bed reactor (c) multi stage reactor (d) CFRI fixed bed multi tubular reactor

To obtain gasoline as major product from fixed bed type of reactors and maintaining minimum temperature gradient across the catalyst bed the hot gas recycle (HGR) and Oil circulation (OC) reactors (fig. 2a, fig. 2b) were designed and tested at Pilot Plant [3,4"] level. The Operating Temperature for HGR was considerably higher relative to conventional fixed bed F-T reactor system. In the OC reactor catalyst bed temperature was relatively lower and could be more accurately controlled in comparison to HGR reactor.



(a) (b)

Fig 2 (a) Hot gas recycle reactor (b) oil circulation reactor

F-T synthesis being a highly exothermic reaction, removal of heat of reaction instantaneously is of prime importance. With the above objective and also to produce gasoline as main product fixed fluidized bed (FFS) reactor system was developed in early 50s (fig. 3a), but it was not successful [5] at that time. It could be brought by SASOL to successful commercial scale operation in late 80s [6]. When FFS system failed, entrained fluid1zed system F-T reactor (£FS) (fig. 3b) was initially developed by KELLOG and put to commercial scale [7] by mid 50s at SASOL Works.

From the view point of precise controlling of reaction temperature and variably selectivity of the F-T catalyst by hanging operating conditions, slurry phase reactor system (f1g. 4) was studied. Semi-commercial scale slurry phase reactor was claimed to be operated successfully as early as mid 50s [8]. Its commercial scale development in mid 90s had been reported [6] by SASOL

Table 1 F-T synthesis reactors and their main feature

Type of reactor	Status	Structural features	Operating Temp. (°C)	Approx. Heat Transfer coefficient (kcal/m^2.hr. °C)	Major product
Old fixed bed (German)	Industrial scale (ohsolate)	Shell & double tube (concentric)	220-260	30	Diesel oil and wax
Improved fixed bed (Arge)	Commercial	Shell & Tube	220-260	150	Diesel oil and wax.
Multi bed	Pilot scale	Shell & Tube and Tray		NA	
Tubular-cum Tray	Pilot scale	Shell & Tube and Tray	220-260	150-170 Tubular section & mainly as sensible heat from Tray	Diesel oil & Wax or gasoline & Diesel oil
Hot gas recycle	Pilot scale	Single catalyst bed (Cylindrical shell)	300-350	*	Gasoline
Oil recirculation	Pilot scale	Single catalyst bed. (Cylindrical shell)	220-270	*	Gasoline
Fixed fluidized bed.	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	300-330	450	Gasoline & Chemicals
Circulating fluidized system	Commercial	Cylindrical shell with two cooling zones Top & bottom connected through piping loop	300-330	450	Gasoline & Chemicals
Slurry phase	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	200-320	200	Gasoline/ Diesel oil/Eax.

