# APPENDIX D

# FISCHER-TROPSCH REACTOR SELECTION

## A comparison of slurry versus fixed-bed reactor design principles for methanol and Fischer-Tropsch distillate production.

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# Fischer-Tropsch Reactor Selection

## Introduction

Bechtel is currently carrying out for the DOE an economic comparison of fixed-bed versus slurry reactors for several applications, including Fischer-Tropsch synthesis. This paper is a report on the first phase of this study; a review of reactor design principles.

## Types of Fischer-Tropsch Reactors

The challenge in Fischer-Tropsch reactor design is to remove the large heat of reaction, some 55,000 to 60,000 kJ/kgmol (24,000 to 26000 Btu/lbmol) of synthesis gas reacted. For Fischer-Tropsch operations directed at gasoline production (i.e. values of the chain propagation probability factor of about 0.6) two types of reactor have been used:

1. The entrained fluidized-bed with riser coolers, called the Synthol reactor, used at Sasol.
2. The fixed fluidized-bed with internal cooling coils used at the Carthage-Hydrocol plant at Brownsville, Texas.

For waxy distillate production at values of the chain growth factor of about 0.9, the above reactor types are not satisfactory because the high molecular weight products cause fluidization problems. There is a great deal of interest in this type of operation today because yields of light gases and oxygenates are reduced and because an easily upgraded, high quality distillate is produced. Gasoline and other products produced in Synthol type operations require extensive upgrading before they are marketable. While numerous reactor types have been proposed for distillate production, the selection boils down to two main candidates:

3. The low conversion per pass, fixed-bed, tubular reactor used at Sasol (the ARGE reactors).
4. The higher conversion per pass, slurry bubble column reactor with internal cooling coils demonstrated by Rheinprussen in the 1950's.

It is of interest to note that for natural-gas-based Fischer-Tropsch distillate designs, Shell has selected the tubular fixed-bed for their new

plant in Malaysia, whereas Statoil has recently announced a slurry reactor design for the same type of application.

Methanol Experience

The experience of Air Products with the liquid phase methanol process in the LaPorte demonstration unit is pertinent to any discussion of slurry reactors. This process was invented by Chem Systems to provide adequate heat removal in their once-through methanol process. Since there is no external gas recycle to remove part of the heat of reaction as sensible heat, heat evolution per unit volume of reactor is high and the best way of removing this heat seemed to be in a slurry reactor where a high heat flux [20 $kW/m^2$ or 6300 $Btu/(h \cdot ft^2)$] may be used because the rapid circulation of the liquid phase gives very uniform liquid temperatures.

In the course of their experimental work, Air Products investigated three types of slurry reactor:

1. An ebullating-bed system with liquid circulation through an external heat exchanger.
2. An entrained-bed system with slurry circulation through the external heat exchanger.
3. A slurry bubble column reactor with internal cooling coils.

The entrained-bed system was favored over the ebullating-bed because smaller particles could be used, giving higher effective catalyst activity. Both types required an external circulation pump and, ultimately the internally cooled, slurry bubble column reactor was chosen as the simplest and least costly design. Only about 4% of the reactor volume is occupied by the cooling coils, but heat removal has been limiting and a more practical design would increase this figure. The LaPorte reactor is operated with a superficial gas velocity of 0.15 m/s[1] and a catalyst concentration of 35 wt% or higher. Above 35 wt%, mass transfer limitations become significant [Studer, et.al. (1989)]. Typically, space velocity is in the range of 6 to 10 $Nm^3/(h \cdot kgCat)$, the same as in fixed-bed methanol and the approach to equilibrium is similar at the same space velocity.

The primary application of the low conversion, once-through methanol process is in the coproduction of methanol and power in integrated gasification-combined cycle designs, an application selected in Clean Coal

[1] Multiply by m/s by 3.28 to obtain corresponding velocity in ft/s.

3 for further evaluation. The slurry reactor is not proposed as a replacement for conventional fixed-bed reactors in high yield, conventional, recycle methanol designs, although Air Products has suggested a novel two-step design with a slurry reactor operating once-through in the first step.

