The addition of HZSM-5 to the Fischer-Tropsch process for improved gasoline production

by

Frederick Gideon Botes

A thesis submitted in partial fulfillment of the requirements for the degree of

Taught Masters in Chemical Engineering - Catalysis

at the University of Cape Town

Supervisors: Prof. C. O'Conner
Mr W. Böhringer

June 2002

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to:

- Sasol Technology, for their financial and technical support of the project.

- Walter Böhringer, for his invaluable technical inputs, witty and amusing remarks, late night hours put in to read through the text, knowledgeable and not so amusing comments on the text, interesting shoes, as well as ... wonderful and insightful post-grad courses !

- Lynville Leukes, for his dedication and tenacity in the laboratory, as well as a constant positive attitude when helping to perform the experiments.

- Philip Gibson, for his constant support, being always available, his prompt feedback when required, and for not interfering too much in the project.

- My computer, for never failing to disappoint me and enduring tons of abuse screamed at it.

SYNOPSIS

The Fischer-Tropsch process has two important disadvantages with regard to the production of gasoline. Firstly, the carbon number distribution of the product spectrum follows the statistical Schulz-Flory function. This means that principally hydrocarbons of all lengths are produced and that the gasoline selectivity is limited to a theoretical maximum value of about 48%. Secondly, the Fischer-Tropsch process produces mainly linear olefins and paraffins. Because of the low octane value of these compounds, the gasoline requires extensive work-up to improve the octane number. The above two limitations of the Fischer-Tropsch process can at least in part be addressed by the addition of an acidic co-catalyst to the system. The cracking of longer chain hydrocarbons and the oligomerisation of light olefins would increase the yield of gasoline range products. Skeletal isomerisation and aromatisation are also facile reactions over acidic zeolites. The branched and aromatics hydrocarbons formed by these reactions have a high octane value. Consequently, using a zeolite in combination with a Fischer-Tropsch catalyst will increase the selectivity and quality (octane value) of the gasoline range products.

A literature survey revealed that a number of patents and papers have been published on the subject of adding an acidic co-catalyst to a syngas conversion function. Even though a range of different catalyst combinations have been tested, not all of these seem feasible for commercial application. The reason is that, in order to obtain the desired reactions over an acid catalyst, a synthesis temperature in excess of 300°C is generally required. Whereas other metals active for Fischer-Tropsch (cobalt and ruthenium) have high methane selectivities at such a high operating temperature, an iron catalyst can produce an acceptable product spectrum. This limits the choice of the Fischer-Tropsch function to an alkali-promoted iron catalyst if both catalysts of the bifunctional system are to be contained in the same reactor. With regard to the acidic co-catalyst, there is reasonable consensus in the literature that HZSM-5 is the most preferred choice, because of the following reasons: its shape selective properties essentially limit the liquid fraction of the product spectrum to the gasoline boiling range; it has a high acidity that gives it a high activity for acid catalysed reactions; HZSM-5 has a high resistance to coke formation and a high hydrothermal stability. The synthesis results published on the bifunctional process were quite encouraging and proved in principle that it has enormous benefits over the normal FT process as far as gasoline production is concerned. Based on the information obtained from the literature, it was decided to study the conversion of synthesis gas to hydrocarbons with a bifunctional catalyst system comprising an alkali-promoted iron Fischer-Tropsch catalyst and an acidic ZSM-5 zeolite. It was further decided to operate the bifunctional process more or less at the conditions of Sasol's High Temperature Fischer-Tropsch process as published in the open literature.

A preliminary experimental investigation was performed in a fixed bed microreactor. For this program, a sodium-promoted precipitated iron catalyst was employed as the syngas conversion function. Three commercial HZSM-5 zeolites with different aluminium contents were tested as co-catalysts. These were referred to as the "high acidity" zeolite

(silica / alumina molar ratio of 30), the "medium acidity" zeolite (silica / alumina molar ratio of 80) and the "low acidity" zeolite (silica / alumina molar ratio of 280). Two configurations of the bifunctional process were tested in the fixed bed reactor, namely the physical admixture of the two catalysts, as well as a dual layer arrangement where the catalysts were separated by inert material. For every experiment performed in the fixed bed reactor, the catalyst bed was diluted with inert carborundum in an attempt to obtain a more even temperature distribution across the bed.

The most important conclusion of the preliminary investigation was that the fixed bed microreactor was not an adequate set-up to study the addition of HZSM-5 to the HTFT process. For the baseline FT run, carbon deposition on the iron catalyst led to plugging of the packed bed and the run had to be shut down after about a week on line due to an increase in the pressure drop over the reactor. The deposited carbon not only affected the operation of the process, but also had a serious influence on the product selectivity as a result of alkali migration from the iron catalyst to the carbon. Consequently, the performance of the FT catalyst became consistent with that of a low alkali catalyst, producing a light product spectrum rich in paraffins that would neither be acceptable for a commercial process, nor be optimal for conversion over an acid catalyst. The inadequacy of the fixed bed reactor set-up was even more pronounced when HZSM-5 powder was physically admixed with the iron catalyst. Presumably, the fine zeolite powder decreased the void space of the reactor bed, so that the deposition of carbon on the iron catalyst plugged the bed more quickly. Some of the data obtained during the fixed bed reactor experiments (especially the CO conversions) varied erratically and this was ascribed to a maldistribution (channelling) of gas in the catalyst bed due to non-homogeneous packing of the particles and uneven carbon deposition.

Since the operating problems of the fixed bed microreactor had such a detrimental effect on the product selectivities obtained during the experiments, the two configurations of the bifunctional process could not be compared quantitatively with each other or with the baseline FT run. However, the following findings were evident from the experimental results:

- The condensable product fraction from the bifunctional process contained a large amount of naphthenes and aromatics. This represents a gasoline fraction with a much higher octane value than the predominantly linear hydrocarbons of the traditional Fischer-Tropsch product.

- Zeolite deactivation was not noted for the bifunctional process with the catalytic functions in physical admixture. This was ascribed to the low olefin selectivity of the iron catalyst in this arrangement due to excessive loss of alkali. To the contrary, deactivation of the HZSM-5 was observed for the dual bed configuration of the bifunctional process, especially for the case where the "high acidity" HZSM-5 was employed as the acidic co-catalyst. The deactivation was ascribed to the higher olefin selectivity of the FT catalyst in this arrangement, which increased the concentration of coke precursors on the catalyst surface. These

observations highlighted the need to study zeolite deactivation under more realistic HTFT operating conditions.

- Because of the low alkali level of the iron catalyst employed in this study, the migration of alkali when the two catalysts were in physical admixture had a more significant influence on the selectivity of the iron catalyst than on the activity of the zeolite.

Due to the limited success of the preliminary investigation in the fixed bed reactor, it was decided to perform the follow-up set of experiments in a Berty microreactor. In this type of reactor, the catalyst is contained in a very thin bed. There is also a very high rate of gas circulation inside the reactor, so that the reactor behaves approximately like a CSTR. The high internal recycle rate ensures an even distribution of temperature in the thin catalyst bed. A further advantage of the Berty reactor is that carbon deposition on the iron catalyst does not impact severely on the operation of the reactor. A fused iron FT catalyst with a low alkali content was obtained from Sasol for the purpose of the follow-up investigation. The "high acidity" and "low acidity" HZSM-5 zeolites used during the preliminary investigation were employed as the acid catalyst function during the Berty experiments. The stability of the fused iron catalyst with respect to activity and selectivity over the course of a two week baseline FT run showed that the Berty reactor set-up was quite appropriate to study the HTFT process and the addition of an acidic co-catalyst to the process.

The effect of contact between the two catalytic functions was investigated by physically mixing the iron catalyst and the zeolite. A severe shift in the selectivity of the FT catalyst towards light paraffins was observed, which indicated extensive migration of alkali from the iron to the zeolite. Since light paraffins are of low value and cannot readily be converted to higher value products over the acid catalyst function, the commercial viability of the bifunctional process in this configuration is doubtful. Furthermore, the prospect of having both catalytic functions on one particle is thus not feasible with the current combination of catalysts. It is envisaged that a commercial bifunctional process will be operated in fluidised bed reactors. In such a fluidised system, the extent of alkali transfer is expected to be dependent on the overall time of contact during collisions between the different particles. Experiments have shown that the one extreme (continuqus contact) is not a commercially viable process. Therefore, all further bifunctional process runs in the Berty reactor were performed in a "dual layer" configuration, where the two catalysts were separated by a wire mesh. Even though this represents the best case scenario of the bifunctional process performed in a fluidised bed reactor, the two layer set-up in a Berty microreactor is currently the most realistic way to investigate the process on laboratory scale.

For the bifunctional process in the "dual layer" configuration, significant HZSM-5 deactivation was observed. This was presumably due to the large amount of olefins produced by the iron catalyst. As expected, the deactivation rate was related to the aluminium content of the zeolite, with the "high acidity" zeolite deactivating more

rapidly. In fact, the deactivation of the "high acidity" HZSM-5 was so severe that it's activity seemed to drop below that of the "low acidity" HZSM-5 after about 150 hours of synthesis. Experimental results have also shown that the addition of a highly active zeolite to the HTFT process does not necessarily improve the gasoline selectivity. The large amount of aromatics formed over such an active catalyst is accompanied by the formation of light paraffins, which fall outside the gasoline range. However, the addition of the less active "low acidity" HZSM-5 to the HTFT process resulted in an increase of around 25% to 35% in the gasoline selectivity throughout the course of the run. In addition, the liquid fraction from the bifunctional process was rich in aromatic, naphthenic and branched compounds. This product will therefore have a much higher octane number than the predominantly linear aliphatic compounds produced by the traditional HTFT process.

During the Berty microreactor experiments, substantial increases in the gasoline selectivity and quality (octane value) was observed upon the addition of HZSM-5 to the HTFT process. These positive results suggest that the bifunctional process definitely has potential as a commercially viable process, and it is recommended that the process be researched further. The main technical challenges that need to be attended to are the issues of alkali migration from the iron catalyst to the zeolite and the deactivation of the acid catalyst function.

CONTENTS

NOMENCLATURE

SYMBOLS

A^{TCD}	Area of compound on GC-TCD chromatogram
A^{FID}	Area of compound on GC-FID chromatogram
n	Number of carbon atoms in a specific hydrocarbon compound
$\dot{n}_i$	Molar flow rate of compound i, *mol / s*
r_{FT}	Rate of Fischer-Tropsch reaction, *mol CO consumed / s*
r_{WGS}	Rate of water-gas-shift reaction, *mol CO consumed / s*
S	Hydrocarbon selectivity (based on amount of carbon converted to hydrocarbons), *carbon atom %*
S_n	Combined selectivity of hydrocarbons containing n carbon atoms, *carbon atom %*
χ	Conversion, *%*
Ψ	GC-TCD calibration factor of compound relative to argon

SUBSCRIPTS

HC	Arbitrary hydrocarbon compound

SUPERSCRIPTS

in	Inlet
out	Outlet

General acronyms

CSTR Continuous stirred tank reactor

FT Fischer-Tropsch

HTFT High Temperature Fischer-Tropsch

LTFT Low Temperature Fischer-Tropsch

CHAPTER 1

INTRODUCTION

Sasol, a South African petrochemical company, produces synthetic liquid fuels from coal by means of the Fischer-Tropsch process. Thereby, low value coal is converted to higher value products. However, this synfuel production route has some limitations with respect to the gasoline selectivity and quality. These limitations can at least in part be addressed by adding an acid catalyst (e.g. zeolite) to the process. Consequently, it has been decided to investigate the combination of a Fischer-Tropsch catalyst and an acidic co-catalyst as an option to improve the synthetic fuel production process.

1.1 SYNTHETIC FUEL PRODUCTION WITH THE FISCHER-TROPSCH PROCESS

1.1.1 Technical aspects and limitations

It is generally accepted that the Fischer-Tropsch process is a type of polymerisation reaction that takes place on the surface of the catalyst (*Anderson*, 1956; *Dry*, 1981; *Schulz* et al., 1988a; *Schulz* et al., 1988b; *Udaya* et al., 1990). Long chain hydrocarbons are built up in a stepwise manner by adding carbon atoms one at a time. This growth process is terminated when the hydrocarbon molecules desorb. The carbon number distribution of the product is thus determined by the competition between growth and desorption, and can be described by a statistical function referred to as the Schulz-Flory distribution. The probability of growth of a certain adsorbed hydrocarbon species is the parameter of the Schulz-Flory distribution. It is commonly referred to as the α value and, in the ideal case, assumed to be independent of the hydrocarbon chain length.

The Schulz-Flory product distribution provides a disadvantage with regard to the selectivity of liquid fuels in the Fischer-Tropsch process. Principally, hydrocarbons of all chain lengths are produced, so that there is a maximum fuel selectivity at a certain optimum value of α. The gasoline selectivity (defined as the C_5 to C_{11} carbon number fraction) and the diesel selectivity (defined as the C_{12} to C_{18} carbon number fraction) are presented as functions of α for the theoretical case of a single α value by *Dry* (1981, 1996). From these figures it is clear that the gasoline and diesel selectivities are limited to values of about 48% (for an optimised α value of 0.76) and 25% (for an optimised α value of 0.88), respectively, while the combined liquid fuels selectivity has a theoretical maximum value of around 65% (for an optimised α value of 0.82). Furthermore, the High-temperature Fischer-Tropsch process, which produces almost all Sasol's synthetic gasoline, is performed in fluidised bed reactors. This places a constraint on the value of α, since the significant production of wax will result in a loss of fluidisation of the catalyst bed. Consequently, the optimum fuel yield might not even be achievable.

