

CHAPTER 3

PILOT PLANT VERIFICATION OF CHEMFT CATALYST

3.1 OVERVIEW

This chapter assesses whether reactor conditions and product selectivities established for the ChemFT catalyst on laboratory scale are applicable to a pilot plant scale reactor. An overview is given of some literature on reactor operation parameters that can be expected to have an influence on the catalyst performance when evaluation is done on larger reactors. Selectivity data obtained from pilot plant scale testing with a few kilograms of catalyst is compared to that from the laboratory scale reactor. The pilot plant reactor referred to is a tubular slurry reactor. Deviations in the results are related to design and scale-up parameters.

3.2 LITERATURE SURVEY

3.2.1 Introduction

Laboratory-bench-scale stirred slurry reactors are widely considered best suited for fundamental studies as such reactors can be operated to ensure the absence of interphase and intraphase concentration and temperature gradients (Zimmerman and Bukur, 1990). Laboratory-bench-scale reactors do however make the collection of sample in sufficient quantities difficult and time consuming due to the small amounts of catalyst used in such reactors (most often a few grams of catalyst). A number of reactor parameters need consideration when scaling experimentation up to a bigger scale such as pilot plant or commercial scale.

Developments in FT reactor technology have seen reactors being designed for production capacities in excess of 2500 bbl/day (Krishna and Sie, 2000). Such single reactor capacities are more than two orders of magnitude higher than those of classical reactors operated before or

during World War II. Issues such as heat transfer rate and selectivity related to mass transfer pose the biggest challenge when scaling from micro scale lab data to full-scale plants.

3.2.2 Parameters influencing catalyst/reactor performance

Perego and Peratello (1999) summarise the phenomena involved in all catalytic processes in addition to the desired catalytic reaction as:

- Side or interfering chemical reactions,
- Thermodynamic, physical and chemical equilibrium,
- Heat transfer,
- Mass transfer between phases or even within a given phase,
- Flows of fluids (free convection or forced convection) of granular solids.

It is understandable that the aforementioned phenomena will be influenced by variables such as reactor geometry and size. Data should be free from the abovementioned influences or they should be accounted for in the design of experimental reactors. The understanding of such phenomena can be accomplished by the development of a reactor model (mathematical) which describes the various aspects. If such a model is present one can easily find model equations whose parameters depend only on the macroscopic variables of the reactor, i.e. pressure, temperature and space velocity (Perego and Peratello, 1999).

The University of Amsterdam has performed much experimental research and published various articles on the design and scale-up of slurry phase reactors during the last decade (Krishna and Sie, 2000). The following overview will thus mainly focus on published results from the University of Amsterdam for the purpose of relating it to the ChemFT catalyst performance to be expected on large-scale reactors.

3.2.2.1 Influence of gas bubble size on reactor flow regime

The bubble size present throughout the reactor will determine the flow regime present within the reactor. This means that a slurry reactor can operate in either a homogeneous flow regime as seen at low gas flow rates and thus small bubbles (1 – 10 mm) uniformly distributed into the slurry phase, or in a heterogeneous (churn-turbulent) flow regime. A heterogeneous regime would develop with increasing gas flows as the small bubbles combine in clusters to form large bubbles

(20 – 70 mm). Such large bubbles would travel through the reactor in a manner similar to plug-flow at high velocities (between 1 and 2 m/s) (Maretto and Krishna, 1999). Together with the large bubbles will be small bubbles “entrained” in the slurry. The heterogeneous regime is the most optimal one for FT synthesis due to the favourable mixing, temperature control and presence of higher catalyst concentrations.

It follows that hold-up of gas bubbles within the reactor will be a very important parameter to be estimated for slurry reactor design and scale-up. Gas hold-up is influenced by factors such as catalyst concentration, column diameter, reactor pressure, gas linear velocity and the physical properties of the gas and liquid (Wilkinson, 1991). Gas hold-up will therefore influence properties of the system such as mass and heat transfer. Rostrup-Nielsen (2000) points out the importance of carrying out scale-up with real feedstock to check non-linear effects and to identify possible impact of impurities.

3.2.2.2 Catalyst concentration influence on gas hold-up

Reactor catalyst particle concentration is one of the parameters that have the greatest influence on the gas hold-up in the system. Small catalyst particle (mean diameter of about 38 μm) addition will enhance the coalescence of small bubbles thereby decreasing the hold-up of this population as the range of small bubble size increases while the large bubble hold-up remains practically independent of the slurry concentration (Krishna and Maretto, 1998). This relates to an increase in the small bubble rise velocity and consequently the total gas hold-up will decrease with increased solids concentration. This is due to the slurry viscosity effect. De Swart *et al.* (1996) showed that the small bubble population is virtually destroyed when the slurry concentration approaches 30 volume percent.