Reactor Sizing Considerations

Conversion in a Fischer-Tropsch reactor is also correlated with space velocity per unit weight of catalyst. Satterfield, et. al. (1983) found that there was little difference between a slurry reactor and a fixed-bed reactor when expressed in these terms. Equivalent product distributions were observed. These tests were run under conditions where mass transfer resistances were virtually eliminated but, roughly speaking, the gas-liquid mass transfer resistance in the slurry reactor and the intraparticle resistance in the fixed-bed reactor are of similar magnitude. The same generalization is true of a methanol reactor.

While the rate of reaction is proportional to catalyst weight, the size and cost of the reactor is more closely related to the volume of the reactor[2]. How then does space velocity per unit *weight* of catalyst compare with space velocity per unit *volume* of catalyst and how much of the total volume is occupied by the heads, cooling coils and other internals? This question will be addressed for typical design values of catalyst concentration, particle density and gas holdup.

While essentially all of the experimental slurry F-T work appears to have been performed at slurry concentrations less than 25% and at superficial velocities less than 0.10 m/s, there does not appear to be any reason why a slurry Fischer-Tropsch reactor cannot be operated at the same conditions as a slurry methanol reactor. The systems are very similar. The primary differences are that the liquid phase in the F-T system is the product itself, molecular weight about 400, whereas the preferred liquid in the methanol reactor is Witco-40, a saturated mineral oil of about 340 molecular weight. Liquid densities are similar and so are the gas densities, the higher pressure in the methanol reactor being compensated for by a generally lower $H_2/CO$ ratio and thus a higher molecular weight gas in the F-T reactor. Use of the critical density concept of Roy, et. al.

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[2] Cost is more directly related to vessel weight. Since wall thickness is related to diameter, reactor weight is determined by the same dimensional factors which determine volume and there is a rough proportionality.

(1964), indicates that up to 65 wt% solids could be suspended in either the F-T or methanol slurry systems.

In their review of Rheinprussen operations, Kolbel and Ralek (1980) state that "The optimum concentration of the catalyst in suspension proved to be about 10 wt% in terms of the iron present in the catalyst. Lower concentrations reduce the reactor efficiency, and higher concentrations up to 20% can be used, but they increase the viscosity of the suspension and thus decrease the interfacial area, which affects mass transfer and hence may cause a loss in conversion" (10 wt% iron corresponds to about 14.3 % slurry concentration). Part of this reluctance to increase slurry concentration may have had to do with physical limitations of the equipment on heat removal. It may also be tied in with a reluctance to go higher than about 0.10 m/s inlet gas velocity. Higher gas velocities will improve mass transfer, and should improve overall conversion, provided gas holdup remains reasonable.

Some Fischer-Tropsch modelling efforts have predicted a loss in conversion at superficial velocities above 0.09 m/s [Deckwer (1982)], but these results are confounded by the use of a simplified gas holdup expression which gives much too high a gas holdup (and therefore too low a catalyst holdup) at superficial velocities above 0.04 to 0.05 m/s. Operation at 0.15 m/s inlet superficial velocity and 35 wt% slurry concentration appears as feasible in a Fischer-Tropsch as in a methanol slurry reactor.

Assuming a 35 wt% catalyst concentration, a particle density of 1,500 $kg/m^3$ and a liquid density of 670 $kg/m^3$ at reaction temperature[3], the slurry density is 830 $kg/m^3$ and the catalyst concentration in $kg/m^3$ of unaerated slurry becomes 290. The recent data of Bukur (1987) indicate that at 15 m/s superficial velocity the maximum gas holdup in these systems, without foaming, is roughly 27%. With contraction in the gas flow due to reaction, a somewhat lower gas holdup is predicted - say about 25%. The weight of catalyst per unit volume of aerated slurry is thus about 218 $kg/m^3$. Adding an additional 15% for the heat transfer coils and 20% for disengaging space, the catalyst loading becomes about 150 $kg/m^3$ of reactor shell volume. It is, of course, possible that a non-supported catalyst of higher intrinsic density could be used, but even if the particle density is doubled, the catalyst loading increases only to

[3] 1,000 $kg/m^3$ is one $g/cm^3$ and corresponds to 62.4 $lb/ft^3$

about 165 kg/m$^3$ of overall reactor volume. Table 1 summarizes the calculation for this case and for a fixed-bed reactor.