A further characteristic of the Fischer-Tropsch product spectrum is that it mainly consists of linear hydrocarbons (*Dry*, 1981). This is a disadvantage with respect to

gasoline quality, because linear molecules have a very low octane number. For example, n-hexane, 3-methylpentane and 2,3-dimethylbutane have octane values of 25, 75 and 101, respectively, which shows that the octane rating of hydrocarbons increase dramatically with increased branching. Fischer-Tropsch gasoline thus requires either further work-up to convert the product to molecules with a higher octane number or the addition of high-octane compounds to the petrol pool (*Horsley* et al., 1993). To the contrary, linear hydrocarbons are desirable as diesel fuel, since it has a high cetane number. However, as already indicated, it is not possible to obtain a high diesel yield directly with the Fischer-Tropsch process.

In view of the above considerations, it has been proposed that there are only two general directions for the further commercialisation of synthetic fuel production via the Fischer-Tropsch synthesis (*Xu* et al., 1998):

- The production of wax via a Fischer-Tropsch process with a high α value, followed by hydrocracking to produce mainly diesel range fuels (see also *Espinoza* et al., 1999; *Schulz*, 1999).

- The conversion of the Fischer-Tropsch product spectrum to high octane gasoline by using a zeolitic co-catalyst.

1.1.2 Economic perspective

Sasol has reported that, with the advent of its new Sasol Advanced Synthol (SAS) reactors, it can build and operate a High-temperature Fischer-Tropsch (HTFT) synthetic fuels plant economically at an oil price of about US$ 23 / barrel (*Steynberg* et al., 1999). The added revenue of chemicals recovered from the product stream (mainly linear 1-olefins and oxygenates) improves the economics to around US$ 16 / barrel. It is thus clear that some of the components in the HTFT product spectrum have a very high value as chemicals. Since olefins and oxygenates are very reactive over acid catalysts, the addition of a zeolite to the process will destroy the high value chemicals, with a resultant loss in revenue.

Diesel production from Fischer-Tropsch via highly selective wax production with subsequent hydrocracking seems to be economically viable under certain circumstances, for example the conversion of remote natural gas or stranded gas (gas associated with deposits of crude oil) to liquid products that can be transported easily (*Schulz*, 1999). However, this probably requires quite a few process steps, such as reforming (for syngas production), Fischer-Tropsch, hydrocracking and a shift converter (for the production of CO-free hydrogen for hydrocracking). The latter two process steps can in principle be omitted for a Fischer-Tropsch / zeolite combination process, since the synthesis step will directly produce high quality gasoline that does not require any further upgrading. Another option would be the integration of the combination process with the Sasol Synthetic Fuels plant (Sasol's current main synfuels production facility). This might provide the company with a strategic position in the South African fuel industry, especially with regard to unleaded petrol. For instance, optimisation of certain reactors for chemicals production and others for fuel production might improve the overall quality of the fuel without compromising the production of chemicals. Therefore, even if a free standing combination process

would not be economically viable, the addition of zeolites to the Fischer-Tropsch process warrants further investigation.

1.2 Background on acid catalysis

Whereas the Fischer-Tropsch product spectrum is very far from the thermodynamic equilibrium, the products of acid catalysed reactions are generally much closer to equilibrium.

1.2.1 Thermodynamic aspects of hydrocarbon distributions

In general it can be said that, at severe conditions, the overall thermodynamic driving force for hydrocarbon conversion follows the disproportionation route. The result of this driving force is that two fractions of hydrocarbons are produced, namely one with a higher and one with a lower hydrogen / carbon ratio than the feed. Therefore, as the disproportionation proceeds, one part of the hydrocarbons will be converted to light paraffins and eventually to methane or hydrogen gas as the hydrogen content of this fraction increases. The other fraction will become richer in carbon and will thus be converted to aromatics and eventually to coke or graphite.

The thermodynamic equilibrium distribution of a pool of paraffins or olefins has the following general characteristics:

- The carbon number distribution is dependent on the temperature. The higher the temperature, the shorter the hydrocarbon chains.

- Branched hydrocarbons are thermodynamically favoured over linear molecules. However, as the temperature increases, the fraction of linear hydrocarbons in the equilibrium mixture increases (*Horsley* et al., 1993). Furthermore, the longer the molecule, the higher the number of possible branched isomers, and consequently the lower the percentage of linear molecules at the thermodynamic equilibrium.

- For olefins, internal double bonds are thermodynamically favoured over terminal double bonds. Therefore, a very low percentage of the olefins are linear 1-olefins as in the Fischer-Tropsch product spectrum.

In view of these thermodynamic considerations, one expects an acid catalyst to convert the Fischer-Tropsch product spectrum (which consist mainly of linear paraffins and linear 1-olefins, with a Schulz-Flory carbon number distribution) into a very broad product spectrum consisting of highly branched paraffins and olefins (with a carbon number distribution peaking at the lighter end of or below the gasoline range), as well as a substantial amount of aromatics. The higher the conversion over the acid catalyst, the more extensive the disproportionation of hydrocarbons would be. Therefore, at high conversions over the acid catalyst, the product spectrum would consist mainly of light paraffins (the fraction with the high hydrogen to carbon ratio) and aromatics (the fraction with the low hydrogen to carbon ratio).

1.2.2 Acid catalysed reactions (*Horsley* et al., 1993; *Moulijn* et al., 1993; *Nieuwenhuys* et al., 1993; *Udaya* et al., 1990)

The mechanism of acid catalysed reactions involves the formation of carbenium ions. These carbenium ions are very reactive and can undergo intramolecular reactions as well as intermolecular reactions. The selectivity of the products formed during these reactions is very often dependent on the stability of the different types of carbenium ions. It is well known that tertiary carbenium ions are much more stable than secondary carbenium ions. Primary carbenium ions are so unstable that reactions involving their formation are very slow and often disregarded.

With the exception of ethylene, olefins are very reactive over acidic zeolite catalysts (*Varma* et al., 1986; *Varma* et al., 1987). The double bond is easily protonated by the strong Brønsted acid sites to form a carbenium ion, which readily reacts further as explained. The protonation of ethylene requires the formation of a primary carbenium ion, which is the reason for the lower reactivity of this olefin. Paraffins are much less reactive over zeolites than olefins, because carbenium ions are required to be formed by means of hydride (H^-) transfer either to a Lewis acid site (which might be present on the zeolite) or to another carbenium ion.

Once a carbenium ion has been formed, the positive charge rapidly migrates from one carbon atom to another by means of H-shift. If such a carbenium ion is deprotonated (e.g. by transferring a proton to another olefin molecule or back to the acid site of the catalyst), an olefin will be formed with the double bond most likely in an internal position. This is the reason that double bond isomerisation of olefins occurs rapidly over zeolites. Skeletal isomerisation of carbenium ions is thought to occur via the formation of a protonated cyclopropyl intermediate and is also a fast reaction in the presence of an acid catalyst. The high stability of tertiary carbenium ions favours the formation of branched isomers, as does the thermodynamic driving force. Consequently, linear molecules are quickly converted to branched hydrocarbons.

Carbenium ions can undergo cracking to smaller molecules by means of β-scission, as well as recombination to form larger molecules (oligomerisation). Stoichiometrically, these reactions can be represented as follows:

1 large olefin $\rightleftarrows$ *2 small olefins* ...[1.1]

1 large paraffin $\rightleftarrows$ *1 small paraffin + 1 small olefin* ...[1.2]

Aromatisation is the most difficult of the acid catalysed reactions and therefore also occurs slower than the reactions discussed above. By means of isomerisation and oligomerisation, cyclic carbenium ions can be formed. Successive abstraction of protons and hydride ions then results in the formation of an aromatic ring. During the formation of the aromatic ring, protons and hydride ions are transferred to other olefins to form paraffins. Stoicheometrically, the aromatisation reaction can be represented as follows:

4 olefins $\rightleftarrows$ *1 aromatic ring + 3 paraffins* ...[1.3]

1.2.3 Importance of the hydrogen / carbon ratio

As explained previously, olefins are very reactive over acidic zeolites and undergo a variety of reactions. Long chain paraffins are easily cracked over the zeolite to yield a mixture of lighter olefins and paraffins. C_3 to C_5 paraffins cannot easily undergo acid catalysed cracking, since this will require the formation of unstable primary carbenium ions. Therefore, light paraffins, together with aromatics, are the stable end products of zeolite catalysed reactions. Whereas aromatics are desired components (they improve the octane value of the gasoline dramatically), light paraffins have a low fuel value and are undesirable. Because of stoichiometric reasons, the initial hydrogen / carbon ratio of the hydrocarbon feed will determine the highest possibly ratio of aromatics to paraffins of the final product. A lower hydrogen / carbon ratio (i.e. a highly olefinic feed) will result in more aromatics relative to light paraffins, which is a more valuable product. Therefore, if the aim is to enhance gasoline production by adding an acidic co-catalyst to the Fischer-Tropsch process, a Fischer-Tropsch catalyst that produces a heavy, highly olefinic product spectrum should preferably be selected.

CHAPTER 2

LITERATURE REVIEW

The combination of a Fischer-Tropsch catalyst with a zeolite for the production of high quality gasoline have been investigated by various companies (most notably Mobil) who have published their findings predominantly in the form of patents. Reports in the open literature on this subject are limited, but some of the findings have been quite encouraging. The two catalytic functions have been combined in a variety of ways, ranging from a single reactor containing both catalytic functions (taking advantage of a possible synergistic effect between the two catalysts) to a dual reactor arrangement with the two catalytic functions in subsequent reactors (so that the operating parameters of the reactors can be optimised individually). The most important literature on the combination process will subsequently be reviewed.

2.1 BIFUNCTIONAL CATALYSTS FOR SYNGAS CONVERSION

The bifunctional system for producing high quality gasoline directly from syngas contains two catalytic functions. Firstly, the carbon monoxide hydrogenation function produces hydrocarbons (preferably highly olefinic or oxygenated compounds) from syngas. Secondly, an acid catalyst function (such as a shape selective zeolite) converts the mainly olefinic or oxygenated hydrocarbons to a gasoline fraction rich in aromatics, naphthenes and branched aliphatics. Even though there is a variety of CO hydrogenation catalysts that can be considered for the purpose of the bifunctional process (e.g. methanol synthesis catalysts), the current project will be restricted to Fischer-Tropsch catalysts. An excellent review of the literature on the bifunctional process is presented by *Udaya* et al. (1990).

2.1.1 The Fischer-Tropsch function

2.1.1.1 General consideration of the Fischer-Tropsch function

For a bifunctional process to be effective, the Fischer-Tropsch function should have the following two characteristics:

- It must have a low methane selectivity (i.e. high α value), so that the excessive formation of light paraffins is avoided. These light paraffins have a low fuel value and are too unreactive to be easily converted to gasoline range components or other useful products.

- It must have a high selectivity for olefins and oxygenates. Not only are these compounds very reactive over zeolites, but they also have a lower hydrogen / carbon ratio than paraffins. This favours the formation of aromatics for stoichiometric reasons.

In order to obtain the desired hydrocarbon reactions over zeolite catalysts, reaction temperatures above 300°C are generally required (*Guan* et al., 1996; *Müller* et al., 1982). Since cobalt and ruthenium as Fischer-Tropsch catalysts have a very high methane selectivity at such high temperatures, they are not expected to be effective in the bifunctional process (*Schulz* et al., 1991). The increase in methane formation with increasing temperature is less excessive for iron based FT catalysts than for cobalt or ruthenium based catalysts (*Schulz*, 1999). For example, Sasol's Synthol process, which utilises a fused iron catalyst, have a fairly low methane selectivity (about 10%), even though the reaction temperature is well above 300°C (*Dry*, 1981). Furthermore, a highly olefinic product spectrum can be obtained with an iron based catalyst. These qualities make iron based FT catalysts ideal for application in the bifunctional process. However, iron catalysts need alkali promotion to attain the desired activity and selectivity (*Schulz*, 1999). Migration of the alkali and subsequent poisoning of the acid sites on the zeolite is a great concern for the bifunctional process (*Butter* et al., 1981).

2.1.1.2 Iron based FT catalysts

During very early attempts at the Mobil Oil Corporation to combine a CO reduction catalyst with a zeolite, an iron catalyst was mixed with HZSM-5 to convert syngas to branched and aromatic hydrocarbons (*Caesar* et al., 1979; *Chang* et al., 1978; *Chang* et al., 1979). A commercial ammonia synthesis catalyst (potassium promoted fused iron catalyst) was ball milled together with the ZSM-5 and an alumina binder, after which it was pressed into pellets to provide an intimate mixture of the two catalytic functions. Impregnation of the zeolite with an $Fe(NO_3)_3$ solution to yield a catalyst containing 3% iron by weight was also tested. Experiments performed with the fused iron / HZSM-5 composite catalyst at 370°C resulted in a very low selectivity (less than 9% on a weight basis) for the C_5^+ hydrocarbons (*Chang* et al., 1978). However, at lower temperatures (around 325°C), the C_5^+ fraction comprised 55 to 65% of the overall hydrocarbon product (*Caesar* et al., 1979). The addition of the zeolite to the iron catalyst changed the Fischer-Tropsch product spectrum, with its Schulz-Flory distribution, significantly. The carbon number distribution was essentially constant over the C_4 to C_9 range and abruptly terminated at C_{11}; consequently, the liquid product was confined to gasoline range hydrocarbons. It was also found that the liquid product was rich in aromatics (up to 40%) and branched hydrocarbons, with a corresponding decrease in olefins, in comparison to the normal Fischer-Tropsch product. As expected, very little linear 1-olefins were present in the product of the bifunctional process.