Factors which favour a heterogeneous operating regime such as increased solids concentration and increased gas velocity, also increase the heat transfer coefficient (Krishna and Sie, 2000).

3.2.2.3 Column diameter influence on gas hold-up

Reactor column diameter is another design parameter with a strong influence on the gas hold-up (although up to a limit). This is due to the influence of the diameter on the rise velocity of the bubbles. Increased diameter increases the rise velocity of large bubbles while the small bubble hold-up is almost independent of the column diameter. The influence on the large bubble rise

velocity is due to reduced “wall” effects at increased column diameters. This effect is dependent on the ratio of the bubble diameter to the column diameter. Krishna and Maretto (1998) shows that slug flow can be obtained in small diameter columns (diameter less than 0.1 m) at superficial gas velocities greater than 0.3 m/s, but slug flow is not possible in larger columns (diameter greater than 1 m). It can be seen that scaling-up from a 0.1 m diameter pilot plant to a 7 m diameter commercial reactor is not straightforward. The statement is made by the above mentioned researchers that the smallest scale pilot plant, for obtaining representative conversion levels in the pilot scale and commercial scale reactors, should be 1 m in diameter.

Due to the “wall” effect it appears that strong downwardly directed liquid velocity is present at the wall region and upwardly directed velocity in the central core. This effect results in liquid recirculation that is the cause of liquid phase dispersion and backmixing (Krishna and Sie, 2000).

3.2.2.4 Reactor pressure influence on gas hold-up

Reactor system pressure increases will result in increased gas density. Krishna and Maretto (1998) show that gas density is about 1.3 kg/m^3 for cases such as cold-flow studies carried out at atmospheric pressure compared to a syngas density of 7 kg/m^3 at 30 bar typical FT operation. The effect of increased gas density is two-fold; namely that it delays transition from the homogeneous to the heterogeneous regime and that the large bubble hold-up at the regime transition point is increased thereby influencing the voidage at the regime transition point. This is an opposite effect to that of increasing solids concentration. Krishna and Sie (2000) found the small bubble rise velocity to be very weakly dependent on the gas density in pure liquids.

3.2.2.5 Gas hold-up influence on mass and heat transfer

Catalyst particles used in slurry reactors are in the size diameter range of 38 to $150 \text{ }\mu\text{m}$. Intraparticle diffusion is normally not a limiting factor in that range. Krishna and Sie (2000) report that for operation in the homogeneous regime with catalyst of relatively low activity present in low concentration, gas-liquid mass transfer is unlikely to be a limiting factor. This statement is made in view of the large surface area of the small bubbles and their long residence time in the liquid. The use of more active catalysts in higher concentration operating in the heterogeneous regime results in gas-liquid mass transfer limitations.

The hydrodynamics of a slurry reactor operating in the heterogeneous regime see the large bubbles frequently coalesce and break-up. This means that the large bubbles would continually disappear and reappear. De Swart *et al.* (1996) explains that the exchange of gas between various bubble classes occurs at a very high rate, which is higher than the characteristic renewal rate for mass transfer. This would mean that, whereas the largest bubbles mainly represent the gas throughput, the interfacial area of the smaller bubbles largely determines gas-liquid mass transfer. Physical properties such as low surface tension, low liquid viscosity and a high gas density all promote bubble break-up in a bubble column, which leads to a decrease in the number of large fast moving bubbles and therefore result in a higher gas hold-up. Wilkinson (1991) confirms that increased gas density leads to smaller bubbles on average and a higher gas hold-up (higher density normally associated with increased reactor pressure or the use of a higher molecular weight gas) which results in an increase in the volumetric mass transfer coefficient.

3.3 EXPERIMENTAL

3.3.1 Pilot plant reactor description

The pilot plant reactor is a tubular slurry bed reactor capable of operating at pressures up to 65 bar(g). This particular reactor is 7.8 meter long with a 5 cm inside diameter ending in an expansion section at the top, which is 2.5 meter long with a 20 cm inside diameter. The reactor system is equipped to handle gas recycle. Up to 7 kg of catalyst can be loaded into this reactor compared to the 20 g of catalyst used on the lab-scale reactor. This scale-up of dimensions still falls far short of commercial size reactors, which can load more than a 100 tons of catalyst for some applications, but comparison of data should however still give some indication of what can be expected when reactors are scaled-up.