A fixed-bed reactor with the 1500 kg/m$^3$ particle density and a bed void fraction of 37% will have a catalyst loading of 945 kg/m$^3$ of reaction volume. In this case, the heat transfer tubes and headers take up about 40% of the reactor volume and the heads add an additional 25% bringing the catalyst loading to about 425 kg/m$^3$ of total reactor volume - more than 2 and 1/2 times that of the slurry reactor. The particle density of 1500 kg/m$^3$ is intended to represent a conservative value for supported precipitated iron catalyst. Supported cobalt catalysts appear to have lower particle densities but a higher activity per unit weight of catalyst so that the productivity per unit volume of reactor is the equivalent of or higher than iron based catalyst.

While this analysis shows that a slurry reactor must have twice the volume of a fixed-bed reactor for comparable operating conditions, it is not likely that operating conditions will be the same. The superficial velocity restriction on a slurry reactor makes it generally unsuitable for low conversion, high recycle operation. In methanol reactor design where there is an equilibrium limitation on conversion per pass, the slurry reactor, for high ultimate conversion levels, will be designed for higher pressure to increase conversion per pass, reduce recycle and increase gas density. Even so, reported space velocities per unit weight of catalyst appear to be comparable.

There are other differences. Temperature profiles will be different, for example. The slurry reactor will use continuous catalyst makeup from a prereduction system, whereas the fixed-bed reactor requires periodic shutdowns for catalyst replacement. Productivity per unit weight of catalyst consumption is believed to remain constant. The heat transfer tubes add significantly more to the weight of the fixed-bed reactor than the slurry reactor, but the shell of the slurry reactor must be designed for reaction pressure (60 to 100 atm in the methanol case, 15 to 30 atm for Fischer-Tropsch) whereas the shell of the fixed-bed reactor is designed for steam side pressure which ranges from 20 to 40 atmospheres.

These differences must be quantified in a more detailed study. Clearly, however, we can agree with Air Products' conclusion that the proper niche for slurry phase methanol is in the "once through methanol" application. There is little or no incentive to consider a slurry reactor for a recycle methanol operation except, perhaps, as a first stage reactor.

Natural Gas Based Fischer-Tropsch Synthesis

The natural gas based Fischer-Tropsch plant is operated at close to 2.0 $H_2/CO$ ratio. The reactor design presents a somewhat different situation from methanol, in that recycle is not required by equilibrium limitations but is required in the fixed-bed reactor in order to achieve a mass velocity adequate for good heat transfer. A conversion per pass of 35 to 40% appears to be the practical limit in a fixed-bed F-T reactor, requiring a recycle to fresh feed ratio of about 2.3. (The ARGE reactors were limited to about 25% conversion per pass and 66% ultimate conversion because of the high level of inerts and methane in the reactor feed gas. With a natural gas feed and combined reforming or partial oxidation to produce synthesis gas, a lower inerts level is readily achievable and ultimate conversions of over 90% are possible.)

A slurry F-T reactor is not limited in this manner and can go to higher per-pass conversion levels. The limiting factor on conversion in the slurry bubble column is backmixing, particularly of the liquid phase, which makes it necessary to use lower space velocities to achieve a given conversion level than would be required in a plug flow reactor. Three simplified models have been used to investigate the effect of backmixing:

Model 1 - plug flow, no axial mixing of either phase
Model 2 - gas phase plug flow, liquid phase fully backmixed
Model 3 - CSTR, both phases fully backmixed

These simplified models are based on the conversion rate being proportional to hydrogen concentration and on an overall gas contraction factor, $\alpha$, which is assumed constant with conversion. The model equations are summarized in an addendum to this paper.

Figure 1 shows space velocity requirements to achieve a given conversion level in a plug flow and a fully backmixed slurry reactor at two levels of the contraction factor, 0.0 and -0.5. Contraction factors of -0.5 to -0.6 are typical of F-T synthesis. Space velocity in Figure 1, is combined with the overall rate constant, K, in the dimensionless Stanton Number, K/SV. The overall rate constant combines the mass transfer rate constant, $K_M$, and the reaction rate constant, $K_R$, in the form of a summation of resistances:

$$1/K = 1/K_R + 1/K_M$$

Model 2, which approaches most closely what would be expected from a large, low L/D, F-T reactor, has the interesting characteristic that it reduces to Model 1 when mass transfer controls, ($K_R >> K_M$), and to Model 3, when reaction rate controls, ($K_M >> K_R$). Figure 2 shows the situation when $K_M = K_R$.