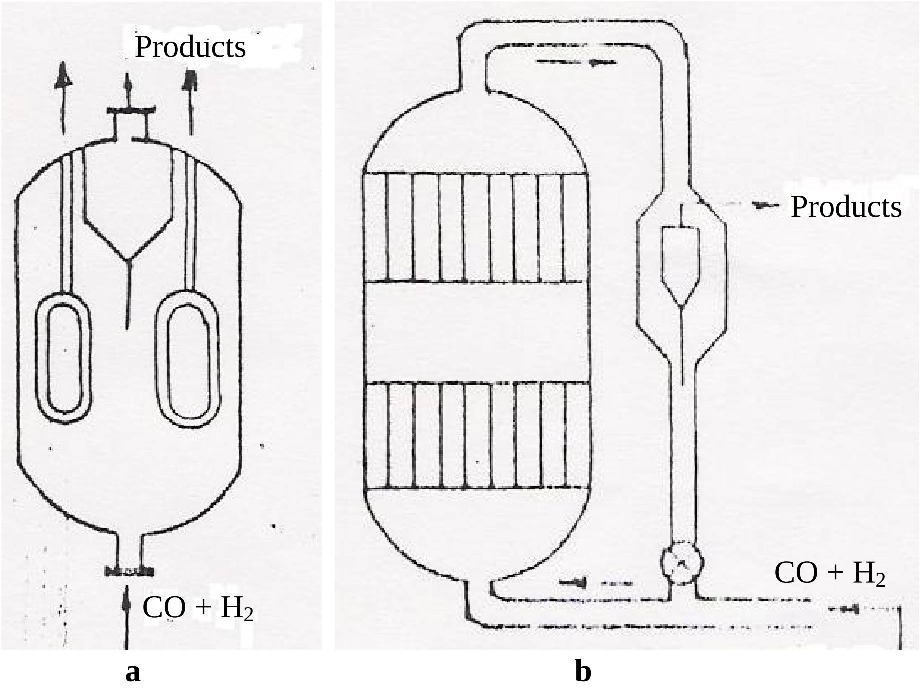


Fig 3 (a) dense phase fluidized bed reactor (b) slurry phase reactor

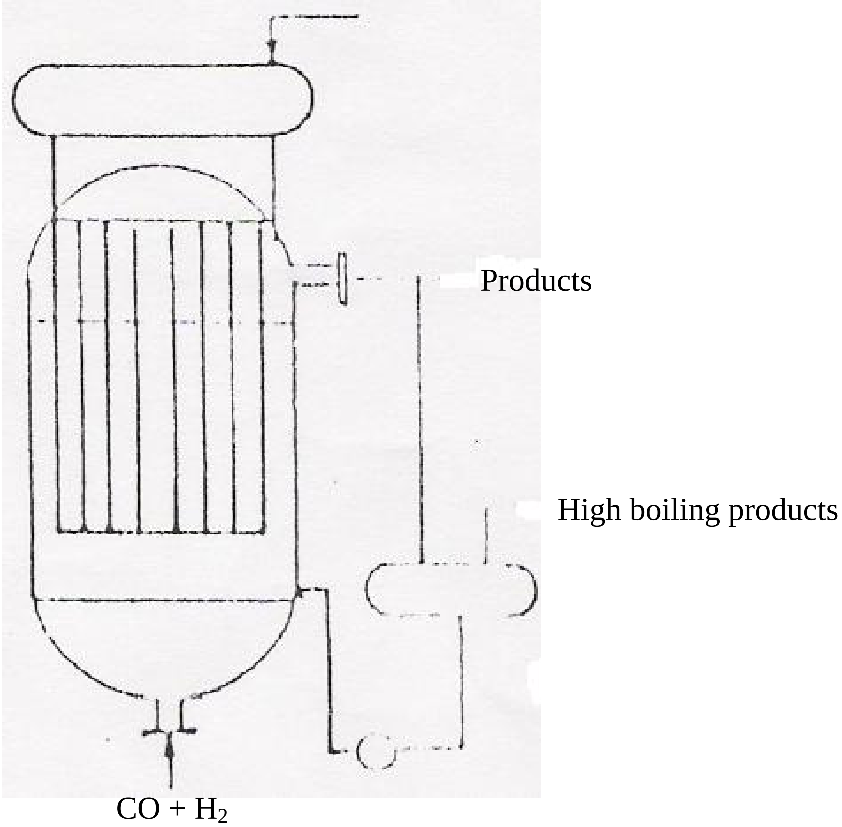


Fig 4. Slurry Phase Reactor

Design-Development of F-T Reactors and Catalysts

(1) Reactors

The following important factors have governed the design development of F-T synthesis catalytic reactors:

- the rate of a heterogeneous gas-solid catalytic vapour of catalyst required for specific phase reaction determines the volume production of desired product.

- the productivity of a reactor in turn depends on the catalyst capacity of the reactor and mechanical design limitation.

- the F-T synthesis products are consumed in terms of million tones. To minimize capital and operating cost the number of reactors for a particular plant capacity should be as minimum as possible by having high capacity reactor.

- the F-T synthesis reaction being highly exothermic (670 Kcl/ Nm^3 CO +H_2 converted), higher the productivity higher is the heat load on reactor. Hence high heat transfer coefficient has to be obtained by proper design of t he reactor and process condition to maintain near isothermal condition of the catalyst bed

- for a multi product reaction system like F-T synthesis selection of the type of reactor depends on desired product like gasoline or wax and corresponding process conditions.

- the design of a reactor involves material balance, energy balance and reaction kinetics. The main objective interrelationship between the F-T reactor and catalyst is examined based on relevant basic design correlations containing the term catalyst covering the above aspects. For different type of heterogeneous catalysts, material and energy balances differ slightly from the basic balance of a vapour phase heterogeneous catalytic reaction. The material and energy balances at steady state for heterogeneous catalytic reactors i8 represented [9] by correlations as follows:

Mass transfer to catalyst surface = mass transfer into catalyst particle= rate of reaction

$K_GA_S (c_b-c_s) = A_SD_{eff} (dc/dr_i) = 4 \pi r_i^2 dr_i \eta$ rate ---------- (1)

Heat transfer from surface = heat generated by reaction

Hg AS (Ts-Tb) = ($4 \pi r_i^2 dr_i \eta$ rate) ΔH --------- - (2)

Simultaneous solution of the above equations yields information on temperature and concentration gradients within the catalyst pellet. The distribution of reaction species and temperature through space and time can be obtained from such balances. From the equations relating to mass transfer that it is seen parameters As' C. "and pares are of relevance in catalyst and catalytic reactor interrelationship. The interrelationship will also be evident from various mathematical correlations used in determining heat transfer coefficients with respect to different reactor configuration and further it will be found that this factor plays a very important role in the development of F-T synthesis reactors and catalysts.

The important factor for reactor design, the reaction kinetic is examined first for the interrelationship. F-T synthesis reaction mechanism has been discussed [10, 11, 12] extensively over the last eighty years. The mechanism is very complex as consecutive and parallel reactions occur simultaneously producing hundreds of components. As a result, for Designing r-T reactor a rate equation truly representing synthesis step is difficult to derive. A few of the reactions which account major types of ""-T products formation i.e. olefins, paraffins and oxygenates are given below.

$$n\,CO + 2n\,H_2 \longrightarrow C_n H_{2n} + n\,H_2O \qquad \text{..........................(i)}$$

$$n\,CO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O \qquad \text{.........................(ii)}$$

$$n\,CO + 2nH_2 \longrightarrow C_nH_{2n+2}\,O_{(n-1)}\,H_2O \qquad \text{........................ (iii)}$$

$$n\,CO + n\,H_2O \longrightarrow n\,H_2 + n\,CO_2 \qquad \text{........................ (iv)}$$

steps (i) and (iii) are conventionally accepted as primary and steps (ii) & (iv) are secondary products forming reactions on iron F-T catalyst. For the present objective synthesis reaction is represented by

$$A + B \longrightarrow R + S \qquad \text{…………….(v)}$$

and assuming surface reaction viz. hydrogenation *01* chemisorbed species betueen adjacent active sites

$$Am + Bm \longrightarrow \_Rm + Sm \qquad \text{… . ………..... (vi)}$$

being the slowest step is rate controlling. Such concept in F-T synthesis is an accepted [13, 14 1 basis for LHHW type rate equation which include active site term. Considering dual site mechanism fundamental rate equation (eqn) is

$$r = \kappa[P_AP_B - (P_RP_S/K)] \,/\, (1 + K_AP_A + K_BP_B + K_RP_R + K_SP_S)^2 \qquad \text{……………(3)}$$

where mass transfer resistance does not exist. Though full derivation of eqn - (3) is not needed, involvement of active sites in design and interrelationship between reactor and catalyst will be evident from certain steps in the process of derivation.