In a later Mobil patent (*Butter* et al., 1981), it is stated that the addition of alkali promoters to the iron based FT function of the bifunctional process is undesirable, since these promoters tend to migrate to the zeolite with a resultant poisoning of the acid sites. In this patent it is claimed that unpromoted iron in combination with a zeolite is in fact capable of converting syngas to olefinic or aromatic naphta with a low selectivity for methane. However, during catalyst manufacturing, large amounts of sodium silicate and sodium zirconium silicate was added to the preparation mixture together with the zeolite and the iron powder. It is therefore questionable whether the iron was totally unaffected by the alkali in the preparation mixture, especially in light of the fact that an unpromoted iron based FT catalyst is expected to produce much

higher quantities of methane at a synthesis temperature of 300°C than was reported in the patent.

Shamsi et al. (1986) investigated the effect of the preparation procedure on the performance of iron / HZSM-5 bifunctional catalysts. The preparation procedures included the direct decomposition of $(C_5H_5Fe(CO)_2)_2$ on ZSM-5, impregnation of ZSM-5 with an aqueous solution of iron nitrate and the physical admixture of precipitated iron oxide with ZSM-5. All these catalysts portrayed the typical selectivity trends, namely essentially no products heavier than the gasoline range were produced and the product spectrum was rich in aromatics with a corresponding loss of olefins. It was found that, even though the method of preparation did not affect the extent of syngas conversion, it did have a significant influence on the selectivity of aromatics. The physically admixed catalyst produced significantly more aromatics than the nitrate impregnated catalyst, with the organometallic impregnated catalyst having the lowest selectivity for aromatics. Infrared studies with chemisorbed pyridine indicated that ion exchange of Fe^{2+} and Fe^{3+} ions for acidic protons occurred during the nitrate impregnation of ZSM-5, resulting in a decrease in the number of acid sites. This lowered the production of aromatics. Since no ion exchange occurred during the organometallic decomposition, the low aromatics selectivity of this catalyst was ascribed to pore blockage and poisoning of the acid sites by a carbonaceous residue formed during catalyst preparation.

The conversion of syngas with a low H_2/CO ratio (0.66) over a composite catalyst containing potassium promoted iron as Fischer-Tropsch component, HZSM-5 as zeolite and alumina as a binder was also studied (*Niederberger*, 1988; *Schulz* et al., 1991). Both fused and precipitated iron catalysts were used. The composite catalysts were prepared by mixing powders of HZSM-5 and the iron catalyst into an aluminium hydroxide gel, followed by drying and grinding. The experiments were mainly performed at a temperature of 325°C. The addition of the zeolite to the iron catalyst resulted in the normal changes to the Fischer-Tropsch product spectrum, namely a higher selectivity for gasoline range products, isomerisation of the linear hydrocarbons to branched molecules and a high production rate of aromatics. There were little olefins left in the C_2 to C_5 fraction, since these were converted to higher hydrocarbons (via cyclisation and aromatisation) and to light paraffins (via hydrogen transfer during aromatisation). The C_7 to C_{12} fraction consisted mainly of alkylbenzenes, with naphthenes being present only in minor amounts. The addition of alumina to the Fischer-Tropsch catalyst reduced the effect of potassium as a promoter for iron, presumably because of the migration of alkali away from the iron phase. However, there was not a significant exchange of potassium ions for the acidic protons of the zeolite, since the activity of the zeolite could be fully restored after burning off the coke deposits. The alumina binder seemingly acted as a barrier between the iron catalyst and the HZSM-5 which trapped the potassium ions, preventing poisoning of the acidic sites on the zeolite.

During the above study, the time on stream behaviour of the bifunctinoal catalyst was also investigated. It was found that the HZSM-5 component deactivated faster than the Fischer-Tropsch component. However, the slight decrease in the aromatic content of the liquid product after 120 hours on stream indicates merely a minor deactivation of the HZSM-5. It was further stated that the useful lifetime of the HZSM-5 could possibly be extended by raising the reaction temperature by 10°C or 20°C. The

composite catalyst was regenerated by oxidation of the coke with diluted air, followed by reduction of the metal component with hydrogen. As mentioned already, the activity of the zeolite was fully restored. Surprisingly, it appeared as though the Fischer-Tropsch component was reconstructed to a more stable state by the subsequent synthesis and regeneration cycles, resulting in a higher activity and more favourable selectivity (lower methane production). Furthermore, it was also found that regeneration of the catalyst became easier with increasing number of synthesis / regeneration cycles.

2.1.1.3 Iron-manganese based FT catalysts

In an article by *Müller* et al. (1982), it is stated that the Fischer-Tropsch function of the combination process should give the lightest, most olefin and oxygenate rich product possible, while providing for a low ageing rate and a low coking tendency. Since it was believed that a manganese / iron precipitated catalyst complied better to these requirements than a fused iron catalyst or an iron impregnated zeolitic catalyst, such a Mn/Fe catalyst was chosen as the syngas conversion function of the combination catalyst. It must, however, be borne in mind that a light product spectrum also implies a high methane selectivity, with a corresponding low selectivity of gasoline range products from the combination catalyst. Therefore, even though a reasonably high aromatics production rate could be achieved with the Mn/Fe/HZSM-5 bifunctional catalysts at synthesis conditions of 310°C and 12 bar, the methane selectivity was sometimes as high as 26%.

An iron / manganese catalyst in combination with an HY-zeolite was studied by *Egiebor* et al. (1989) for converting syngas to high octane gasoline. Synthesis was performed at temperatures ranging from 300°C to 370°C and a pressure of 21 bar. Little experimental data is presented, but the selectivity of hydrocarbon gases (presumably C_1 to C_4 hydrocarbons) is reported to be around 50%. There was a reasonable production of C_{20+} hydrocarbons, so it does not seem as if this system was able to target the gasoline range effectively.

Fe/Mn catalysts, pure and promoted with various metals, were tested by *Baerns* et al. (1994) for possible application as the Fischer-Tropsch component in the bifunctional process. Even though the catalysts that contained Pd or Rh had a high syngas conversion activity, they produced essentially only paraffinic hydrocarbons due to the strong hydrogenation ability of the noble metals. These were thus deemed unsuitable for the bifunctional process. It was concluded that the Cu promoted catalyst was the preferred choice as the Fischer-Tropsch function of the combination process, because of its high selectivity for C_2 to C_4 olefins. However, this conclusion is questionable, since the Cu promoted catalyst had a much lighter product spectrum than the K promoted Fe/Mn catalyst (e.g. the methane selectivity was about double at the fairly low synthesis temperature of 270°C and a pressure of 11 bar). The light product spectrum was the reason for the higher C_2 to C_4 olefin selectivity. In actual fact, the product spectrum of the K promoted catalyst was far more olefinic than that of any of the other catalysts. It thus appears as though even Fe/Mn catalysts can benefit from alkali promotion when applied to the bifunctional process. The unpromoted and Cu promoted Fe/Mn catalysts were tested in combination with HZSM-5 and gallium substituted ZSM-5. The selectivity for aromatics was not as high as that reported by

some other researchers, which could in part be due to the low overall olefin selectivity of the Fischer-Tropsch function.

Unpromoted Fe/Mn and copper promoted Fe/Mn catalysts were also tested in combination with HZSM-5 and GaZSM-5 by *Guan* et al. (1996). Reaction temperatures were varied between 270°C and 300°C, while the total pressure was 11 bar. Using HZSM-5 as zeolite, the yield of aromatics was very low. It was found that the addition of copper to the Fe/Mn catalyst increased the aromatics yield slightly. This was attributed to the fact that copper promotion improves the selectivity of C_2 to C_4 olefins of such Fischer-Tropsch catalysts. The only means to obtain an adequate yield of aromatics was to use a Ga substituted ZSM-5 zeolite. However, this catalyst system deactivated very fast (the syngas conversion, as well as the aromatic selectivity, dropped steeply) and the catalyst could not be regenerated successfully. This behaviour of the catalyst was attributed to the migration of gallium to the active centres of the Fe/Mn catalyst, thereby affecting both the activities of the Fischer-Tropsch function (decrease in syngas conversion) and the acid function (decline in aromatisation activity).

In general, it seems as if the use of a Fe/Mn catalyst as the Fischer-Tropsch function of a bifunctional process results in a lower aromatics yield than when a potassium promoted iron catalyst is employed. The reason for this is clearly the light product spectrum obtained with the Fe/Mn catalysts. Such a product spectrum will inevitably contain a substantial amount of C_1 to C_4 paraffins that cannot readily be converted to gasoline range components over the acid catalyst. The long chain aliphatics contained in a heavier product spectrum are easily cracked down to lighter hydrocarbons, and this contributes to the pool of light, reactive olefins that can be converted over the zeolite. In this light, the notion by some researchers that the FT catalyst function of a bifunctional process should produce mainly light olefins is questionable.

2.1.1.4 Cobalt based FT catalysts

Stencel et al. (1983) found that impregnating HZSM-5 with cobalt nitrate leads to the exchange of cobalt ions for acidic protons. These exchanged cobalt ions were non-reducible and found not to be active for syngas conversion. Only the cobalt exterior to the ZSM-5 structure was active for syngas conversion. It was also shown that the physical mixing of precipitated cobalt oxide with HZSM-5 did not result in any cobalt ion exchange, so that the HZSM-5 still had a high number of Brønsted acid sites. Consequently, the production of aromatics from synthesis gas with the physically admixed catalyst was higher than for the impregnated cobalt catalysts.

In a later study, *Shamsi* et al. (1984) investigated the effect of preparation procedure on the properties and syngas conversion performance of cobalt / HZSM-5 bifunctional systems. Three different preparation procedures were employed: the direct decomposition of $C_5H_5Co(CO)_2$ on ZSM-5; impregnation of ZSM-5 with an aqueous solution of cobalt nitrate; the physical admixture of precipitated cobalt oxide with ZSM-5. It was again found that, whereas no ion exchange took place for the physically admixed catalyst, it did take place for the impregnated catalysts. Furthermore, it was reported that the extent of ion exchange was considerably less for the organometallic-impregnated catalyst than for the solution-impregnated catalyst.

Synthesis tests were performed at 280°C, 21 bar and an H_2/CO ratio of one. The aromatics production by the physically admixed catalysts was much higher than for the impregnated catalysts. This was possibly due to the fact that ion exchange of acidic protons for cobalt ions for the case of the impregnated catalysts reduced the acidity of the zeolite function. Surprisingly, there was a trend in the experimental results that a higher aromatics selectivity was accompanied by an increase in methane production. The most plausible explanation for the increased methane was that the exothermic aromatisation reaction (in addition to the exothermic FT reaction) caused a deviation from isothermal operation of the catalyst bed (*Gormley* et al., 1988). Consequently, the actual synthesis temperature was suspected to be much higher than the 280°C aimed for. This emphasises the problem of using cobalt as Fischer-Tropsch component in the bifunctional process, namely that at a temperature high enough for sufficient acid catalyst activity, the methane production is excessive.

In a follow-up study, *Rao* et al. (1985) investigated the effect of promoting the cobalt component of a physically admixed cobalt / ZSM-5 bifunctional system with thoria. The same synthesis conditions were employed as previously, namely a temperature of 280°C, a pressure of 21 bar and an H_2/CO ratio of one. Even at these moderate conditions, the methane selectivity was very high (sometimes above 30%) when no thoria was added to the cobalt catalyst. By promoting the catalyst with thoria, the methane selectivity decreased markedly with a corresponding increase in gasoline range products. However, the yield of aromatics also decreased significantly, as did the number of Brønsted acid sites of the zeolite, which was attributed to an exchange of H^+-ions upon the addition of thoria to the catalyst. The Co/Th/HZSM-5 catalysts could produce gasoline range hydrocarbons with a selectivity of 65%, while the aromatic content of the liquid product was about 20%. However, these results were obtained in the first 24h period of synthesis and no long term behaviour of the catalyst was reported.

Co/Mn catalysts were used in combination with different forms of ZSM-5 zeolites by *Bäurle* et al. (1993) and *Baerns* et al. (1994). In the Co/Mn system, cobalt was regarded as the active component and manganese as the promoter. The addition of manganese lowered the activity of the FT catalyst for syngas conversion, but also suppressed the formation of methane and enhanced the production of olefins. Generally, the selectivity towards aromatics was low when this type of FT catalyst was used in the bifunctional process. The use of Ga exchanged ZSM-5 did not lead to better results than HZSM-5 on account of a high catalyst deactivation rate.