In Figure 3 the space time yield (STY), in Nm3 syngas converted/(h·m3), is plotted versus conversion per pass for a Model 2 reactor, based on the curve shown in Figure 2. Two prediction lines are shown, the upper one being an ideal case with no inerts and the lower one being a more realistic case with 1.5% inerts in the feed gas and 95% ultimate conversion. Conditions for this plot are 533 °K and 1500 kPa. In the ideal case STY = GHSV times conversion per pass, and the ultimate conversion is 100%.

Figure 3 also shows the recycle to fresh feed ratio (R/FF) required at varying levels of conversion per pass for the same two cases. The gain in productivity at low conversion per pass is offset by a higher recycle ratio, [R/FF ratio = (1 ÷ conversion per pass - 1)], so there is an engineering evaluation to be made as to the best conversion level to design for. From heat transfer considerations, the fixed-bed reactor works best *low* conversion per pass, below 50%. The slurry reactor requires a *high* conversion per pass because of superficial velocity limitations. Nevertheless, it is apparent from Figure 3 that conversion levels over 90% should be avoided because of the sharp dropoff in STY and 80% conversion per pass may be a good compromise between recycle requirements and high productivity.

The fixed-bed reactor has the advantage that it behaves like a plug flow reactor, though the difference between models at 35 to 40% conversion is small. Since the fixed-bed reactor runs at a lower average temperature, it has a lower STY than would be read off from Figure 3. The trade-off between a slurry reactor and a fixed-bed reactor for the natural gas case is not obvious, a more detailed engineering and cost evaluation being required. This is not a part of Bechtel's assignment, which is concerned only with coal based plants.

The Coal Based Fischer-Tropsch Design

A coal based Fischer-Tropsch plant for distillate production differs fundamentally from a natural gas based plant because of the composition of the raw synthesis gas. A natural gas plant using partial oxidation will

produce a synthesis gas with a $H_2/CO$ ratio of slightly under 2, the stoichiometric ratio for the reaction:

$$2H_2 + CO \rightarrow -CH_2- + H_2O \qquad (1)$$

In this case, the water gas shift reaction is not desired since it produces unwanted $CO_2$. Most of the recent developments in natural gas processing use cobalt type catalysts which do not have this activity.

A modern coal gasifier of the Texaco or Dow design produces a synthesis gas with a $H_2/CO$ ratio of about 0.75, a Shell gasifier produces something under 0.5 $H_2/CO$ ratio. A 0.667 ratio is stoichiometric for a F-T reactor, without steam addition, where the catalyst has high water gas shift activity. Precipitated iron catalysts have this activity. The reactions involved are reaction number (1) plus:

$$H_2O + CO \leftrightarrow H_2 + CO_2 \qquad (2)$$

giving the overall reaction:

$$H_2 + 2CO \rightarrow -CH_2- + CO_2 \qquad (3)$$

Because equilibrium in reaction 2 heavily favors $CO_2$ production at F-T conditions, reaction 3 predominates over reaction 1.

In this scenario, shift and $CO_2$ removal are not required prior to Fischer-Tropsch synthesis. This has the dual advantage of eliminating a separate reaction step with its steam requirement and simplifying the gas purification step. $CO_2$ removal after synthesis is more straightforward.

A slurry reactor may be ideal for low $H_2/CO$ ratio synthesis for the following reasons:

1. Low $H_2/CO$ ratio can lead to carbon formation via the Boudouard reaction:

$$2CO \leftrightarrow CO_2 + C\downarrow \qquad (4)$$

A slurry reactor, however, raises the $H_2/CO$ ratio that the catalyst actually sees owing to combination of a higher mass transfer coefficient for hydrogen and a higher CO consumption by reaction 2..

2. Even if carbon formation does occur, the slurry reactor offers the possibility for its removal.

3. Catalyst deactivation can be handled by means of periodic catalyst withdrawal and addition, whereas replacement of fixed-bed catalyst requires a shutdown.

4. Distillate production requires low reaction temperatures for good yield. Because of uniform temperatures, a slurry reactor can be run continuously at end of run temperature for the fixed-bed reactor and give equivalent yield distribution. This gives both high reactor productivity and the potential for higher pressure steam generation.

Weighed against these advantages are the need to provide for product removal and separation from the catalyst as well as facilities for continuous addition of preactivated catalyst.