$$A + m \leftrightarrows Am \qquad K_4 = C_A/P_AC_m \qquad \text{..........................(4)}$$

$$B + m \leftrightarrows Bm \qquad K_5 = C_B/P_BC_m \qquad \text{...........................(5)}$$

$$Am + Bm \leftrightarrows Rm + Sm \qquad K_6 = C_RC_S/C_AC_B \qquad \text{………………. (6)}$$

$$Rm \leftrightarrows R + m \qquad K_7 = P_RC_m/C_R \qquad \text{......................... (7)}$$

$$Sm \leftrightarrows S + m \qquad K8 = P_SC_m/C_s \qquad \text{………………. (8)}$$

Step (6) being rate controlling

$$r = \kappa_6 C_A C_B - \kappa_6' C_R C_S \qquad \ldots\ldots\ldots\ldots\ldots\ldots..\ (9)$$

Substituting the values of CA,CB,CR,CS, from equations (4), (5), (7) and (8) into equation (9)

$$r = \kappa_6 K_4 K_5 P_A P_B C_m C_m - \kappa_6' (P_R P_S\ C_m C_m / K_7 K_8) \qquad \ldots\ldots\ldots\ldots\ldots\ldots..\ (10)$$

$$= C_m^2\ [\kappa_6 K_4 K_5 P_A P_B - \kappa_6' (P_R P_S / K_7 K_8)] \qquad \ldots\ldots\ldots\ldots\ldots\ldots..\ (11)$$

Now, $C_A + C_B + C_R + C_S + C_m = M$

Or, $M = K_4 P_A C_m + K_5 P_B C_m + (P_R C_m / K_7) + (P_S C_m / K_8) + C_m$

$= C_m\ [K_4 P_A + K_5 P_B + (P_R/K_7) + (P_S/K_8) + 1]$

Or. $C_m = M / [K_4 P_A + K_5 P_B + (P_R/K_7) + (P_S/K_8) + 1]$ .... (12)

$C_m^2 = M^2 / [K_4 P_A + K_5 P_B + (P_R/K_7) + (P_S/K_8) + 1]^2$ .... (13)

Substituting eqn (13) into eqn (11)

$$r = M^2\ [\kappa_6 K_4 K_5 P_A P_B - \kappa_6' (P_R P_S / K_7 K_8)] / [K_4 P_A + K_5 P_B + (P_R/K_7) + (P_S/K_8) + 1]^2 \ \ldots.\ (14)$$

Now, $(\kappa_6 / \kappa_6') = K_6$ or, $\kappa_6' = \kappa_6 / K_6$

$K_4 = K_A$, $K_5 = K_B$, $K_7 = 1/K_R$, $K_8 = 1/K_S$

and overall reaction rate constant 'κ' being

$\kappa = M^2\ \kappa_6 K_4 K_5$ and overall reaction equilibrium constant

$K = K_4 K_5 K_6 K_7 K_8$, steps (4) – (8) add upto the overall reaction

Eqn. (14) becomes

$$r = M^2\ [\kappa_6 k_4 k_5 P_A P_B - \kappa_6 (P_R P_S / k_6 k_7 k_8) - k_4 k_5 / k_4 k_5] / [1 + k_4 P_A + k_5 k_8 + (P_A/P_R) + (Ps/k_8)] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (15)$$

and further derivation leads to eqn. (3). The interrelationship between catalyst and catalytic reactor is evident from the term 'M' in eqn. (15), an intermediate step in the derivation final rate equation. Two significant facts are revealed during the derivation. first, all active sites do not take part in the reaction as evident from the definition of the term 'M' and secondly the overall rate constant κ being equal to $M^2 \kappa_6 k_4 k_5$ can be written as $k\ \alpha k_6 k_4 k_b$ where M becomes a constant and taken to second power. This shows involvement of two active sites in the controlling step. Since f-T synthesis is a first order reaction [15] and for such reaction rate constant is a direct measure of the activity of the catalyst [16] the same depends on M. For a reactor designer the estimation of active sites in catalyst mass gives an idea how effectively reactor volume is utilized. Accordingly, concentration of active sites *in* two typical iron and cobalt based F-T catalysts has been estimated [17] by author which is proposed to be shown in a separate publication. It is found that concentration of active sites on total number of metal site basis in iron and cobalt catalysts is 1.20 and 2.60 percent respectively, which is extremely low. The concentration of active sites in term of number per unit mass is in the range of 10^{18} - 10^{19}/ gm which apparently give an idea that the value is not insignificant. Since volume of the reactors depends on mass of the catalyst, it is seen that very small fraction of the reactor is utilized in reality.

From reactor design view point for multi product reaction systems as in the areas of petroleum and F-T synthesis, application of 'Space velocity' parameter is also effective to calculate catalyst volume as rate equation and gives an idea of catalyst efficacy when compared with similar catalytic processes. Table-2 [181 shows that F-T catalyst takes less gas load compared to ammonia and methanol synthesis catalysts. It is worth noting that ammonia synthesis catalyst can also be used for r-T synthesis.