2.1.1.5 Combinations of FT metals

In an article by *Chen* et al. (1994) it is stated that the use of multi-metallic catalysts seems to be a very promising technique for overcoming selectivity problems in the Fischer-Tropsch process. Even though the article did not concern the bifunctional process per se, this idea should be taken note of, since an FT catalyst that does not contain mobile promoters and still has an acceptable product spectrum may be beneficial to the bifunctional process. In the article, reference is made to previous studies on the topic of multi-metallic FT catalysts. It is discussed how combinations of conventional Fischer-Tropsch metals (Fe, Co, Ni and Ru) have resulted in catalysts with desirable properties, such as having a high olefin selectivity. In the experimental

study by *Chen* et al. (1994), a cobalt / molybdenum catalyst was tested (without the addition of an acidic co-catalyst), and it was found that the addition of molybdenum to cobalt improved the olefin content of the FT product spectrum. However, accepting the point made in the article that the catalyst and operating conditions were not optimised for a low methane yield, the methane selectivity was too high to consider this system for the purpose of the bifunctional process.

Multi-metallic FT catalysts have in fact been tested by some researchers in combination with acidic co-catalysts. For on such study, *Rao* et al. (1980) argued that cobalt can be added to the iron Fischer-Tropsch function of the bifunctional system to control the extent of the water-gas shift reaction. Thus, by changing the ratio of cobalt to iron in the bimetallic FT catalyst, syngas with a wide range of H_2/CO ratios can be used. However, the methane selectivities of the Fe/Co bimetallic FT catalysts were very high when it was tested in combination with HZSM-5 at a synthesis temperature of 280°C and a total pressure of 21 bar. Even though the data is quite limited, it seems as if an increase in the cobalt content of the FT catalyst function resulted in a decrease in the octane value of the gasoline product from the Fe/Co/HZSM-5 bifunctional system.

Zirconia-based cobalt / nickel catalysts have also been tested as the Fischer-Tropsch function in combination with HZSM-5 (*Bruce* et al., 1984; *Varma* et al., 1986; *Varma* et al., 1987). It was found that syngas could be converted to aromatics with a selectivity of 35% at the mild temperature of 280°C when HZSM-5 was mixed with the FT catalyst. However, the temperature could not be raised above 280°C, because this resulted in excessive methane formation, as well as catalyst deactivation due to carbon deposition on the cobalt / nickel component. This shows that the combination of nickel and cobalt could not suppress the tendencies of these to two metals to produce excessive methane at elevated temperatures. Furthermore, it was stated that the Co/Ni FT component usually deactivated faster than the HZSM-5 component (*Varma* et al., 1987). This seems to indicate that a synthesis temperature of 280°C is already too high for the cobalt / nickel FT function, since most other researchers have found that the lifetime of the bifunctional catalyst system was limited by zeolite deactivation.

It was also stated by *Jothimurugesan* et al. (1998) that the use of alloys of two or more group VIII metals as a Fischer-Tropsch catalyst has certain advantages over monometallic catalysts, namely that the methane selectivity is lower and that the Fischer-Tropsch activity is higher. Different combinations of Co, Ni and Fe were tested as bimetallic FT catalysts and their performances were compared to the single metal catalysts. It was concluded that the alloying of two metals enhanced the performance of the catalyst in comparison to single metal systems. However, it must be noted that unpromoted single metal catalysts were used, which will perform very differently from promoted catalysts developed for industrial application. The conclusion regarding the benefits of bimetallic FT catalysts is thus questionable. The bimetallic FT catalysts were then tested in combination with HZSM-5. However, at 250°C and 10 bar, the aromatics production of these bifunctional systems were very low. Increasing the temperature to improve the yield of aromatic compounds would not be an option for this system, since higher reaction temperatures resulted in excessive methane formation.

2.1.2 The zeolite function

The aim of the bifunctional process is to produce high octane gasoline selectively. ZSM-5 has been the preferred zeolite for this application because of the following reasons (*Jothimurugesan* et al., 1998; *Udaya* et al., 1990):

- ZSM-5 has medium size pores that give it shape-selective properties. Consequently, the formation of aromatic compounds above about C_{10} is avoided, so that there is a sharp cut-off in the product spectrum at the upper limit of the gasoline boiling range.

- HZSM-5 has a high acidity and can therefore catalyse the oligomerisation, isomerisation, cracking and (in particular) aromatisation reactions effectively.

- The medium size pores of ZSM-5 prevent the formation of large molecules (most importantly polyaromatics) that can act as coke precursors; consequently, ZSM-5 has a high resistance to coke formation.

- ZSM-5 is stable under hydrothermal conditions and is resistant to dealumination under typical Fischer-Tropsch conditions.

The acidity of the HZSM-5, which is dependent on the silica / alumina ratio, influences the performance of the zeolite. For example, silicalite has the same crystal structure as ZSM-5, but has a very low aluminium content. It therefore also has a low activity with regard to acid catalysed reactions. When silicalite was combined with a Fischer-Tropsch catalyst, *Rao* et al. (1980) found that the product spectrum was rich in olefins and oxygenates, but contained almost no aromatics. *Müller* et al. (1982) reported that the use of silicalite in the bifunctional process led to isomerisation of the Fischer-Tropsch products and an increase in the C_5^+ fraction (presumably because of oligomerisation of the light olefins), but that only small amounts of aromatic compounds were formed. However, in both these publications it is evident that when HZSM-5 with a silica /alumina ratio of about 30 to 40 is used in the bifunctional process, the olefins and oxygenates are almost completely consumed and a product spectrum rich in aromatics is obtained.

Fischer-Tropsch catalysts with a high selectivity for C_2 to C_4 olefins (Fe/Mn and Co/Mn based catalysts) have been used to test the effect of Ga substitution on the performance of HZSM-5 in the bifunctional process (*Baerns* et al., 1994; *Bäurle* et al., 1993; *Guan* et al., 1996). When normal HZSM-5 was used in the bifunctional process, the yield of aromatics was generally quite low. When GaZSM-5 was used in combination with Fe/Mn or Co/Mn catalysts, higher yields of aromatics were achieved. This is possibly due to the homolytic hydrogenation / dehydrogenation properties of GaZSM-5, i.e. paraffins were dehydrogenated to olefins that were subsequently converted over the acid sites. Despite the high selectivity for aromatics achieved with bifunctional catalyst systems containing Ga-ZSM5, these catalyst systems had a strong deactivation rate and the activity could not be restored by subsequent cycles of oxidation and reduction (*Baerns* et al., 1994). The irreversible deactivation was ascribed to the migration of gallium species from the zeolite to the Fischer-Tropsch function.

Hammer et al. (1994) investigated the use of different zeolites (mordenite, erionite, ZSM-11, ZSM-12, as well as zeolites L, omega and beta) in combination with a Fischer-Tropsch catalyst. The synthesis runs were started at 200°C and every 24 hours the temperature was raised by 10°C. The total running time per experiment was about 14 days. The results are not presented very clearly in the publication, but it was stated that the zeolites with larger pores are more resistant to fast blocking by carbon deposition than the zeolites with narrower pores. However, it should be noted that, for the first few days of each experiment, the reaction temperature was quite low. At higher operating temperatures (which would be more suitable for a commercial process) the predominant mechanism of zeolite deactivation may be different, so that the relevancy of the conclusion in the publication is doubtful.

Egiebor et al. (1989) tested a wide pore HY cracking catalyst in combination with a Fe/Mn Fischer-Tropsch catalyst at temperatures ranging from 300°C to 370°C. It was reported that the addition of the acid catalyst increased the formation of isomers and aromatics in the C_{20-} range. However, despite the presence of the HY cracking catalyst, a reasonable amount of components in the C_{20+} range was still produced. It was found that the selectivity towards C_{20+} hydrocarbons could be decreased by varying the process conditions, e.g. increasing the H_2/CO ratio of the feed gas or increasing the reaction temperature. These changes in process conditions are known to shift the product spectrum of an FT catalyst towards the lighter end (*Dry*, 1981). In addition, an increase in temperature would have increased the cracking ability of the zeolite. Therefore, even though a limited amount of data is presented in the publication, it seems as if the HY zeolite did not have sufficient intrinsic activity to crack all the heavy components in the FT product spectrum to the desired carbon number range. This emphasizes the importance of using an acidic co-catalyst with a high activity for the purpose of the bifunctional process. Furthermore, the wide pores of the HY zeolite would have allowed for the formation of aromatics heavier than the gasoline range. This may have contributed to the production of hydrocarbons above C_{11}.

In view of the above discussion, HZSM-5 seems to be the best choice as the acid catalyst function of the bifunctional process. The silica / alumina ratio of the zeolite is a parameter that can be varied and will have a significant influence on the performance of the catalyst (*Barthomeuf*, 1987; *Horsley* et al., 1993). At sufficiently low aluminium content, the aluminium atoms will be adequately spaced so that the acid sites do not interfere with each other (*Barthomeuf*, 1987). Under such conditions, the acid strength of the sites is independent of the silica / alumina ratio. However, at higher aluminium contents, an increase in the number of aluminium atoms increases the interaction between the aluminium atoms and therefore causes a decrease in the strength of the acid sites (*Barthomeuf*, 1987). Furthermore, the number of acid sites increases with increasing aluminium content of the zeolite. Since the rates of the different acid catalysed reactions depend on both the number and the strength of the acid sites, the silica / alumina ratio of HZSM-5 is expected to have an important influence on the activity and selectivity of the bifunctional process. In addition, the silica / alumina ratio also has an effect on the coking tendency of the zeolite. It is therefore expected that there will be an optimum aluminium content of the HZSM-5 for application in the bifunctional process. This optimum will probably depend on the product spectrum produced by the Fischer-Tropsch function, as well as

the process conditions. The effect of the silica / alumina ratio should therefore be investigated as part of the experimental program.

2.2 INTIMACY OF MIXING OF THE TWO CATALYTIC FUNCTIONS

In the literature, a variety of different methods have been used to combine the two catalytic functions of the bifunctional process:

- The metal active for the Fischer-Tropsch reaction has been supported on the acidic zeolite by means of the decomposition of an organometallic compound on the zeolite or the impregnation of the zeolite with an inorganic metal salt (e.g. *Shamsi* et al., 1984; *Shamsi* et al., 1986; *Stencel* et al., 1983).

- Finely ground Fischer-Tropsch and zeolite catalyst particles have been physically admixed. Sometimes this mixture was pressed into pellets with or without the addition of a binder (e.g. *Niederberger*, 1988; *Rao* et al., 1985; *Schulz* et al., 1991; *Shamsi* et al., 1984; *Shamsi* et al., 1986).

- The two catalysts have been placed in the same reactor, but in subsequent beds, with the zeolite containing section following the Fischer-Tropsch catalyst bed (*Bruce* et al., 1984). This method can also be extended to a "sandwich" design, consisting of alternating layers of Fischer-Tropsch catalyst and zeolite.

- The two catalytic functions can be contained in different reactors. Synthesis gas is then first converted to predominantly linear hydrocarbons in the first reactor containing the Fischer-Tropsch catalyst, after which the hydrocarbons are converted to branched and aromatic compounds over an acid catalyst in the second reactor. This configuration has been referred to as the follow-bed arrangement or the dual reactor configuration (e.g. *Baerns* et al., 1994; *Bäurle* et al., 1993; *Varma* et al., 1987).

A very important consequence of the configuration of the bifunctional process is the intimacy of contact obtained between the two catalytic functions. At the one extreme (zeolite supported catalysts), the two functions are in very close contact, while in the other extreme (dual reactor arrangement) the two functions are completely separated. The intimacy of mixing may determine the effect that the different catalytic sites have on each other, it could influence the hydrocarbon product selectivity (e.g. by a type of synergistic effect) and it will have an effect on the operation of the bifunctional process.

2.2.1 The influence of the two catalytic sites on each other

It has been found that the impregnation of an acidic zeolite support with a metal salt results in ion exchange of the metal ions for acidic protons on the zeolite (*Shamsi* et al., 1984; *Shamsi* et al., 1986; *Stencel* et al., 1983). This affects both catalytic functions of the combination process, since the non-reducible metal species that are

formed after ion exchange are not active for syngas conversion and the acidity of the zeolite is reduced. Even though the decomposition of an organometallic compound on the zeolite resulted in a much lower degree of ion exchange, these catalysts also had a low activity with regard to acid catalysed reactions. This was ascribed to blockage of the zeolite pores and poisoning of the acid sites by a carbonaceous residue that was formed during the catalyst preparation procedure (*Shamsi* et al., 1986). No ion exchange between the Fischer-Tropsch base metal and the acidic protons was found for physically admixed catalysts.

Iron based Fischer-Tropsch catalysts need alkali promotion (usually potassium is employed) to attain the desired activity and selectivity (*Schulz*, 1999). Under normal Fischer-Tropsch synthesis conditions, the potassium is mobile and migration to the zeolite will lead to poisoning of the acid sites (*Butter* et al., 1981). This poisoning occurs not only for impregnated catalysts, but also for physically admixed composite catalysts. The addition of a binder (such as alumina) to physically admixed catalysts pressed into pellets can serve as a trap for the potassium. This successfully protects the acidic sites from poisoning, but results in a lowering of the potassium content of the iron catalyst, thereby affecting the performance of the Fischer-Tropsch function of the bifunctional process (*Niederberger*, 1988; *Schulz* et al., 1991).