Figure 3.1 gives a flow diagram of the reactor system. Either APG gas from the commercial plant for synthesis or hydrogen for reduction purposes is fed to a feed compressor. This fresh feed ties into the recycle gas feed line whereafter the total feed is preheated to about 120°C before flowing through a filtering system. The heated total feed enters the reactor bottom to bubble upwards through the wax / catalyst slurry medium. Flow rates through the reactor are controlled to ensure that the catalyst remains in the pipe section of the reactor (7.8 m section) while preventing any settling of catalyst. The wax level within the reactor is controlled by

means of a filtration system in the expansion section. A slurry return line ensures continuous mixing within the reaction zone to maintain a uniform temperature profile over the reactor.

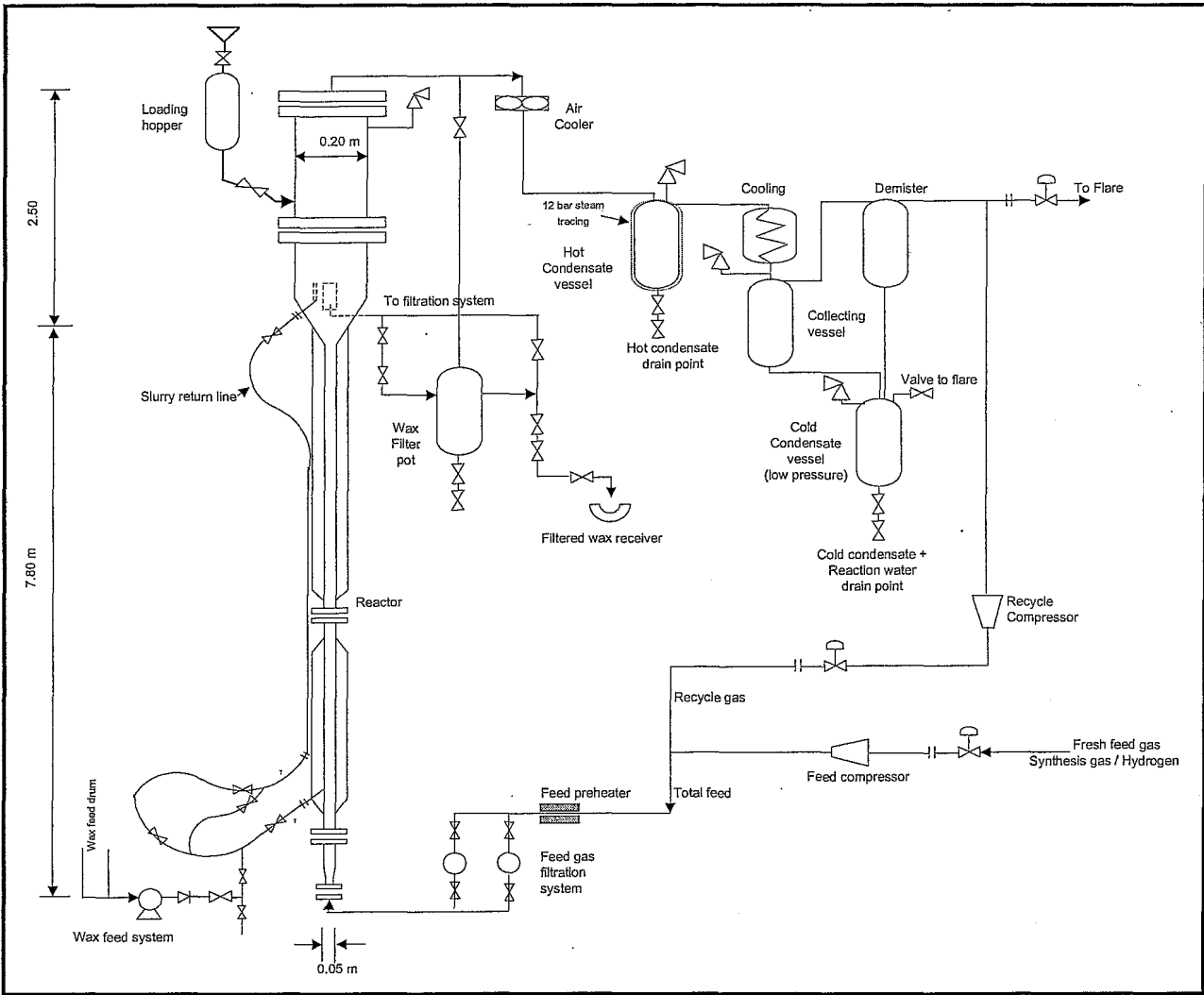


Figure 3.1: Pilot plant reactor system flow diagram

Unreacted gas together with the gas-phase product stream exits the reactor top after which it is cooled by an air cooler to about 80°C. Heavier condensed product is collected and drained at the hot condensate vessel. This vessel is traced by 12 bar(g) steam lines to ensure that reaction water is not drained at this point (controlled at about 170°C). The gaseous stream from the hot condensate vessel is cooled with a water cooler to around 30°C. Reaction water and cold condensate product are collected and drained at the cold condensate vessel. This vessel is operated at atmospheric pressure. A demister ensures that gas exiting from the cold section is dry before it is flared or recycled.