TABLE . 2. Space - Time - Yield of A Few Industrial Catalytic Processes.

s.no	Synthesis	Operating press (atm)	Tempareature (°C)	Space velocity * (V/V-hr)x 10^3	S.T.Y. (Ton/m^3 catalyst/day)
1	Methanol	150-350	300-390	18-30	20-25
2	Ammonia	200-300	400-550	10-20	12-14
3	Hydrocarbons	10-30	220-325	1.5-4.5	1.5-4

* Space velocity based on made up plus recycle gas. From reference [18].

After studying the rate equation aspect for catalyst and catalytic reactor interrelationship, the mass transfer phenomenon and its role in the interrelationship is examined. Studies on mass transfer resistance during F-T synthesis have shown [19, 15] the absence of film diffusion. During F-T synthesis catalyst is covered and pores are filled with liquid hydrocarbons at temperature below 290 °C [15 land resistance to pore diffusion has been found to exist. In fact, fluidized bed F-T a synthesis is carried out at 300 °C and above to prevent hydrocarbon deposition and defluidization of F-T catalyst during the reaction. In fluidized bed synthesis existence of mass transfer resistance is expected to be insignificant because of catalyst size employed. During investigation, diffusivity through the "absorbed hydrocarbon layer (01) has to be taken into account since this factor is one of the important link between the catalyst and catalytic reactor design. Diffusivity in the pores of the r-T catalyst has been reported ~5] to be as low as 5~0 percent of that in the bulk liquid and explain why diffusion in the catalyst pores is the important slow step.

To examine how the effectiveness factor of F-T catalyst is influenced by diffusion in hydrocarbon filled pores, η values have been calculated as ~ for catalysts covered with liquid hydrocarbons during synthesis and as '~d when catalyst ~s not covered with liquid hydrocarbons. The later condition can be obtained by using catalyst and maintaining operating conditions which produce low molecular weight hydrocarbons as only products. The basic data on diffusion and physical properties of catalyst have been obtained from literature [5]. The size of the catalyst particles employed in the studies were 1.0 and 3.0 mm. For calculation purpose spherical shape has been assumed and for catalyst covered with liquid hydrocarbon Shatterfield eqn. (16) is used [20]

$$\eta_{li} = 3/\phi_{li} \left[(1/\tanh \phi_{li}) - (1/\phi_{li}) \right] \qquad \text{.............................(16)}$$

Where for F-T synthesis

$$\phi_{li} = r_0 \sqrt{\ } r\, \ell_s / D_{li} H_A C_{A0}^{n} \qquad \text{.............................(17)}$$

$$\text{and } H_A = H_A' \ell_w RT/22400 \qquad \text{.....…………………..(18)}$$

When catalyst is not covered with oil, equation (16) could not be used as value of Thiele modules ϕ_d being very small, values of ϕ_d and $\tanh\phi_d$ became identical. Since for different catalyst shapes η values at given ϕ can be estimated with an error less than 15 percent [16] using equation (19)

$$\eta_d = \tanh\phi_d/\phi_d \qquad \text{. ………………..... (19)}$$

$$\text{Where } \phi_d = r_0 \sqrt{\ } 2k_s/D_{er} \qquad \text{…………………..(20)}$$

is used to calculated η_d. The parameters involved to determine the values of ϕ under two different conditions during F-T synthesis are significantly different. The values of parameters used in eqns. (16) - (20) are given in the nomenclature.

The values of moduli $\phi_{li,}$ ϕ_d and effectiveness factor η_{li} η_d are determined with liquid hydrocarbon covered and liquid hydrocarbon free catalyst of 1.0 mm and 3.0 diameters. The data are presented in Table 3.

Table 3. Effect of Catalyst size and liquid hydrocarbon presence on Thiele modulus and effectiveness factor.

Catalyst		ϕ_{li}	ϕ_d	η_{li}	η_d
State	Size (Dia. Mm)				
Liquid hydrocarbon covered	1.0	2.54	-	0.75	-
Not covered with liquid hydrocarbon	1.0		0.03	-	1.0
Liquid hydrocarbon	3.0	7.48	-	0.40	-

The data show absence of pore diffusion limitation in the liquid hydrocarbon free catalyst, while in the liquid hydrocarbon covered catalyst *it* exists, marginally. Considering the size of the catalyst i.e. 1.0 mm *dia* absence of pore diffusion limitation in the former is expected. However, even the small decrease in n_{li} value with liquid hydrocarbon covered catalyst show the effect on diffusivity in pores filled with liquid hydrocarbon.

Further, to examine the effect of variation in catalyst particle size on pore diffusion the values of ϕ_{li} and η_{li} have been determined with 3.0 mm dia particle covered with liquid hydrocarbon. The values are shown in Table-3. The data show that significant pore diffusion limitation has set in with the increase in catalyst particle size. This is one of the reasons for difficulties faced during scaling up of such catalytic reactor. From the correlations (17) and (20) it is seen that the size of catalyst and pores and diffusion limitation are important factors in determining the required volume of the catalyst and hence reactor volume. For surface phenomenon rate controlling reaction if pore diffusion resistance exists, it is better to replace rate equation by an equivalent first order rate expression which can be combined with other steps to yield an overall rate expression. Pore diffusion is accounted for by a separate multiplicative correction term η. The η term involves not only diffusion term but a surface reaction term as well in the form of rate constant κ .

In designing catalytic reactor, heat transfer aspect is an important area especially for a highly exothermic reaction like F-T synthesis. The reactor design should include provision for instantaneous removal of heat of reaction to maintain near isothermal condition of the bed. Otherwise, apart from carbon deposition and catalyst deactivation there will be deviation from the desired selectivity in such a multi product reaction system.