Rao et al. (1985) added thoria as a promoter to a precipitated cobalt catalyst to decrease the methane selectivity and increase the olefin selectivity of the Fischer-Tropsch catalyst. However, it was found that thoria addition resulted in a decrease in the number of Brønsted acid sites of HZSM-5 when the composite catalyst was produced by means of physical admixture of the two catalytic functions. This was attributed to an exchange of H^+-ions upon the addition of thoria. No solution to this problem was presented in the paper, and it is unclear whether the use of an alumina binder will prevent the decrease of acidic protons on the zeolite.

Modification of the zeolite function can also have an influence on the Fischer-Tropsch active sites when the two catalytic functions are in close association. For example, when gallium substituted ZSM-5 was mechanically mixed with Fe/Mn and Co/Mn Fischer-Tropsch catalysts, the syngas conversion activity of the catalyst decreased steeply with time on line. The activity of the catalyst could not be restored by means of regeneration, and the deactivation was ascribed to the migration of gallium to the Fischer-Tropsch sites (*Baerns* et al., 1994; *Bäurle* et al. 1993; *Guan* et al., 1996).

2.2.2 Synergism between catalytic functions regarding synthesis performance

There has been some discussion in the literature about a synergistic effect between the two catalytic functions of the bifunctional process. *Chang* et al. (1979) found that the addition of HZSM-5 to a typical Zn/Cr methanol synthesis catalyst lowered the formation of methane. It was concluded that, since methane is a stable (unreactive) end product, its suppression by the zeolite was the result of the scavenging of a methane precursor from the syngas conversion function. However, this effect was not observed with an iron based Fischer-Tropsch catalyst in combination with a zeolite. Consequently, it was assumed that the methane precursor is either more strongly bound to the iron surface or methane formation is governed by another mechanism on the iron catalyst (e.g. via carbide intermediates). *Jothimurugesan* et al. (1998) did

find a lowering in the methane selectivity when HZSM-5 was added to a typical Fischer-Tropsch catalyst and ascribed this to the ability of the zeolite to intercept methane precursors.

Other researchers have also reported a synergistic effect when a zeolite was used in conjunction with a Fischer-Tropsch catalyst. The limited chain length of the hydrocarbon product has been attributed to the scavenging of desorbed olefins by the zeolite before they could readsorb onto the Fischer-Trophch catalyst and grow into longer chain molecules (*Caesar* et al., 1979; *Rao* et al., 1980; *Udaya* et al., 1990). *Müller* et al. (1982) proposed a similar mechanism, whereby the reaction of olefins on the zeolite function changes the equilibrium between adsorbed olefins on the metal surface and olefins in the gas phase. Consequently, all steps in the chain propagation process of the Fischer-Tropsch reaction will be affected by this shift in equilibrium. However, these explanations for the limited chain length of the hydrocarbon product of the bifunctional process seems odd, since the cracking of long chain aliphatic compounds over the acid sites and the shape selective properties of the HZSM-5 that restrict the formation of large aromatics are most probably the reasons that heavy hydrocarbons are not present in the final product. *Bruce* et al. (1984) stated that, when the hydrogenation activity of the Fischer-Tropsch function is high, an intimate mixture of the two catalytic functions is expected to be beneficial, since the acid catalysed reactions will be in competition with the hydrogenation reaction. Consequently, the olefins will be reacted away by the zeolite before they can readsorb and be hydrogenated on the metal surface. This seems to be a more plausible proposal for a possible synergistic effect between the two catalytic functions.

2.2.3. Operation of the bifunctional process

From a process operating perspective, there are distinct advantages in having the two catalytic functions in different reactors (*Baerns* et al., 1994; *Udaya* et al., 1990). The two reactors can be operated at different temperatures, so that the performance of the Fischer-Tropsch catalyst and the zeolite can be optimised individually. This is desirable, since the temperatures required for high zeolite activity and low coking tendency generally lead to high methane selectivities over Fischer-Tropsch catalysts. Furthermore, it is easier to regenerate each catalyst individually, since different regeneration procedures are required for the two catalytic functions. The coke formed on the zeolite must be burned off, while Fischer-Tropsch catalysts are active in the reduced metal state; consequently, a two-step regeneration procedure (oxidation followed by reduction) is required when the two catalysts are combined in the same reactor vessel. Therefore, unless there is some kind of synergism when the two catalytic functions are in intimate contact, the dual reactor configuration will probably be preferred over the mixed reactor bed.

Some researchers claimed to have obtained better results with the dual reactor configuration than with mixed bed reactors when the zeolite containing reactor was operated at a higher temperature than the Fischer-Tropsch reactor (e.g. *Baerns* et al., 1994; *Bäurle* et al., 1993). However, it must be borne in mind that the benefit of different reactor temperatures will be more pronounced for cobalt based catalysts than for iron based catalysts, since the methane selectivity of a cobalt catalyst is very sensitive to an increase in temperature. A possible synergistic effect may outweigh

the disadvantages of having the two catalysts in the same reactor when the Fischer-Trsopch function is an iron based catalyst.

2.3 PROCESS PARAMETERS

Not much information is available in the literature on the effect of process parameters on the bifunctional process, since most studies focused on the evaluation of different catalysts and the methods of combining the catalytic functions.

2.3.1 The effect of temperature on the bifunctional process

Temperature seems to be the most important operating parameter of the bifunctional process. It is well known that an increase in the synthesis temperature causes the Fischer-Tropsch product spectrum to shift towards lighter hydrocarbons, which is accompanied by an increase in the methane selectivity (*Dry*, 1981; *Dry*, 1996; *Schulz*, 1999). As already mentioned, this increase is more pronounced for cobalt based catalysts than for iron based catalysts (*Schulz*, 1999). On the other hand, temperatures in excess of about 300°C are generally needed to ensure adequate zeolite activity (*Gaun* et al., 1996; *Müller* et al., 1982). Furthermore, the rate of coke formation on HZSM-5 is dependent on the temperature, and the lowest coking rate is generally achieved at a temperature of around 370°C (*Horsley* et al., 1993).

When cobalt based Fischer-Tropsch catalysts were used in combination with HZSM-5, the synthesis temperature generally did not exceed 280°C (e.g. *Bruce* et al., 1984; *Rao* et al., 1985; *Shamsi* et al., 1984). When iron-based Fischer-Tropsch catalysts were employed, synthesis temperatures of between 300°C and 370°C have frequently been used (e.g. *Caesar* et al., 1979; *Chang* et al., 1979; *Egiebor* et al., 1989; *Müller* et al., 1982; *Niederberger*, 1988). *Niederberger* et al. (1988) investigated the effect of temperature on the bifunctional process for an iron catalyst in admixture with HZSM-5. It was found that, as the temperature was increased from 275°C to 350°C, there was an increase in the CO hydrogenation rate, an increase in the methane selectivity, and an increase in the conversion over the zeolite (with a resultant increase in aromatics). Clearly, an increase in the reaction temperature had both beneficial and detrimental effects. This emphasises the importance of establishing an optimum operating temperature for the bifunctional process when the two catalytic functions are contained in the same reactor.

2.3.2 The effect of pressure on the bifunctional process

For the Fischer-Tropsch process, an increase in total pressure over the range of 1 to 20 bar generally results in a heavier product spectrum for both iron and cobalt based catalysts (*Dry*, 1981). It is thus expected that a low pressure for the bifunctional process will contribute to a high methane selectivity (with a corresponding decrease in gasoline range products).

Not much attention has been paid to the effect of pressure on the bifunctional process. Most experiments were performed at pressures between 10 and 20 bar, but a total

pressure of 1 bar (which resulted in fairly high methane selectivities) has even been employed (*Bruce* et al., 1984). *Niederberger* et al. (1988) found that an increase in the pressure from about 12 to 50 bar resulted in a higher rate of CO hydrogenation, a lower paraffin selectivity, and a faster rate of HZSM-5 deactivation. The reason for the increased HZSM-5 coking rate may have been the higher partial pressure of olefins and other unsaturated products due to the increased CO conversion and the higher total pressure.

2.3.3 The effect of the syngas H_2/CO ratio on the bifunctional process

For the Fischer-Tropsch process, a higher H_2/CO ratio in the reactor leads to a lighter and less olefinic hydrocarbon product spectrum (*Dry*, 1981). As explained previously, a Fischer-Tropsch product spectrum with a high hydrogen / carbon ratio is undesirable for the bifunctional process, because it will increase the ratio of light paraffins to aromatics in the final product. On the other hand, it is also known that hydrogen inhibits coke formation on zeolites during acid catalysed hydrocarbon reactions. This stabilising effect is possibly due to the reaction of hydrogen with the carbenium ions involved in coke formation (*Horsley*, 1993). An increase in the H_2/CO ratio may therefore decrease the aromatics selectivity of the bifunctional process, but also lower the coke formation rate on the zeolite.

Niederberger et al. (1988) varied the H_2/CO ratio of the syngas feed to the bifunctional process from 0.49 to 1.16. It was found that a higher hydrogen content in the syngas led to an increase in the paraffin selectivity and effected a slower deactivation rate of the HZSM-5. The higher H_2/CO ratio of the syngas may, of course, have had an indirect influence on the deactivation rate of the zeolite, because of the lower olefin selectivity of the Fischer-Tropsch catalyst. Other researchers did not investigate the effect of the syngas H_2/CO ratio and most studies on the bifunctional process were performed at a fairly low H_2/CO ratio of around 1.

CHAPTER 3

PROJECT OUTLINE

Reports in the literature have shown that the bifunctional process has tremendous potental for the production of high quality gasoline. For example, a gasoline fraction that forms nearly 70% of the total hydrocarbon product has been obtained in some experimental studies on the bifunctional process, while research octane numbers in excess of 90 for the liquid product have been reported in some publications (*Udaya*, 1990). Therefore, it is recommended that the concept be investigated further. This chapter briefly considers the economic context of the bifunctional process and provides an outline of the most important technical aspects that can be included in an experimental investigation.

3.1 ECONOMIC CONTEXT OF THE BIFUNCTIONAL PROCESS

It has been reported that a High-temperature Fischer-Tropsch synthetic fuels plant can be built and operated economically when the crude oil price is around US$ 23 / barrel. The recovery of chemicals from the product stream improves this value to around US$ 16 / barrel. The addition of a zeolite to the process will increase the selectivity of gasoline range products and also improve the quality of the fuel (increase the octane value). However, the high value chemicals are very reactive over acid catalysts and will therefore be destroyed upon addition of the zeolite. It therefore seems as if a free standing bifunctional process becomes economically viable at an oil price of somewhere between US$ 16 and US$ 23 / barrel, but probably closer to the upper limit of this range.

Notwithstanding this unfavourable economic position, the bifunctional process may find application in certain specific situations. Natural gas and stranded gas from crude oil recovery in remote locations can, in principle, be converted to gasoline with a high octane number in merely a few process steps. This route to convert syngas to synthetic liquid fuels may be simpler than the production of wax with a Fischer-Tropsch process followed by hydrocracking to preferentially obtain a diesel fraction. Furthermore, integration of the bifunctional process with Sasol's existing synthetic fuel production facilities may improve the economics of the bifunctional process and provide the company with a strategic position with regard to unleaded petrol. Therefore, it is justified to investigate the combination of a zeolites with a Fischer-Tropsch catalyst further.

3.2 SYNERGY BETWEEN CATALYTIC FUNCTIONS (INTIMACY OF CONTACT)

There has been some speculation in the literature about the ability of the zeolite function to scavenge hydrocarbon species growing on the surface of the Fischer-Tropsch catalyst or to intercept desorbed olefins before they can readsorb onto the metal surface and be hydrogenated. If this is indeed the case, the intimacy of contact between the two catalytic functions would have an important influence on the efficiency of the bifunctional process. On the other hand, if no such synergistic effect

exists, it would be desirable to have the two catalytic functions in subsequent reactors for the following reasons: the operating temperatures of the two reactors can be optimised individually; the two catalytic functions can be regenerated individually; the migration of promoters from the Fischer-Tropsch catalyst to the zeolite (with subsequent poisoning of the acid sites) will be avoided; some valuable chemicals can be extracted from the Fischer-Tropsch product slate before conversion over the acid catalyst.

In view of the above, it is important to investigate the effect of the intimacy of contact between the two catalytic functions and to determine whether or not there is a synergistic effect when the two catalysts are in close contact.

3.3 Catalysts

Even though a wide range of Fischer-Tropsch catalysts have been tested in combination with zeolites, it seems as if an alkali promoted iron catalyst would be the preferred choice for this application. Iron based Fischer-Tropsch catalysts can be operated at the high temperatures required for sufficient zeolite performance without producing excessive amounts of methane and also have a product slate rich in olefins and oxygenates. Furthermore, the heavier molecules produced by alkali promoted iron catalysts (in comparison to Fe/Mn systems) can easily be cracked down to lower olefins by the zeolite and subsequently undergo aromatisation reactions. The level of alkali promotion, which will determine the primary Fischer-Tropsch product spectrum, can be varied to optimise the overall performance of the bifunctional process.

As discussed previously, HZSM-5 is the preferred choice of zeolite for the bifunctional process, because of its excellent properties as a gasoline production catalyst. The silica / alumina ratio determines the acidity of the zeolite and therefore influences the synthesis performance and deactivation rate (coking tendency) of the catalyst. Consequently, the effect of the silica / alumina ratio of HZSM-5 is also an important aspect that should be investigated.