Catalyst and melted wax are loaded into the reactor with the aid of a loading hopper, while additional wax can be fed to the reactor during operation with the wax feed system. Gas sample points allow sampling of the fresh feed, total feed and tail gas leaving the system. Gas samples are analysed with a mass spectrometer for conversion calculations and mass balances.

3.3.2 Pilot plant reactor experimental conditions

3.3.2.1 Catalyst loading

Catalyst from the same prepared batch was used for the pilot plant test and laboratory evaluation. 5 kg of unreduced ChemFT catalyst was mixed with commercial FT wax to produce a homogeneous mixture. The wax / catalyst mixture was heated to 180°C in the loading hopper with the aid of 12 bar(g) steam. The reactor already loaded with some clean FT wax was operating at 180°C, 20 bar(g) with the hydrogen linear velocity through the reactor set to 0.3 m/s (i.e. 21 m³_n/h). The hydrogen flow rate corresponds to a GHSV of 4200 ml/gcat/h. The wax / catalyst slurry was added to the reactor load and the reactor temperature slowly increased to 240°C.

3.3.2.2 Catalyst reduction

Reduction of a 5 kg ChemFT catalyst sample took place in-situ at 240°C, 20 bar(g) and a hydrogen linear velocity through the reactor of 0.3 m/s. Reduction conditions were maintained for a period of 20 hours. All vessels were drained after completion of reduction.

3.3.2.3 Synthesis conditions

On completion of the reduction, the reactor temperature was decreased to 200°C while maintaining the hydrogen flow rate (similar procedure than that used on laboratory scale experiments). Upon reaching 200°C the synthesis gas was introduced step-wise at increments of 1 m³_n/h every 15 minutes, while simultaneously decreasing the hydrogen flow rate. After having replaced all the hydrogen with synthesis gas, the reactor pressure was increased to 45 bar(g) with the feed gas flow rate adjusted accordingly to ensure 0.3 m/s linear velocity.

Reactor temperature was slowly increased to 240°C and the linear velocity adjusted to ensure a CO+CO₂ conversion level of 40 % (same as laboratory data). The reactor was operated in a

once-through mode before recycle was introduced for the last condition. Table 3.1 shows the final conditions used for the pilot plant evaluation.

Table 3.1: Pilot plant reactor experimental conditions

Condition	Pressure	Gas linear Velocity	Temperature	CO+CO ₂ conversion	Duration	Recycle ratio
1	45 bar(g)	0.17	240°C	40 %	5 days	0
2	45 bar(g)	0.17	240°C	60 %	5 days	1.4

3.4 RESULTS AND DISCUSSION

The pilot plant test run lasted 75 days, during which time a number of different operating conditions were investigated. Reference conditions added to the test program assured reproducibility of the results obtained. Only the data from those conditions relevant to the comparison of laboratory data are shown here. Table 3.2 provides the relevant operating data and results of the pilot plant investigation when using once-through and recycle operation. All the data was obtained at a operating pressure of 45 bar(g) and 240°C reactor temperature. Such conditions are similar to that used in the laboratory investigations and will thus enable comparison. More comprehensive summaries of the results are given in Appendix 7 together with that from the laboratory reactor, which will be used for comparison.

Selectivity data obtained from the pilot plant reactor operation can be compared to selectivity data obtained on the laboratory stirred slurry reactor operated at 45 bar(g), 240°C and a CO+CO₂ conversion of 40 % (data obtained from Appendix 7). Figure 3.2 compares the total product selectivity of the pilot plant cases to that obtained in the laboratory. Pilot plant once-through operation has increased olefin selectivity compared to the recycle condition, with similar alcohol selectivity. This result confirms the influence of higher conversion observed under Section 2.4.2.4, i.e. reduced olefin selectivity with little change in alcohol selectivity. Recycle conditions see unsaturated products being converted to paraffinic products together with increased internal olefins. The product selectivity obtained from the laboratory reactor agrees better with that of the recycle condition despite the difference in conversion.