Since the fixed-bed reactor is not applicable to low $H_2/CO$ ratio operation, our DOE study will evaluate fixed-bed operation at a 2 to 1 ratio versus slurry bubble column operation at the low ratio out of a Shell gasifier. Because of the hydrogen deficiency, steam will be added to conform with stoichiometry. The two processing schemes will be quite different between the gasifier and the downstream processing units. These, however, will be kept essentially unchanged. It is expected that the slurry reactor system will have an advantage under these assumptions and we hope to quantify this advantage in the remainder of our study.

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# Addendum

## Limiting Fischer-Tropsch Models

### Model 1
Plug Flow Both Phases

$$(1 + \alpha^*)\cdot\ln(1 - X_H) + \alpha^*\cdot X_H = - K/SV$$

### Model 2
Plug Flow Gas - Fully Mixed Liquid

$$((\alpha^*\cdot X_H + (1 + \alpha^*\cdot Y)\cdot\ln(1 - x_H/Y))/(1 + \alpha^*\cdot n) = K_M/SV$$

where

$$Y = (1 - n)/(1 + \alpha^*\cdot n)$$

$$n = X_H/(K_R/SV)$$

### Model 3
Both Phases Completely Mixed

$$X_H\cdot(1 + \alpha^*\cdot X_H)/(1 - X_H) = K/SV$$

In all cases:

$$K_R = k_H\cdot\varepsilon_L/H_H, \qquad K_M = k_La/H_H$$

$$K = \frac{K_R.K_M}{K_R + K_M}$$

$$SV = \frac{GHSV}{3600} \times \frac{T}{273} \times \frac{101.3}{P}$$

Models 1 and 2 follow the derivations of Deckwer ((1981) and Bukur (1983) and all models assume the reaction is first order in hydrogen concentration.

## Notation

| | |
|---|---|
| a | gas-liquid interfacial area, $m^{-1}$ |
| C'Cat | catalyst concentration, $kg/m^3$ |
| $C_{HG}$ | hydrogen concentration in gas phase, kg mole/$m^3$ |
| $C^*_{HL}$ | hydrogen concentration,liquid, in equilibrium with gas, kg mole/$m^3$ |
| $C_{HL}$ | hydrogen concentration in the liquid phase, kg mole/$m^3$ |
| D | I.D. of reactor, m |
| GHSV | Gas hourly space velocity, $Nm^3$ $(H_2+CO)/[h \cdot m^3$ reactor volume], (reactor volume is expanded slurry height times cross section area) |
| H | solubility coefficient of hydrogen = $C_{HG}/C^*_{HL}$ |
| I | Inlet ratio of $CO/H_2$ |
| $k_L$ | liquid side mass transfer coefficient, m/s |
| $k_H$ | effective reaction rate constant for hydrogen consumption, $s^{-1}$ (note that to agree with space velocity in $Nm^3/[s \cdot kgCat]$, $k_H$ = $k_H' \cdot C'Cat$ where $k_H'$ is in $m^3/[kg \cdot s]$ |
| L | Length of expanded slurry bed, m |
| P | pressure, kPa |
| r | rate of hydrogen consumption, $r = k_H \cdot C_{HL}$, kg moles/$[m^3 \cdot s]$ |
| SV | Space velocity in actual $m^3$ inlet gas/$[s \cdot m^3]$ |
| T | temperature, °K |
| U | Usage ratio of $CO/H_2$ |
| $X_H$ | hydrogen fractional conversion per pass (If U = I, $X_H = X_{CO}$) |
| $\alpha$ | contraction factor, $\alpha=[m^3/s(X_{H_2+CO=1})-m^3/s(inlet)]/[m^3/s(inlet)]$ |
| $\alpha^*$ | contraction factor modified for $H_2$ conversion, $\alpha^* = \alpha \cdot (1+U)/(1+I)$ |
| $\varepsilon_L$ | fractional liquid hold-up |

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Table 1

Comparison of Catalyst Loadings
kg/m3

| | Slurry Reactor | Fixed-Bed Reactor |
|---|---|---|
| Particle density, kg/m3 | 3100 | 1500 |
| Liquid density, kg/m3 | 670 | |
| Slurry density, kg/m3 | 922 | |
| Slurry concentration, kg/m3 | 323 | |
| Gas holdup or voids, % | 25 | 37 |
| Loading (reaction volume), kg/m3 | 242 | 945 |
| Heat transfer tubes, % | 15 | 40 |
| Heads & Disengagement, % | 20 | 25 |
| Loading (reactor volume), kg/m3 | 165 | 425 |