It has been mentioned earlier that different type of F-T reactors have been designed and tested so far. Considering variation in reactor types discussion on heat transfer machanism will reveal more information on catalyst and catalytic reactor interrelationship.

In the area of heterogeneous gas-solid catalytic vapour phase reaction the fixed bed reactor system is most common both for initial testing of the catalyst and industrial application. In F-T synthesis single bed, multi bed, shell and tube type fixed bed reactors have been studied [4, 21, and 22]. The generalized correlation f or fixed bed reactor wall heat transfer coefficient is expressed [23] as

$$h_m\ D_t/K_g = f\ \ D_t^{0.17}\ (D_pG/\mu)\ (C_p\mu/K_g) \text{……………………}(21)$$

The maximum value of 'f' and in turn coefficient h_m is obtained when D_p/D_t has a value of 0;16. Beyond this value i.e. if D_p is increased rate of heat transfer by convection and through the reactor wall decreases. In such cases heat of reaction is removed mainly as sensible heat. In multi bed reactor with large diameter, interstage cooling/Cold Gas Injection/high ratio gas recycle techniques are employed. However, for F-T synthesis industrial scale multi bed reactor system Fi g. 1c has not yet been successful because of limitation of allowable temperature gradient. Semi-pilot scale process development unit along with the objective of examining viability of an integrated reactor consisting of tubular followed by catalyst tray Fig. 1d was designed by author and studies were undertaken [24]. The design was based on maintaining controlled conversion. Such combination can overcome limitation of catalyst tube length, increase catalyst holding capacity and make reactor maintenance relatively simpler.

The first industrial scale F-T reactor Fig. 1a used during second World War was of shell and tube type. The catalyst tube inside the shell was concentric double tube [25]. The width of the annular space for catalyst was limited to 8mm so that centre of the catalyst bed was only 4 mm away from cooling tube wall.

This was necessary to control the temperature and maintain near isothermal condition of the catalyst bed. Not only fabrication of such concentric catalyst tube was cumbersome, but reactor catalyst holding capacity was also diminished. During implementation of SASOL-I project the improved fixed bed shell and tube reactor Fig. 1a was designed and installed. The catalyst tube was not concentric. The number of tubes were almost same in both the reactor. By increasing only the length of the catalyst tube two and half, times in the improved fixed bed reactor and application of appropriate design principle the productivity could be increased twenty times to that of earlier shell and tube reactor Fig. 1a. As a result heat load on catalyst bed increased correspondingly.

The efficiency of removal of heat of reaction from the catalyst bed to the cooling medium depends on achieving optimum overall heat transfer coefficient 'U’. In shell and tube type catalytic reactor when heat generation is from inside of the tube packed with catalyst, the value of corresponding heat transfer coefficient '$h’_m$ can be calculated from the following correlations [2, 6] depending on D_p/D_t

$h_m = (0.813/e^{6Dp/Dt})\ (DpG_0/\mu)^{0.9}$ for D_p/D_t upto 0.35 ....(22)

and $h_m\ 0.125\ (K_g/D_p)\ (D_pG_0/\mu)^{0.75}$ for D_p/D_t from 0.35 – 0.60 …………………..(23)

The three correlations (21), (22), (23) show that catalyst particle/pellet diameter and its size ratio w.r.t. catalyst tube/cylinder play important role in designing such reactor. To obtain desired 'h_m' value the parameter G_o has the greatest influence and for such catalytic tubular reactor. The parameters under discussion clearly show the interrelationship between catalyst and catalytic reactor.

$G_o = f(S_v, R_r)$

Two special type of fixed bed F-T reactor viz. hot gas recycle Fig. 2a and oil circulation reactors Fig. 2b were investigated at pilot level by earlier investigators [3, 4]. The objectives of these reactors were to operate at higher temperature for synthesizing gasoline as main product and to remove highly exothermic heat of reaction as sensible heat by directly contacting the catalyst bed with cooling medium viz. recycle gas at very high ratio and cooling oil thereby eliminating d_p/d_t ratio limitation and making the reactors design relatively simple. The catalysts used in these reactors were non conventional and reactor specific. In HGR reactor good temperature control (< 10 °C) across the catalyst bed was obtained by maintaining a very high recycle ratio of $40^{\#}$ against the normal recycle ratio of 2 - 4 which was employed in fixed and fluidized bed F-T reactors system. In OC reactor cooling all flow rate of about 5-6 cm/Sec was maintained to obtain catalyst bed expansion of about 20.0 percent to prevent catalyst agglomeration and temperature differential across the bed below 5 °C. The catalysts used in these reactors were carbon steel turnings; steel wool, fused iron granules and steel shot. One of the important properties of these catalysts was to provide high void volume, nearly 90 percent in the catalyst bed.

Due to high exotherm1city of f-T synthesis reaction and requirement of near isothermal condition of the catalyst bed, maintaining high conversion per pass and desired product selectivity, high output per unit fixed bed reactor volume becomes difficult. Also catalyst replacement without taking the reactor off-stream is not possible. To overcome some of these short-comings fluidized bed F-T reactor system is more appropriate from the view point of higher heat transfer rate, selectivity towards straight run gasoline with higher octane number and near isothermal condition of the bed. Such reactors may be dense phase i.e. fixed fluidized bed (FFD) or lean phase i.e. entrained fluidized system (EFS) - In fluidized bed reactor the heat transfer coefficient relating to heat flow between catalyst bed and cooling surface is correlated by the following type of equation [27}

$$h_m D_p/k_g = 0.16\,(C_s\,\ell_s\,D_p^{1.5}\,g_c^{0.5}/k_g)\,(D_p G_f\,E_\phi/\mu R') \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

Further, the basic equation for minimum fluidization mass velocity (G_{mf}) is [26]

$$G_{mf} = 688\,D_p^{1.82}\,[\ell_F(\ell\,s' - \ell_{\mathcal{F}})]/\,\mu^{0.88} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$$

Comparing eqns. (22) and (23) for fixed fluidized bed reactor with eqns (24) and (25) it is seen that additional catalyst parameters C_s, ρ_s are involved in fluidization and fluidized bed beat transfer mechanism.