Table 3.2: Operating data and results for pilot plant reactor tests

Operation at 240°C, 45 bar(g)	Pilot Plant Once-through	Pilot Plant Recycle
Data point	1	2
Total Reactor Tail Gas Flow Rate (ml(n) / s)	4662.03	1363.70
Total Reactor Feed Gas Flow Rate (ml(n) / s)	6421.54	6741.00
H ₂ /CO-Feed Ratio (fresh feed)	1.96	1.94
H ₂ /CO – Total Feed Ratio	1.96	2.84
H ₂ /CO-Reactor Ratio	3.03	5.24
Reactor Partial Pressures (bar(g))		
H ₂	23.35	18.65
CO	7.70	3.56
H ₂ O	4.08	1.83
CO ₂	3.61	7.54
% Conversion (overall)		
H ₂	34.71	64.61
CO	57.73	86.88
SYNGAS	42.48	72.17
CO+CO ₂	40.06	62.23

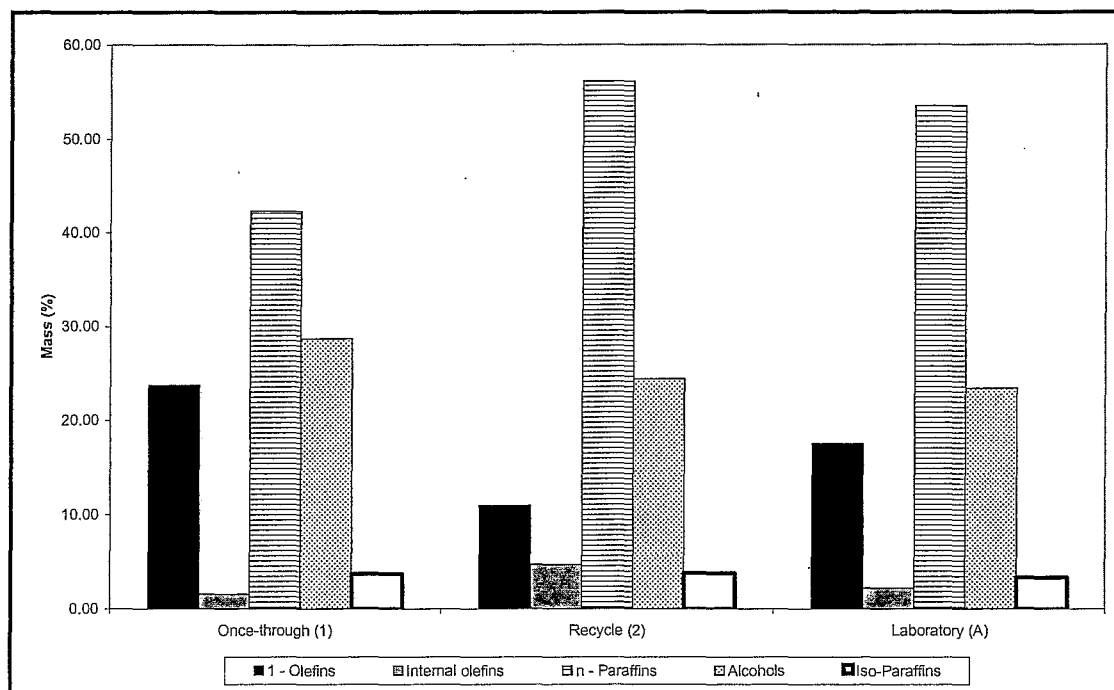


Figure 3.2: ChemFT catalyst Pilot plant and laboratory total product distribution comparison

Figure 3.3 compares the product mass distribution per carbon number of the two pilot plant-operating scenarios (data point 1, which is once-through operation vs. recycle point 2). Figure 3.4 shows the comparison of pilot plant once-through data (data point 1) to the laboratory results, while Figure 3.5 compares the pilot plant recycle data points (data point 2) to the laboratory results.