The migration of alkali from the iron catalyst to the zeolite, with subsequent poisoning of the acid sites, is a serious concern. A binder (e.g. alumina) may act as an alkali migration barrier between the two catalytic functions. Therefore, the addition of a binder to the composite catalyst can be considered.

3.4 Operating parameters

Temperature seems to be the most important operating parameter of the bifunctional process. It has a marked influence on the primary Fischer-Tropsch product spectrum (especially the alpha value). It also has a notable effect on the rate of the acid catalysed reactions, as well as the coke formation rate (deactivation behaviour) of the zeolite. In the event that the bifunctional process is integrated with an existing synfuels production plant, the temperature chosen for the zeolite containing reactors should not impact significantly on the rest of the plant; consequently, it expected that there will not be any external restrictions on the operating temperature of the process.

In view of the above, investigating the effect of temperature on the bifunctional process is considered to be very important.

The H_2/CO ratio of the syngas is expected to have an influence on the product selectivity of the process and on the coking behaviour of the zeolite. A higher H_2/CO ratio will probably increase the selectivity towards light paraffins and lower the HZSM-5 deactivation rate. Optimisation of the H_2/CO ratio of the syngas feed to the bifunctional process can therefore be considered. For the Fischer-Tropsch process, an increase in total pressure over the range of 1 to 20 bar results in a heavier product spectrum, i.e. a lower methane selectivity (*Dry*, 1981). Therefore, it is important to perform the experiments of this project at elevated pressure (preferably around 20 bar) in order to obtain a product spectrum that would be realistic for a commercial process. However, provided that pressure is in that order, pressure seems to be of lesser importance to the optimal performance of the bifunctional process than the other process parameters.

CHAPTER 4

PRELIMINARY EXPERIMENTAL STUDY IN A FIXED BED MICROREACTOR

It is well known that carbon is deposited on the iron catalyst under HTFT synthesis conditions (*Dry*, 1981). Since this will eventually lead to plugging of the catalyst bed, a fixed bed microreactor is generally not the preferred choice for HTFT experiments. However, one of the primary objectives of the experimental study on the bifunctional process was to investigate the effect of the intimacy of contact between the two catalytic functions and to determine whether there is a synergistic effect when the two catalysts are in close association. A packed bed reactor lends itself ideally to investigating such a possible synergistic effect, because the two catalytic functions can be loaded into the reactor in a variety of ways. For example, the catalysts can be loaded as a physical mixture or separately in subsequent layers. Consequently, it was decided to perform a preliminary experimental investigation in a fixed bed microreactor.

During the preliminary investigation, it became clear that the choice of reactor system was in fact not adequate to study the addition of HZSM-5 to the HTFT process. The main problem was that the product spectrum produced by the iron catalyst was neither representative of commercial HTFT operation, nor optimal for conversion over an acid catalyst. The results of the preliminary study are presented in this chapter, but no sound conclusions could be made about the feasibility of the bifunctional process. In the next chapter, the results of a follow-up experimental investigation is reported, for which the benefits of the bifunctional process over the normal HTFT process could be illustrated more clearly.

4.1 EXPERIMENTAL

4.1.1 Catalysts

4.1.1.1 Iron Fischer-Tropsch catalyst

Since the catalyst would not be exposed to the harsh fluidised environment of the commercial HTFT process during laboratory experimentation, there was no need to employ a strong fused iron catalyst as the syngas conversion function. Consequently, a precipitated iron catalyst was rather used during the preliminary study, as such a catalyst is very easily prepared at laboratory scale. It was decided to add sodium to the catalyst as the alkali promoter. Copper was also added to the catalyst to improve the reducibility of the iron (*Dry*, 1981).

For the preparation of the iron catalyst, iron nitrate was dissolved in distilled water to obtain a Fe^{3+} solution of 1 mol / l. The iron was then precipitated by the addition of a 25% ammonia solution to the dissolved iron nitrate whilst stirring fast until a final pH of about 7 was reached. Thereafter, dissolved salts of the promoters (sodium carbonate and copper nitrate) were added to the slurry. The precipitate, together with the mother liquor, was poured into a flat pan and dried overnight in an oven at a temperature of 150°C. The dried precipitated catalyst was put in a ceramic bowl and

calcined in air at 350°C for four hours to decompose the ions introduced to the catalyst during the preparation (nitrate-, carbonate- and ammonium-ions). Caution was taken during calcination, since a very steep temperature ramp might lead to a quick expansion of gases causing excessive break-up of the precipitated particles. The temperature program used for the calcination is presented in Table 4.1.

The calcined precipitate was gently crushed and sieved into a 38 to 150 micron fraction. A summary of the preparation details, as well as the analysed composition of the catalyst, is presented in Table 4.2.

Table 4.1: Temperature program used during calcination of precipitated iron catalyst

Program step	Step time	Final step temperature
Initial condition		Room temperature
Ramp	45 min	150°C
Isothermal	30 min	150°C
Ramp	45 min	250°C
Isothermal	30 min	250°C
Ramp	45 min	350°C
Isothermal	4 h	350°C
Cool down		Room temperature

4.1.1.2 Acid catalyst function

The acid catalysts used during the experimental study were samples of commercial ZSM-5 powder. The zeolites, obtained from *Zeolyst International*, were received in the ammonium form (NH_4ZSM-5) and therefore needed to be calcined to convert them to the acidic form (HZSM-5). For the purpose of the calcination, the zeolite powder was spread over the surface of a ceramic saucer to form a layer with a thickness of about 5 mm. The saucer was then placed in an oven and calcination took place in air at a temperature of 500°C for 16 hours. The temperature program of the calcination procedure is presented in Table 4.3.

Three HZSM-5 zeolites with different aluminium contents were used during the preliminary study. For the purpose of this document, these acid catalysts will be referred to as the "high acidity" zeolite (silica / alumina molar ratio of 30), the "medium acidity" zeolite (silica / alumina molar ratio of 80) and the "low acidity" zeolite (silica / alumina molar ratio of 280). It should be noted that the names of the acid catalysts are related to the number of acid sites (which increases with decreasing silica / alumina ratio) rather than the acid strength of each site (which generally decreases with increasing aluminium content)[i]. In Table 4.4, the most important details of the zeolites are summarised.

[i] A more detailed discussion on the importance of the aluminium content of HZSM-5 is presented Chapter 2, Section 2.1.2

Table 4.2: Preparation details of precipitated iron catalyst (summary)

Precipitation	
Iron precursor	iron nitrate solution
Fe^{3+} concentration	1 mol / l
Precipitation agent	25% ammonia solution
Final pH of precipitation	7
Promoters (added to slurry after precipitation)	
Alkali promoter	sodium carbonate
Reduction promoter	copper nitrate
Drying	
Temperature	150°C
Time	overnight
Calcination (in air)	
Final temperature	350°C
Time	4 hours
Catalyst composition	
Fe (mass %)	61.9
Cu (g / 100 g Fe)	0.58
Na_2O (g / 100 g Fe)	0.24

Table 4.3: Temperature program used during calcination of zeolites

Program step	Step time	Final step temperature
Initial condition		Room temperature
Ramp	2 h	500°C
Isothermal	16 h	500°C
Cool down		Room temperature

4.1.2 Reactor system

The flow rates of the various feed streams to the fixed bed microreactor were controlled by Brooks mass flow controllers. The total feed comprised of argon (which served as an internal standard), bottled syngas (with a H_2/CO ratio of 2) and pure hydrogen (to increase the H_2/CO ratio of the feed to the desired value). The total feed entered the reactor at the top and flowed downwards through the packed bed.

Table 4.4: Details of HZSM-5 zeolites used during preliminary investigation

Reference name (thesis)	*Zeolyst* product number	Silica / alumina (molar ratio)	Surface area (m^2 / g)
"High acidity" HZSM-5	CBV 3024E	30	400
"Medium acidity" HZSM-5	CBV 8014	80	425
"Low acidity "HZSM-5	CBV 28014	280	400

The fixed bed reactor consisted of three sections that screwed into one another to form a hollow tube with an inner diameter of 15 mm. The heights of the three sections, from top to bottom, were 166 mm, 25.5 mm and 53 mm, respectively. The catalyst was housed in the middle section and the bed was held in place with a porous metal plate and a wire mesh at the bottom of the bed. The top section served as a preheater of the feed gas before it entered the catalyst bed. A thin thermowell ran along the centre axis of the reactor tube. A thermocouple, situated inside the thermowell just above the catalyst bed[ii], was used to control the temperature inside the reactor. The whole length of the reactor tube was surrounded by a heating mantle, which supplied the necessary heat in order to keep the reactor at the temperature set-point.

The reactor effluent was passed through a two stage knock-out system. The hot knock-out pot, which was kept at a temperature of 200°C, condensed any waxy hydrocarbons that were formed, since this heavy fraction is a solid or a viscous liquid at room temperature. Downstream from the hot knock-out, a cold pot condensed the light oil and reaction water phases at room temperature. All uncondensed effluent passed through a back-pressure regulator (which maintained the pressure in the reactor system) into the vent system.

The main details about the reactor system are summarised in Table 4.5.

4.1.3 Packing of the fixed bed reactor

It is notoriously difficult to operate the HTFT process in a fixed bed reactor. The deposition of carbon is known to occur on the iron catalyst under HTFT operating conditions, and this will eventually lead to plugging of the catalyst bed (*Dry*, 1981). The situation is aggravated by the large amount of heat generated due to the highly exothermic nature of the Fischer-Tropsch reaction. Under HTFT conditions, all the products are in the gas phase. Gases generally have a much lower heat capacity than liquids, which means that dissipation of heat from the catalyst particles in the HTFT process will not be as effective as for the Low-temperature Fischer Tropsch (LTFT) process. Consequently, operation of a fixed bed reactor at HTFT conditions often leads to hot spots in the catalyst bed, resulting in excessive carbon deposition in some areas that speeds up the plugging of the bed. In view of the above, the catalyst was

[ii] Since the Fischer-Tropsch reaction is highly exothermic and the temperature was measured at the entrance to the catalyst bed, the actual reaction temperature inside the bed may have been higher than the set-point.

diluted with inert carborundum in an attempt to avoid or reduce the severity of hot spots. However, the amount of carborundum that could be added was limited by the volume of the microreactor. The maximum amount of inert material was always loaded.

Table 4.5: Summarised information on fixed bed reactor system

Feed streams	
Argon (internal standard)	bottle
Syngas (H_2/CO ratio = 2)	bottle
Hydrogen	bottle
Reactor dimensions and material	
Internal diameter	15 mm
Top section height	166 mm
Middle section (catalyst bed) height	25.5 mm
Bottom section height	53 mm
Construntion material	Stainless steel 310 (ASTMA 182 Gr. F)
Temperature control	
Temperature measurement	thermocouple
Heat supply	heating mantle
Reactor effluent	
Hot knock-out temperature	200°C
Cold knock-out temperature	ambient

At the start of the experimental program, a Fischer-Tropsch run was performed to serve as a baseline with which to compare the performance of the bifunctional process. For this baseline run, 1 g of iron catalyst was diluted with 6 g of carborundum. Following this, a series of bifunctional process runs were performed where the two catalytic functions were combined by physical admixture of 1 g iron catalyst, 1 g HZSM-5 and 5 g carborundum. Finally, the two catalysts were separated by loading a layer of HZSM-5 (1 g) diluted with carborundum (1 g) at the bottom, a layer of carborundum (1 g) in the middle to avoid contact between the catalytic functions, and a layer of iron catalyst (1 g) diluted with carborundum (3 g) at the top. A summary of the packing configurations for the various experiments is presented in Table 4.6.

It should be noted that the mixing of different materials and the loading of the reactor was done carefully in an attempt to obtain a homogeneous mixture of particles. However, because of the different properties of the materials (particle size and density), segregation would not have been avoided completely as the dry mixtures of particles were poured into the reactor. It is therefore likely that the packing density varied across the reactor bed, which may have led to some bypassing of gas (channelling) during reduction and synthesis.

Table 4.6: Packing configurations of the fixed bed microreactor for the various preliminary experiments

Catalysts and inert material	
Crushed iron catalyst	38 to 150 micron fraction
HZSM-5	powder (as supplied)
Diluent (inert) material	carborundum (180 grit)
Baseline FT run	
Number of layers	1
Iron catalyst	1 g
Diluent material	6 g
Bifunctional process - physical admixture of catalysts	
Number of layers	1
Iron catalyst	1 g
HZSM-5	1 g
Diluent material	5 g
Bifunctional process - separate catalyst layers	
Number of layers	3
Top layer: iron catalyst	1 g
diluent material	3 g
Middle layer: diluent material	1 g
Bottom layer: HZSM-5	1 g
diluent material	1 g

4.1.4 Catalyst activation and synthesis

Before synthesis commenced, the iron catalyst was reduced at 420°C for 16 hours by feeding pure hydrogen to the reactor at a flow rate of 250 ml/min. The HZSM-5, which did not require any additional activation, should not have been affected by the reduction procedure. Following the reduction, the reactor temperature was lowered to the synthesis temperature of 330°C under a flow of hydrogen. After the temperature had stabilised, the various feed gas flow controllers were set to the desired values, which signalled the onset of synthesis. During reduction and synthesis, the total pressure of the reactor was kept at a constant value of 20 bar.