In entrained fluidized system the catalyst particle movement is different from that of fixed fluidized bed reactor. The variation of heat transfer coefficient 'h' with the gas mass velocity 'G' covering the range of dense phase to lean phase has been studied and shows [27] increase in 'h' value with the increase of 'G' and a maximum value 'h_m' is reached at the point of beginning of the lean phase i.e. transportation of catalyst. The value of 'h_m' is also influenced by the conductivity of the gas and catalyst particle size. The maximum value falls with in the range of 250-260 kCal/ m^2. °C. hr. The heat transfer coefficient usually obtained with F-T FFB and EFS reactors are in the range of 450-500 kCal/m^2 °C. hr.

The absence of catalyst particle's thermal conductivity term in the correlations (2) and (21) - (23) shows that its role is not important in fixed bed system. From correlations (2) it is evident that surface area 'A' is also important parameter in fluidized bed heat transfer as in mass transfer. In fluidized system catalyst being in power form its surface area is large and being in constant motion heat transfer coefficient is very high. Hence cooling surface area required in the reactor is much less relative to fixed bed reactor.

In EFS reactor the catalyst is ellutriated serially Fig. 3b through the 'D' riser, reaction zone, separated in the cyclone and finally recirculated through the standpipes. For Catalyst transportation in EFS, superficial gas velocity 'ls' has to be several times higher than that maintained in the FFB reactor. In EFS the reaction zone has two sections - reaction zone and cooling 80ne. To have an idea how the operating conditions differ in these two reactors the ratios of linear velocities through the reactors are presented. The ratios l_{sr}/l_{sf} and l_{st}/l_{sf} ratios are about 10-12 and 40-45 in the reaction and cooling zone tubes respectively of EFS w.r.t. EFS reactor. Though catalyst attrition is natural in fluidized system, the ratios show attrition is more severe in EFS. Hence very high attrition resistant catalyst is necessary.

Earlier, the development of industrial scale slurry phase reactor (Fig. 4) has been mentioned. The operation of such reactor is somewhat similar to dense phase fluidized bed i.e. FFB reactor in the sense that in both the system powder catalyst is circulated in similar manner in fluid medium, operate at low linear velocity, and in laminar range. The slurry phase operation tends toward particulate fluidization and is characterized by a relatively uniform distribution of void space throughout. Eqn. (25) with a correction factor can be applied [27] for voidage upto 80-85 percent and for laminar flow i.e. DpG/μ <:10. In slurry reactor heat transfer rate to cooling tube wall is not of same magnitude as in rrs and is in between fixed bed and FFB.

For desired interaction between slurry and bubble, liquid circulation rate, gas hold up, axial dispersion coefficient etc. it is necessary to find out optimum *H/D* ratio, superficial linear velocity, viscosity of the liquid medium and catalyst loading, Since viscosity is influenced by pressure, temperature and solid content including carbon deposition, the concentration of catalyst in the medium is kept within optimum limit. The size, heat capacity and density of catalyst particle are the physical properties involved in the various correlations used in slurry phase. Hence catalyst loading is the important factor in determining the reactor volume.

Thus the development of industrial scale F-T reactors followed a sequence with the objectives of improved reactor temperature control, desired selectivity, and high productivity along with operating reliability. It would also be seen that along with changes in the reactor types, F-T catalysts also had to be changed for reactor's suitability. With properly designed catalyst slurry phase reactor in comparison to fixed bed reactor could yield higher amount of middle distillate.

Catalysts:

The discussion on the development of F-T catalysts is limited to specific requirement for different type of F-T reactors. Industrial F-T catalysts are based on cobalt and iron metals. Cobalt catalysts have been used mainly in fixed bed type of reactors though it can be used in slurry phase also. It has the advantage when paraffinic nature of products is desired. Iron catalysts have been used in all type of F-T reactors discussed so far.

From reactor and catalyst interrelationship views point both the physico-chemical properties of the catalyst are of relevance. While chemical properties are related to selectivity and determining the reactor volume, various correlations for mass and heat transfer used in designing the heterogeneous catalytic reactor like F-T reactor show involvement of catalyst's physical parameters extensively.

It is evident that four types of F-T reactors are being commercially utilized presently. Over the eighty years thousands of catalysts involving various methods of preparations have been tested. But commercial F-T catalysts are still based on iron and cobalt metals. Similarly catalysts preparations are mainly confined to precipitation and fusion technique corresponding to type of reactor to be employed.

During catalyst development these factors may therefore be taken into account. The precipitated type of catalysts is prepared initially during the development and screening test is carried out in fixed bed reactor. Various types of precipitated catalysts can be prepared. In precipitated F-T catalysts there are supported, unsupported and also a type where support is added at the last stage of precipitation [5, 28] . These F-T catalysts may be duel component and multi component. That desired physico-chemical properties of catalyst for a particular process can to some extent be obtained with different preparation methods has been shown in an earlier publication [28]. The formulation and preparation methods of these catalysts Table - 4 were planned by the present author in late 80s for employing in fixed bed type reactor. The precipitated F-T catalysts are not suitable for all types of F-T reactors. Apart from activity the other chemical property of the F-T catalysts viz. selectivity also influences the selection of the type of the reactor to be used. F-T catalyst with selectivity towards wax synthesis is unsuitable for fluidized bed reactor, since such catalyst leads to caking phenomenon.