Figure 1
COMPARISON OF MODELS
HYDROGEN CONVERSION VS STANTON NUMBER

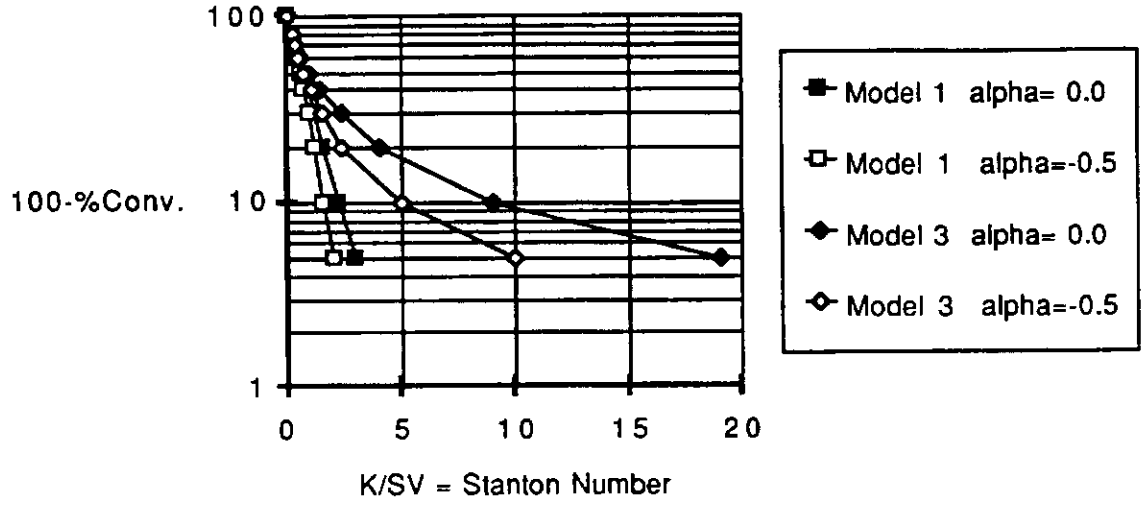


Figure 2
COMPARISON OF MODELS
KR = KL = 2K
$\alpha^* = -0.5$

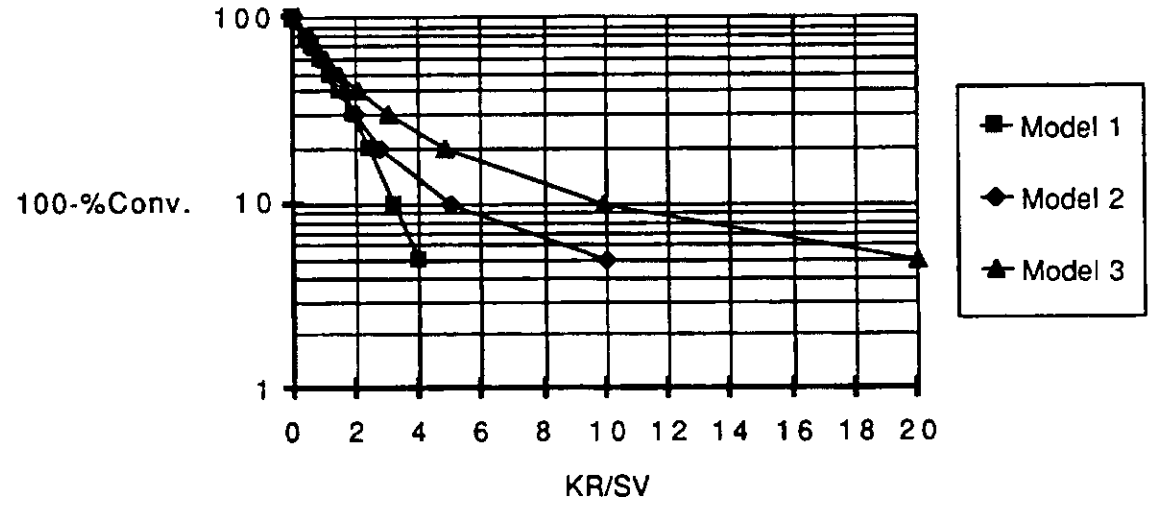

Figure 3
STY AND RECYCLE RATIO
VERSUS CONVERSION PER PASS