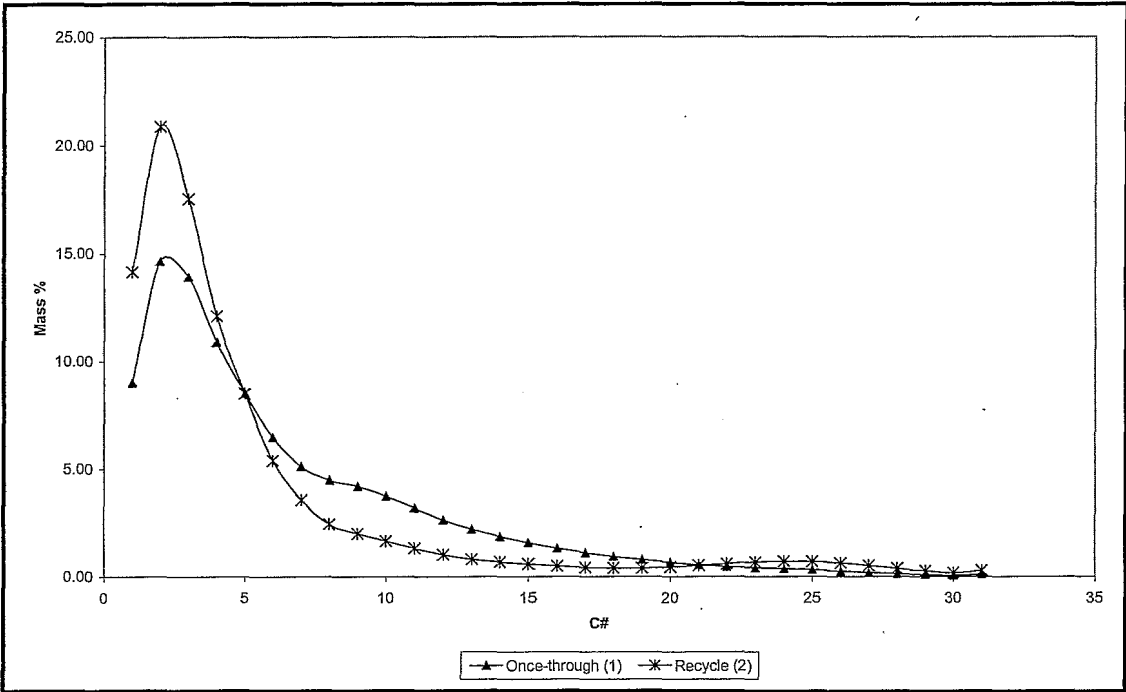


Figure 3.3: ChemFT Pilot plant total product distribution : once-through vs. recycle

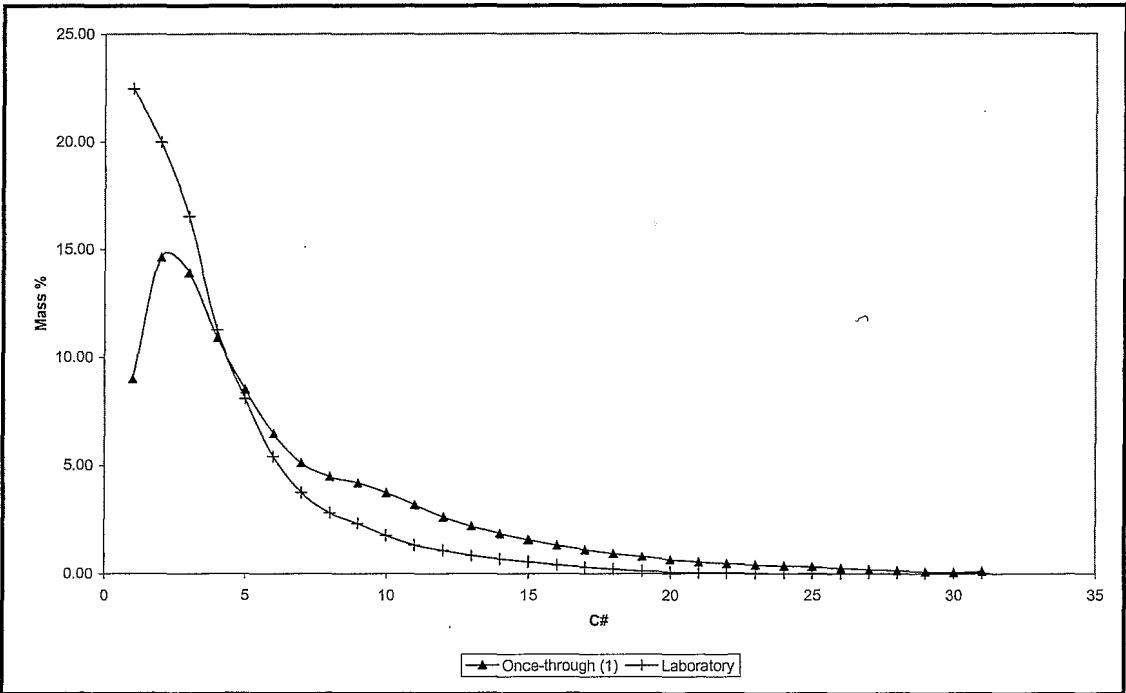


Figure 3.4: ChemFT Total product distribution: pilot plant once-through vs. laboratory