Non conventional F-T catalysts in the form of carbon steel lathe turnings, steel shots and steel wool were prepared with the objective of producing gasoline as main product by operating at high temperature and very high recycle ratio using pilot plant scale fixed bed reactor as mentioned earlier. Fused synthetic magnetite granules as F-T catalyst was also studied at this time in pilot plant level fixed bed reactor at high temperature to synthesize gasoline as main product by circulating cooling oil through the catalyst bed. These studies were carried out by USBM [3, 4] nearly half a century back with the objective of developing simple fixed bed reactors.

Fluidized bed f-T reactors are being operated presently at commercial scale to produce gasoline mainly along with some exygenated organic compounds like alcohols and ketones. Severe attrition of catalyst occurs in these reactors. Hence reactor specific fused mill scale, fused magnetite based attrition resistant catalysts have been developed and are being used. Sintered iron ore based catalyst was also tested. These catalysts require higher operating temperature and accordingly affect reactor design.

Table 4 Change in physico-chemical properties as shown by CO adsorption of series of designed Fe catalysts and prepared by different methods.

Catalysts	Reduction		CO adsorption x 10^2		d (A°)
	Temp (°C)	h	mol/g cat	mmol/ g Fe	
1. Fe: Cu : K_2O : Mn : Al_2O_3	290	8	1.25	1.44	100
100 10 0.5 40 5	350	8	0.93	1.94	87
2. Fe: Cu : K_2O : MgO : Al_2O_3	290	8	1.29	1.70	93
100 10 0.5 15 5	350	8	0.96	1.30	107
3. Fe: Cu : K_2O : Mn : ThO_2	290	8	1.40	2.10	81
100 10 0.5 15 5	350	8	1.45	2.25	80
4. Fe: Cu : K_2O : MgO : SiO_2	350	8	0.27	1.68	73
100 10 0.5 15 500	400	8	0.14	0.87	129
5. Fe: Cu : K_2O : Mn : Kisselghur	350	8	0.27	0.47	176
100 10 2.8 40 22	400	8	0.18	0.31	215
6. Fe: Cu : K_2O : Mn : SiO_2	350	8	0.26	0.45	178
100 10 0.5 40 22	400	8	0.25	0.45	182

From ref. [28]

Over the last few decades, zeolite based, SOSS [Cobalt from $Co(CO)_8$ deposited on alumina and promoted by platium/palladium] Catalyst [18J bimetallic alloy and cluster type catalysts have been investigated. Such catalysts are generally suitable for fixed bed and slurry type of reactors.

It is observed that in pptd. catalyst the term Cs does not appear, but in fused catalyst for fluidizes bed the term appears in eqn.(24). In fact fused catalyst has good heat conducting property which facilitates heat transfer.

The diffrent type of f-T reactors and their relationship with the type of catalysts to be used in each reactor and their physico-chemical properties involved in various design correlations are shown in Tab1e-5.

Conclusion

Nearly a dozen types of F-T reactors have been investigated and amongst these four types are being commercially uti1ised.

The type of FT product desires determines the type of reactor required which in turn influences the type of catalyst to be employed.

Since specific catalysts are necessary to operate these reactors the process offers scope to study the interrelationship between the F-T reactor and the catalyst.

Considering low concentration of active sites in the catalyst mass, a small fraction of the reactor volume is utilized in reality.

Table 5 variation of types of F-T catalysts with different types of F-T reactors.

Type of reactor	Catalyst preparation method	Catalyst		Related catalyst properies
Fixed bed reactor		Shape	Size (μ)	
1 (a) old fixed bed (German) (b) improved fixed bed (Arge) (c) multi bed (d) Tubular-cum-Tray	Precipitated Fe & Co Catalysts	Pellet, Granules	$3x10^3 – 5 x 10^3$	A_{in}, As, $\bar{r}$ L, p_{sd}
2 Hot gas recycle	Lathe turnings Steel Wool sintered iron	Spiral, Pellet	$6x10^3 – 10x 10^3$	A_{in}, As, ε_B, C_s
Oil circulation	Fused iron Oxide, Steel shot, sintered iron	Granules, balls, pellet	$3x10^3 – 10x 10^3$	A_{in}, As, $\bar{r}$ L, A_r
Fixed Fluidized Bed	Fused Magnetite, Mill Scale	Powder	100 – 250	As, A_{in}, , C_s, ρ_s, A_r
Circulating Fluidized Bed	Fused Magnetite, Mill Scale	Powder	80-350	As, A_{in}, , C_s, ρ_s, A_r
Slurry phase	Precipitated Fe & Co Catalysts. Fused iron Oxide	Powder	20-200	As, A_{in}, , ρ_s

Studies have shown that not all the properties of catalysts are important for any particular type of reactor. Relevant physico-chemical properties of reactor specific F-T catalyst are evident from various reactor design correlations.

Acknowledgment

On the occasion of completing one decade of my retirement from Central Fuel Research Institute, Dhanbad, where I learnt and worked on F-T synthesis, I dedicate this paper to the same and my younger colleagues who are pursuing the subject.