Since the main objective of the preliminary experiments was to evaluate different configurations of the bifunctional process, it was decided to keep the synthesis conditions constant for all experimental runs. Initially, an H_2/CO ratio of 2 was chosen for the syngas feed, but a suitable baseline FT run could not be performed under these conditions due to excessive carbon formation that resulted in plugging of the packed bed. Consequently, the H_2/CO ratio of the feed was increased until a reasonable FT baseline run was obtained. The composition of the total feed to the

reactor used for all the experiments, as well as the other details of reduction and synthesis, is presented in Table 4.7.

Table 4.7: Reduction and synthesis conditions for all preliminary experiments performed in the fixed bed microreactor

Reduction conditions	
Reduction gas	hydrogen
Flow rate	250 ml / min
Gas space velocity	250 ml / min / g unreduced iron cat
Temperature	420°C
Pressure	20 bar
Time	16 hours
Feed gas composition (volume %)	
H_2	66
CO	15
Ar	19
Synthesis conditions	
Total flow rate	960 ml / min
Syngas flow rate	778 ml / min
Syngas spave velocity	778 ml / min / g unreduced iron cat
Temperature	330°C
Pressure	20 bar

4.1.5 Gas sampling and product analysis

Since the zeolites were expected to deactivate rapidly under synthesis conditions due to coke formation, about four samples were usually taken over the first eight hours on line. Thereafter, the sampling interval was increased to 24 hours. Samples of the reactor feed and effluent were taken in glass ampoules for later GC analysis. The empty ampoule, which is sealed under vacuum, has a long capillary tube that is pushed through the septum of a sample point into the gas stream. The tip of the capillary tube is then broken off so that a sample of the gas stream is sucked into the ampoule. After sampling, the glass ampoule is sealed off with an open flame. GC's, equipped with special ampoule breakers, are then used to analyse the gas samples. A more detailed description of this glass ampoule technique is presented by *Niederberger* (1988).

The feed gas was sampled from a point on the total feed gas line (upstream from the reactor). The sample point on the reactor effluent line was situated after the hot knock-out pot (so that the presence of waxy hydrocarbons in the glass ampoule was avoided), but before the cold knock-out pot (which ensured that a fairly comprehensive product spectrum was obtained). All samples were analysed on two

gas chromatographs, namely one that was fitted with a thermal conductivity detector (GC-TCD) and another that had a flame ionisation detector (GC-FID). The GC-TCD, which was calibrated with three gas mixtures of known composition, was used to quantify the relative amounts of the permanent gases (Ar, H_2, CO, CO_2 and CH_4). Since the sample contained argon, the carrier gas used for the GC-TCD analysis was helium. However, due to the similar thermal conductivities of hydrogen and helium, a reliable hydrogen analysis is not readily obtained when helium is used as carrier gas. Therefore, the gas sample was split into two fractions by two sample loops of fixed length. Helium was then passed through the one loop to carry the gas components through the separating columns and to a thermal conductivity detector where all the components, except hydrogen, were analysed. Argon was passed through the other sample loop to carry the gas through another set of separating columns to a thermal conductivity detector that analysed the amount of hydrogen. The hydrocarbon product spectrum was analysed with the GC-FID. For this latter analysis, it was assumed that the area on the chromatogram was proportional to the amount of carbon detected for all components that do not contain oxygen. For the oxygenated compounds that were identified in the Fischer-Tropsch product spectrum, appropriate response factors were applied. The two GC's are described in more detail in Tables 4.8 and 4.9.

Table 4.8: Details of GC-TCD

Make	Gow-Mac series 600
Columns	Porapak Q (1.5 m) followed by a 13X molsieve (2 m) in series
Split	Sample loops split sample gas into two fractions
Carrier gas - H_2 analysis	Ar
Carrier gas - other components	He
Oven temperature	60°C (constant)
Detector temperature	100°C

Table 4.9: Details of GC-FID

Make	Perkin Elmer XL
Column	Petrocol DH (150 m)
Carrier gas	H_2
Carrier gas flow velocity	22 cm/s
Split	1:100
Oven temperature	-60°C to 220°C (ramp)

The following aspects were taken into account for the identification of the important components on the GC-FID chromatogram and the lumping of the unidentified peaks:

- The GC-FID has a non-polar column, which means that the components of the product gas are separated more or less according to boiling point.

- Gas chromatography / mass spectroscopy (GC-MS) analyses were performed on some of the condensed hydrocarbon product samples (cold knock-out pot drainings). For this purpose, the same column and similar operating conditions (temperature program, carrier gas velocity, etc.) were employed as for the GC-FID analysis. Since the retention time of each of the various components in the GC-MS column was comparable to that in the GC-FID column, the patterns on the two chromatograms corresponded quite well. Information obtained from the mass spectrometer analysis could therefore be applied to the chromatogram of the GC-FID analysis.

- As explained in previous chapters, the addition of an acid catalyst to the HTFT process will transform the typical Fischer-Tropsch product spectrum to a hydrocarbon distribution that is much closer to thermodynamic equilibrium. For example, a highly active, highly acidic HZSM-5 zeolite will transform the higher carbon number fraction (C_{8+}) almost completely to aromatics (thermodynamically very stable compounds), whereas a deactivated or a low acidity HZSM-5 zeolite will produce less aromatics and more branched aliphatic products. Knowledge of the relative thermodynamic stabilities of different compounds aided in identifying the peaks on the chromatogram.

- The shape selective properties of HZSM-5 were also taken into account (*Horsley* et al., 1993). For example, it is known that the side branches of an aliphatic hydrocarbon are mainly confined to methyl groups, because of steric hindrance effects in the medium sized pores of this zeolite. For the same reason, the side chains on the aromatic rings are essentially methyl or ethyl groups.

- It was expected that the product spectrum obtained during the current set of experiments would bear resemblance to that of previous studies on the bifunctional process, as well as to that of the methanol-to-gasoline (MTG) process. Published chromatograms of the bifunctional process product spectrum (*Niederberger*, 1988) and the MTG product spectrum therefore provided valuable information about the order in which compounds are separated by a non-polar GC column, as well as the relative amounts of different compounds in the product spectrum.

The bifunctional process produces a large number of compounds. Since not all the peaks on the chromatogram could be identified, some of the products were lumped together. Subsequently, it is explained which components in the product spectrum were identified and how the unidentified components were grouped together:

C_{1-5}: A short hydrocarbon chain has limited possibility of branching. For molecules containing three or fewer carbon atoms, branching is not possible at all, while only a few aliphatic isomers exist for the C_4 and C_5 hydrocarbons. Furthermore, the ring of a cyclic compound generally contains at least five carbon atoms, whereas a minimum of six carbon atoms are needed to form an aromatic compound. Therefore, due to the simplicity of the light end of the product spectrum, all components in the C_1 to C_5 carbon number range could be identified. Small amounts of certain alkynes (most notably acetylene) and dienes were present in this part of the product spectrum. Since these

components cannot be formed in appreciable amounts by either the FT catalyst or the zeolite, it is assumed that the thermal cracking of heavier hydrocarbons was responsible for their formation. This probably occurred when the glass ampoules were sealed with an open flame after product sampling. Therefore, the peaks of alkynes and dienes on the chromatogram were ignored.

C_{6-7}: For this carbon number fraction, all the paraffins (both aliphatic and cyclic), linear olefins (terminal and internal) and aromatics (benzene and toluene) were identified. The rest of the peaks on the chromatogram were assumed to be branched olefins. It should be noted that some of the unidentified compounds may have been cyclic olefins.

C_{8-9}: All the aromatics, but only a few aliphatic paraffins, were identified in this range of the product spectrum. Since C_8^+ olefins and paraffins are not expected to be very stable in the presence of HZSM-5 at the prevailing reactor conditions, the unidentified components were assumed to be cyclic compounds. This assumption is fairly accurate for the case of a highly active zeolite, since cyclisation and aromatisation are so extensive that very little other compounds will be left in the heavy end of the product spectrum. However, for a low activity zeolite, these reactions do not proceed to completion, so that a vast number of products (presumably including aliphatic paraffins and olefins) are present in the C_8 to C_9 fraction.

C_{10-11}: It was assumed that only aromatics and naphthenes were present in this fraction in significant amounts. As for the case of the C_8 to C_9 fraction, this assumption will become less valid as the zeolite deactivates.

C_{11+}: Sometimes, for the case of a low aluminium content zeolite or a deactivated zeolite, components heavier than C_{11} aromatics were detected by the GC-FID. However, because of the insignificant amounts, these heavy products were merely lumped together and are not presented along with the other results.

Two typical chromatograms of product gas samples from the bifunctional process are presented in Appendices I and II. These chromatograms correspond to the addition of the "high acidity" and the "low acidity" HZSM-5 zeolites, respectively, to the HTFT process.

4.1.6 Data processing

Since argon is an inert gas that passes through the reactor unconverted, its flow rate out of the reactor is the same as its flow rate into the reactor. Therefore, argon served as an internal standard for the purpose of processing the results of the experiments. The argon flow rate was obtained from the calibration curve of the Brooks mass flow controller. The inlet and outlet flow rates of all the other permanent gases (H_2, CO, CO_2 and CH_4) could therefore be calculated from the results of the GC-TCD analysis by means of the following equation, shown here only for the case of CO:

$$\dot{n}_{CO} = \left[\frac{A_{CO}^{TCD}}{A_{Ar}^{TCD}}\right] \Psi_{CO}\, \dot{n}_{Ar} \qquad \ldots[4.1]$$

Since water is not detected by the GC-TCD, its outlet flow rate must be calculated from the flow rates of the other components. The iron catalyst used for the experiments not only has the ability to catalyse the Fischer-Tropsch reaction, but also has activity for the water-gas-shift reaction. General forms of these two reactions are presented below (*Dry*, 1983):

Fischer-Tropsch: $$CO + 2H_2 \rightarrow (-CH_2-) + H_2O \qquad \ldots[4.2]$$

Water-gas-shift: $$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \ldots[4.3]$$

It is thus clear that water is produced by the Fischer-Tropsch reaction, but consumed by the forward water-gas-shift reaction. Since no water is contained in the feed to the reactor, the outlet flow rate of water can be expressed as follows:

$$\dot{n}_{H_2O}^{out} = r_{FT} - r_{WGS} \qquad \ldots[4.4]$$

Similarly, the consumption of CO and CO_2 can also be expressed in terms of the reaction rates of the two involved reactions:

$$\dot{n}_{CO}^{in} - \dot{n}_{CO}^{out} = r_{FT} + r_{WGS} \qquad \ldots[4.5]$$

$$\dot{n}_{CO_2}^{in} - \dot{n}_{CO_2}^{out} = - r_{WGS} \qquad \ldots[4.6]$$

By combining Equations [4.4] to [4.6], an expression for the outlet flow rate of water is obtained:

$$\dot{n}_{H_2O}^{out} = \left(\dot{n}_{CO}^{in} - \dot{n}_{CO}^{out}\right) + 2\left(\dot{n}_{CO_2}^{in} - \dot{n}_{CO_2}^{out}\right) \qquad \ldots[4.7]$$

With the outlet flow rate of methane known from the expression analogous to Equation [4.1], the outlet flow rates of all the hydrocarbon compounds could be calculated from the results of the GC-FID analysis:

$$\dot{n}_{HC}^{out} = \left[\frac{A_{HC}^{FID}}{n_{HC} A_{CH_4}^{FID}}\right] \dot{n}_{CH_4}^{out} \qquad \ldots[4.8]$$

The flow rates of the various components were then used for further processing of the results. The CO and ($CO+CO_2$) conversions were calculated by means of Equations [4.9] and [4.10], respectively:

$$\chi_{CO} = 100\left[\frac{\dot{n}_{CO}^{in} - \dot{n}_{CO}^{out}}{\dot{n}_{CO}^{in}}\right] \quad \ldots[4.9]$$

$$\chi_{CO+CO_2} = 100\left[\frac{\left(\dot{n}_{CO}^{in} + \dot{n}_{CO_2}^{in}\right) - \left(\dot{n}_{CO}^{out} + \dot{n}_{CO_2}^{out}\right)}{\left(\dot{n}_{CO}^{in} + \dot{n}_{CO_2}^{in}\right)}\right] \quad \ldots[4.10]$$

Even though CO can be converted to CO_2 via the reversible water-gas-shift reaction (Equation [4.3]), this is not considered part of the Fischer-Tropsch (hydrocarbon synthesis) reaction. In this regard, CO_2 is not viewed as a product of CO conversion, but rather as another carbon containing reactant. Carbon entering the reactor as CO and CO_2 can be converted to hydrocarbons or be deposited on the catalyst as solid carbon. However, since it was assumed that the rate of carbon deposition was negligible compared to the formation rate of hydrocarbons, the product selectivities of the process were expressed in terms of the hydrocarbon product spectrum only. The seletivities were expressed on the basis of carbon atom percentage, i.e. the selectivity of a certain hydrocarbon compound was defined as the molar amount of carbon converted to that compound divided by the overall molar amount of carbon converted to hydrocarbons.