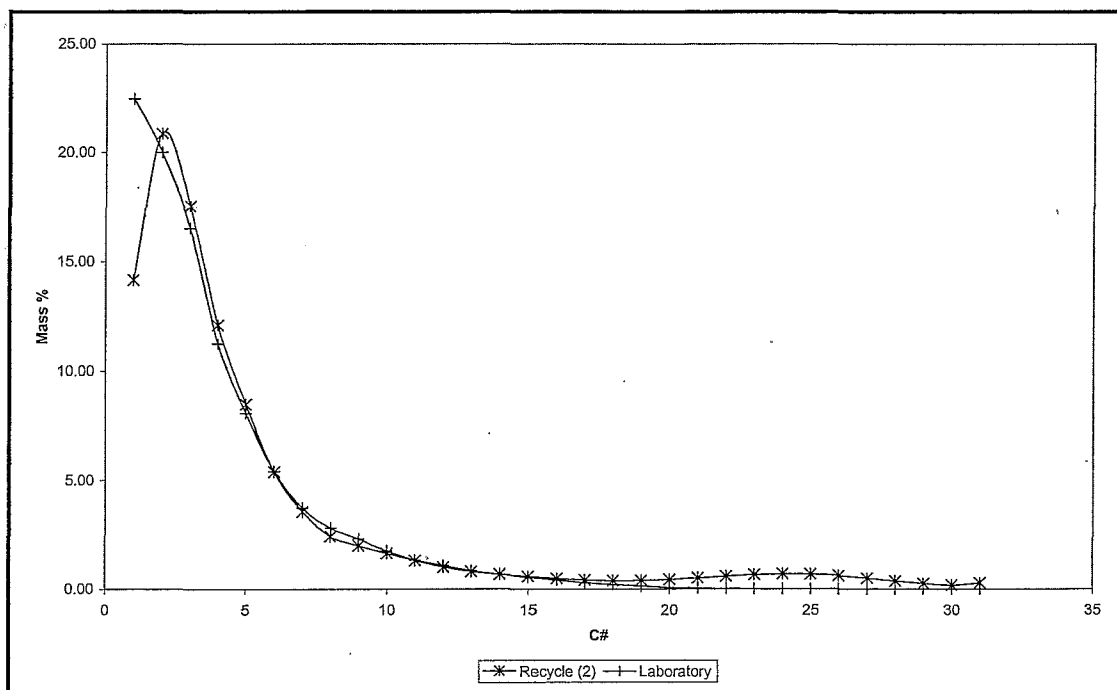


Figure 3.5: ChemFT Total product distribution : pilot plant recycle vs. laboratory

Figures 3.3 to 3.5 confirm that the pilot plant recycle condition gives a similar product distribution to that of the laboratory slurry reactor. Similar growth parameters can be expected for these conditions.

The methane make of the laboratory reactor is more than that reported for both pilot plant conditions. This result is however due to the method used to process the pilot plant data. Laboratory experiments are done with an Argon tracer gas and analyzed with a TCD as discussed in Chapter 2, thus making quantification of the permanent gases easy. Due to the scale of the operation on the pilot plant such a system is not used. Permanent gases are analysed with a MS. An MS does however also pick up other hydrocarbon products and thereby complicating the combination of the more detailed FID analyses with the MS data. A variance in the methane selectivity is thus seen for the different data processing methods. This is especially relevant to the methane as methane is also present in the APG feedgas used. With this in mind the methane selectivity of the pilot plant under recycle conditions compares well with that obtained in the laboratory.

Table 3.3: CH₄ selectivity comparison

CH ₄ C-atom selectivity %	Pilot Plant Once-Through operation	Pilot Plant Recycle operation	Laboratory
TCD with Ar tracer gas			16.3
MS analyses	8.4	15.1	
MS + FID analyses	5.3	8.1	

The pilot plant reactor configuration results in a H₂/CO ratio profile from the bottom to the top of the reactor. Figure 3.6 shows a typical H₂/CO profile for the gas and liquid phases in a 38 m high (diameter 6 m) slurry reactor utilising the same catalyst (in-house simulation on a typical commercial scale slurry reactor). Comparing the data from Table 3.2, the once-through reactor operation in the pilot plant will see an average H₂/CO ratio of about 2.5, while the increased H₂/CO ratio of the total feed in the recycle scenario will result in an average of about 4. Ratios discussed this far imply gas phase ratios, but it can be seen from Figure 3.6 that this will also relate to liquid phase ratios. It can be seen that the liquid and gas phase is in equilibrium, implying that no mass transfer limitations will occur between the two phases, but rather kinetic limitations (if any). Addition of recycle to the pilot plant reactor increases the average H₂/CO ratio to one comparable with that present in the laboratory stirred slurry reactor (CSTR operation).

Laboratory predicted parameters correspond thus more accurately with recycle data points on pilot plant scale than those obtained from once-through operation. It must however be stressed that the accuracy of the partial pressure calculation will influence the accuracy of the reactor model. Pilot plant scale and commercial scale reactor partial pressure determinations are often not as accurate when experimentally determined due to the lack of sufficient measurements in a reactor not displaying CSTR behaviour.