Nomenclature

As - Catalyst pellet/particle's external surface area, cm^2
Aim - Internal surface area of the catalyst pellet/particle, cm^2
K_G - Gas film mass transfer coefficient, g-mole/cm^2 S atm
c_b - Reactant concentration in the bulk gas, g-mole/cm^3
c_s - Reactant concentration at the external surface of the catalyst, g-mole/cm^3
r_i - Integration radius of the Catalyst pellet, cm
h_g' - Gas film heat transfer coefficient, col/cm^2.s.K
T_s - Catalyst surface temperature, K
T_b - Bulk gas temperature, K
ΔH - Heat of reaction, Cal/gm-mole
K - Overall reaction adsorption equillibrium constant
r - Rate of reaction, g-mole/gm-Catalyst. s, 0.455 X 10^{-5}
κ - Overall reaction rate constant
k - First order rate constant forward reaction, s^{-1}
k - First Order rate constant, reverse reaction, s^{-1}
K_4 K_5...K_b - Adsorption equillibrium constants.
$P_AP_BP_RP_S$ - Partial pressure of reactants, A, B, and Products, R. s. atm
c_m - Unoccupied active site on catalyst
M - Total number of Active sites in catalyst.
$C_AC_SC_R$Cs -= Concentration 0 f absorbed reactants, A,B, and Products, R.s.
η - Catalyst effectiveness factor
ϕ - Thiele modulus
li, d - subscript 'li' for Liquid hydrocarbon covered catalyst. and 'd' for catalyst not covered with liquid hydrocarbon.
ϕ_{li} - 2.54 (r0 = 0.051 cm), 7.48 (r0 = 0.151 cm)
ϕ_d - 0.03 (r0 = 0.051 cm)
r_0 - Catalyst pellet/em, Particle radius .051, 0.151
$\bar{r}$ - Average pore radius, Cm, 1.94 X 10^{-6}
ρ_s - Density of Catalyst pellet/particle, g/ml, 1.25
D_{li} - Effective diffusivity in pores filled with liquid hydrocarbon, Cm2/s, 1.90 X 10-5
C^n_{A0} - Initial gas phase H_2 concentration, gm-mole/litre, 0.25
H_A - 0.48 x 10^{-3} lit/gm mole
.H_A' - cc of H_2 / gm waX . atm , 0.26
R - 0. 82 lit. atm/g-mole - K
ρ_w - Density of wax, g/ml, 1.00
De - Effective diffusivity in pores of catalyst not filled with liquid hydrocarbon, cm^2/s, 0.031.
Ks - Rate constant, unit surface basis, cm/s, 0.124 X 10^{-6}
h_m - Mean heat transfer coefficient based on tube wall area, cal/cm^2 s. °C
Kg - Thermal conductivity of fluid, Cal/cm^2 hr.(°C /cm)
Dt - Diameter of the tube, em
Dp - Diameter of catalyst pellet/particle, Cm
G - Superficial masS valocity of fluid based on cross-section of tube, Kg/hr.m^2
Cp - Specific heat of fluid at constant pressure, cal/g-°C

u - Viscosity of fluid, g/hr.cm
f - Coefficient f, 0.14 to 0.Z4 from a graph of f Vs D_p/D_t (Ref.23)
S_v - Space Velocity, hr^{-1}
R_r - Recycle ratio
R' - Bed expansion ratio
$C_{s'}$ - Heat capacity of catalyst, cal/gm °C
D_1 - Effective diffusion coefficient for CO & H_2 gases 1n r-T liquid hydrocarbon, 1.90 X 10^{-4} cm^2/s
G_f - Superficial mass velocity required to fluidize the bed, kg / m^2.hr
E_ϕ - Fluidization efficiency
G_{mf} - Superficial mass velocity .required to incipiently fluidize the bed, Kg/m^2.hr
ℓ_F - Density of feed gas, g/ml
l_{sr} - Linear velocity of feed gas through EFS reactor zone, cm/s
l_{st} - Linear velocity of fleed gas through EFS reactor's cooling tube zone, cm/s
l_{sf} - Linear velocity of feed gas through rrS reactor zone,cml
A_r - Attrition resistance
P_{sd} - Pore size distribution
ε_B - Catalyst bed voidage

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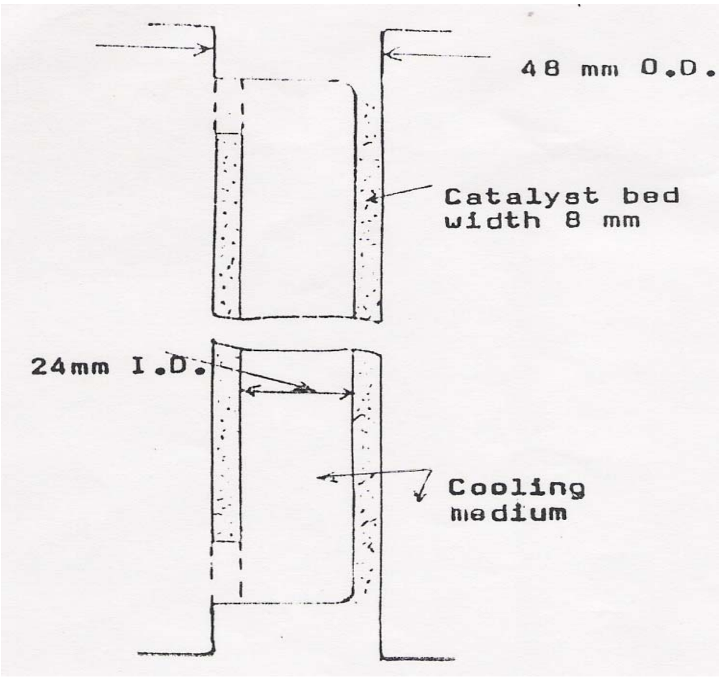

Concentric Tube in shell shown in fig. 1a