The presence of a profile over the pilot plant reactor can be attributed to a number of aspects. Reactors normally see a lower temperature at the bottom due to the feed gas having a lower temperature than the desired reactor operation temperature, which will result in less catalyst activity and thus smaller partial pressure changes at the bottom part of the reactor. A sparger distributing the gas is installed at the reactor inlet thus ensuring that evenly distributed small

bubbles will constitute the majority of bubbles present in the very bottom of the reactor. These smaller bubbles will present a homogeneous flow regime at the bottom of the reactor, explaining the small change in H_2/CO ratio observed for about the first metre presented on Figure 3.6.

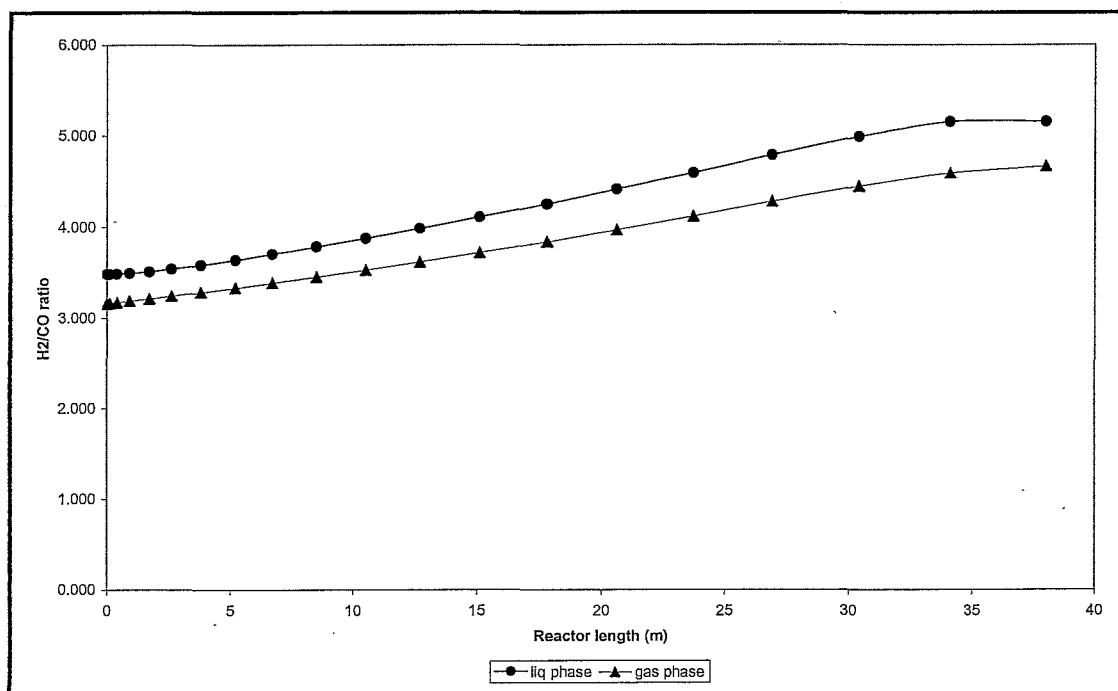


Figure 3.6: A typical $H_2:CO$ profile expected over a tubular slurry reactor

Increased catalyst concentration in the bottom section of the reactor is normally due to natural settling of catalyst, wall effects creating a downward flow at the wall of the reactor as well as the presence of down-comers in some reactors. Krishna and Maretto (1998) explained that the increased catalyst concentration would lead to increased coalescence of small bubbles to form larger bubbles, thereby seeing the homogeneous bubbles size regime developing into a heterogeneous regime. The pilot plant diameter is close to the 0.1 m specified by Krishna and Maretto (1998) for the occurrence of slug flow, thereby enhancing the formation of a heterogeneous regime.

3.5 CONCLUSIONS

Catalyst product selectivity is related to the reactant environment at the point of reaction on the catalyst. It is thus not surprising that the product distribution is similar for conditions where the concentrations of reactants are similar although the reactor configuration differs. Another point of note is that mass transfer can play an important role in determining the product distribution

from a reactor. This influence is limited by the use of a reactor approaching CSTR operation due to its uniform concentration and temperature distribution. The agreement of the recycle condition's distribution to that of the laboratory reactor as well as the fact that the once-through and recycle conditions experienced the same hydrodynamic regimes indicate that mass transfer limitations were negligible in the heterogeneously operated pilot plant slurry reactor. This confirms Maretto and Krishna's (1999) point relating to a slurry bed reactor being very suitable for FT synthesis.

Selectivity data suggests that the main cause for differences in selectivity observable on the pilot plant test is thus the difference of reactant liquid phase concentrations at the point of reaction.

3.6 REFERENCES

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