The overall rate of (CO + CO_2) conversion to hydrocarbons (i.e. the Fischer-Tropsch reaction rate) is the difference between the inlet and outlet flow rates of these two components:

$$r_{FT} = \left(\dot{n}_{CO}^{in} + \dot{n}_{CO_2}^{in}\right) - \left(\dot{n}_{CO}^{out} + \dot{n}_{CO_2}^{out}\right) \quad \ldots[4.11]$$

Note that the above equation can also be obtained by combining Equations [4.5] and [4.6]. The selectivity of a certain hydrocarbon compound can then be expressed as follows:

$$S_{HC} = 100\left[\frac{n_{HC}\dot{n}_{HC}}{r_{FT}}\right] = 100\left[\frac{n_{HC}\dot{n}_{HC}}{\left(\dot{n}_{CO}^{in} + \dot{n}_{CO_2}^{in}\right) - \left(\dot{n}_{CO}^{out} + \dot{n}_{CO_2}^{out}\right)}\right] \quad \ldots[4.12]$$

It should also be noted that not all the product samples were submitted for GC-FID analysis due to the time consuming nature of the method. A comprehensive hydrocarbon product distribution could therefore not be determined for some of the samples. However, since a GC-TCD analysis was available for each sample, the conversion and methane selectivity could be calculated for every data point.

4.2 RESULTS AND DISCUSSION

4.2.1 Baseline Fischer-Tropsch run

4.2.1.1 Process operation

The pressure drop over the packed bed is presented in Figure 4.1 for the full period of synthesis. During the first 80 hours, the pressure drop was not significant, after which it started to increase rapidly. After five and six days on line, the differential pressure over the bed was 1.5 and 2.8 bar, respectively, so that the reactor had to be shut down after the sixth day. During unloading of the catalyst, it was confirmed that the bed was plugged due to carbon formation. The profile of the pressure drop over time on line suggests that the bed void space was sufficient to allow a certain amount of carbon formation without seriously restricting the flow of gas through the bed. Apparently, a threshold amount of carbon was exceeded at around 80 hours on line, so that any additional carbon deposition brought about a significant decrease in the bed voidage. This resulted in a steep rise in the pressure drop during the latter part of the run.

The temperature was measured at the entrance to the catalyst bed for the purpose of temperature control during the fixed bed reactor experiments. Due to the exothermic nature of the Fischer-Tropsch reaction, it is quite probable that the temperature inside the bed was higher than the set-point value. Furthermore, if the packed bed did not consist of a homogeneous mixture of inert material and active catalyst, areas with a high concentration of iron might have led to hot spots inside the bed. If indeed there were areas in the catalyst bed where the actual temperature exceeded the desired synthesis temperature, this would have increased the rate of carbon deposition and aggravated the plugging of the catalyst bed.

4.2.1.2 Conversion (reaction rate)

The CO conversion and the ($CO+CO_2$) conversion are presented as a function of the time on line in Figure 4.2. There was a steep decrease in the conversion over the first few hours, after which the conversion suddenly recovered to the original value where it stayed for the remainder of the run. Even though transformations in the catalyst during the first few hours of synthesis have been reported for studies on iron-based Fischer-Tropsch catalysts, these transformations are normally associated with an increase in the intrinsic activity (see, for example, *Schulz*, 1990). Therefore, the steep decline and subsequent recovery in the conversion was probably not caused by changes in the iron catalyst. Initial temperature effects cannot be excluded as a contributing reason for the transient behaviour of the system.

Since the main objective of the current study is to investigate the feasibility of the bifunctional process, the variation in the conversion during the initial period of synthesis will not be considered further. Suffice to say that, apart from the decline during the first day of synthesis, it seems as if there has in fact been a slight but steady increase in the conversion over the course of the run. This means that the carbon formed on the catalyst particles did not restrict the diffusion of reactants and products to the extent that the reaction rate was affected.

4.2.1.3 Product distribution

4.2.1.3.1 Behaviour of the iron catalyst with time on line

The general effects of the alkali content of an iron catalyst on the product spectrum of the HTFT process have been discussed by *Dry* (1981). It is reported that an increase in the alkali level results in a decrease in the methane selectivity, an increase in the chain growth probability, an increase in the olefin / paraffin ratio of the product and an increase in the selectivity of oxygenated compounds. In other words, the hydrogenation ability of the iron catalyst is decreased by an increase in the alkali content. In order to establish whether there was a change in the alkali content of the active iron phase during the current experiment, the methane selectivity and the olefin / paraffin molar ratios of the C_2 to C_4 carbon number range were considered over the course of the run (Figures 4.3.1 and 4.3.2, respectively). It is clear that the methane selectivity increased and that the product spectrum became more paraffinic with time on line. The observation that the hydrogenating ability of the iron catalyst increased over the synthesis period is also clearly illustrated by the hydrogen / carbon ratio of the overall hydrocarbon product spectrum (Figure 4.3.3) and of the C_{2+} fraction (Figure 4.3.4). These selectivity changes suggest that the iron catalyst progressively became leaner in alkali as the run proceeded.

It is well known that the alkali promoters of the iron catalyst are mobile under HTFT conditions and alkali migration to the free carbon has even been observed (*Dry*, 1981). The diluent material (carborundum) and the excessive amount of free carbon deposited on the catalyst during the run would have provided a large area for the sodium to migrate to. Consequently, the significant change in the selectivity is ascribed to the migration of sodium away from the active iron phase.

4.2.1.3.2 Carbon number distribution

There is general consensus that hydrocarbon chain growth during the Fischer-Tropsch reaction occurs in a stepwise manner, i.e. the adsorbed complex grows by one carbon atom at a time until it desorbs as the product molecule (*Dry*, 1981). If it is assumed that the probability for chain growth (α value) is independent of the number of carbon atoms in the growing species, the carbon number distribution of the product spectrum can be described by the Schulz-Flory equation (*Dry*, 1981):

$$\ln\left[\frac{S_n}{n}\right] = n\ln\alpha + \ln\left[\frac{(1-\alpha)^2}{\alpha}\right] \qquad \ldots[4.13]$$

Therefore, plotting $\ln\left[\frac{S_n}{n}\right]$ versus n should yield a straight line with slope $\ln\alpha$.

It is known that the C_1 and C_2 selectivities of a real Fischer-Tropsch product normally deviate from the ideal Schulz-Flory equation (*Van der Laan*, 1999). Therefore, for the purpose of producing a Schulz-Flory plot of a hydrocarbon product distribution obtained during the current experiment, only the C_{3+} fraction was considered. Two examples of such graphs are presented in Figures 4.4.1 and 4.4.2, corresponding to

hydrocarbon product spectrums obtained after 8 hours and 58 hours on line, respectively. It is clear that early in the run, when the FT product spectrum was still fairly heavy, components up to C_{13} were detected by the GC-FID (see Figure 4.4.1). However, because the product spectrum became lighter as the run progressed, no components heavier than C_{11} were detected after 58 hours on line (see Figure 4.4.2). It is further evident from both these graphs that the measured selectivity of the heavy end of the product spectrum is lower than predicted by the Schulz-Flory relationship. The proposed reason for this is the small amounts of heavier products (C_{11+}) formed during the experiments. The GC-FID presumably did not detect and integrate all the components in the heavy fraction accurately. Furthermore, if any condensation of heavier hydrocarbons occurred during product sampling, it would have had a large effect on the small quantity of the C_{11+} components. These aspects may have led to the underestimation of the heavy cut; hence the downward bend in the Schulz-Flory curve. Therefore, for the purpose of this study, the value of α was calculated from the relative selectivities of compounds in the C_3 to C_{10} carbon number range. The selectivities of the C_{11+} hydrocarbons could then be estimated by extrapolation of the Schulz-Flory line. For all instances, the calculated C_{11+} selectivity constituted less than 3 % (on a carbon atom basis) of the total product spectrum.

Because of the mathematical relationship between the α value and the hydrocarbon selectivities, a large variation in the product spectrum is required to effect a notable change in the calculated value of the chain growth probability. Therefore, the variation in the α value over the course of the run is fairly small (see Figure 4.5). However, the overall trend seems to be that the chain growth probability decreased towards the end of the run, which is in line with the observation that the product spectrum became lighter as the run progressed.

4.2.1.3.3 Discrepancy in the carbon mass balance

By combining the calculated C_{11+} selectivities with the measured selectivities of the C_1 to C_{10} fraction, the total sum of the selectivities could be estimated. Since the selectivities are reported on a carbon atom basis, this is essentially a carbon mass balance. The selectivities added up to values ranging between 70% and 90%. Furthermore, there was a definite trend in the accuracy of the carbon mass balance, since the sum of the selectivities increased over the course of the run (see Figure 4.6). It is understandable that the data processing procedure can propagate and even amplify errors made during the GC-TCD and GC-FID analyses. However, the regular underestimation in the overall sum of the selectivities with a clear trend over the time on line points towards a consistent rather than a random error in the carbon mass balance. The following aspects are proposed as possible causes for the consistent error:

- As mentioned previously, the HTFT product spectrum contains an immense number of compounds, most of which are present in very small quantities. The GC-FID may not detect or integrate accurately each of these components. This problem is especially severe for the heavier end of the product spectrum, since the possible number of isomers vastly increases with increasing hydrocarbon chain length.

- It is possible that some condensation of hydrocarbons occurred during product sampling. If this was indeed the case, the heavier hydrocarbons would have condensed preferentially because of their higher boiling points; consequently, some of the heavy product may not have been contained in the glass ampoule.

- Certain alkynes (most notably acetylene) and dienes are present in the light end of the product spectrum. Since these are assumed to be thermal cracking products of longer chain hydrocarbons (formed when the ampoules were sealed with an open flame), they were omitted from the Fischer-Tropsch product spectrum. However, the combined selectivity of these components was never more than 1%.

- It is often observed that the Fischer-Tropsch product spectrum does not follow an ideal Schulz-Flory distribution, but that the chain growth probability (α value) actually increases with increasing carbon number (*Van der Laan*, 1999). The method used to calculate the selectivities of the heavier hydrocarbons might therefore be an underestimation. However, since these heavier components constituted only a small fraction of the overall hydrocarbon product spectrum (less than 3 % on a carbon atom basis), even a substantial error in their estimated selectivities cannot account for such a large discrepancy in the carbon balance.

- The oxygenates were not included in the product spectrum, but this comprised only about 1 to 2 % of the total hydrocarbon product.

- The carbon deposited on the iron catalyst also consumed CO, but this was not included in the carbon balance. The cumulative amount of unaccounted carbon for the whole run (overall discrepancy in the carbon mass balance) was estimated to be more than 100 g. Even though the amount of carbon in the catalyst bed was not measured, it seems unfeasible that 1 g of iron catalyst (unreduced mass) could have deposited even a significant portion of the unaccounted carbon. This seems to validate the assumption that the rate of carbon deposition on the catalyst was negligible in comparison to the rate of hydrocarbon formation.

It should be noted that all the above aspects are consistent with the observation that the sum of the selectivities improved with time on line. The first four points relate exclusively to an underestimation of the longer chain hydrocarbons, the selectivity of which decreased as the alkali level of the catalyst dropped during the course of the run. Similarly, the selectivity of oxygenates and the rate of carbon formation would also have decreased as the iron catalyst became lean in alkali. However, it has been shown that the last four proposed causes cannot account for the bulk of the "missing" carbon. Therefore, even though all the aspects mentioned may have contributed to the discrepancy in the carbon balance, it appears as though an inaccurate GC-FID analysis of the heavy end of the product spectrum was the main reason. This notion is further supported by the observation that the carbon balance improved upon the addition of a highly active zeolite to the HTFT process during later experiments. The acid catalysed reactions over a highly active zeolite were so extensive that the product spectrum was highly aromatic (i.e. contains fewer compounds) and that virtually no

compounds higher than C_{11} was present due to cracking. This presumably resulted in a more accurate sampling and analysis of the hydrocarbon product.

Since it seems as though the discrepancy in the carbon balance was mostly caused by an underestimation of the heavier hydrocarbons, normalisation of the overall hydrocarbon product spectrum to 100% will result in an overestimation of the light products. On the other hand, it is uncertain to what extent each carbon number fraction has been underestimated. Because it is known that the C_1 and C_2 hydrocarbons often deviate from the Schulz-Flory distribution (*Van der Laan*, 1999), it was decided to scale the calculated selectivities of the C_{3+} components by the required factor in order to force a carbon mass balance. In other words, the selectivities of all the C_{3+} components were multiplied by a certain factor to ensure that the overall hydrocarbon selectivities (from methane onwards) summed up to 100% while the Schulz-Flory product distribution was retained.

4.2.1.3.4 Overall aspects of the product spectrum

The normalised product distributions obtained by following the above method are presented in Figures 4.7.1 to 4.7.3 for various times on line. The methane selectivity (which has previously been presented and discussed in some detail) is not included in these figures, as it would unnecessarily increase the scale of the graphs and distract from the discussion of the rest of the product spectrum. From the figures, it is clear that the C_2 to C_{10} range of the product spectrum is highly olefinic, especially early in the experimental run when the iron catalyst presumably still contained a sufficient amount of sodium. As the synthesis time increased and the product spectrum became more hydrogenated, the selectivities of the light paraffins increased with a corresponding decrease in the olefins. However, even at the end of the run, the olefin selectivity in the C_2 to C_{10} range was still substantially higher than the paraffin selectivity. On all the graphs there also seems to be an exponential decay in the olefin and paraffin selectivities with increasing carbon number. The reason for this is that the product spectrum approximately follows a Schulz-Flory distribution (see Equation [4.13], as well as the discussion in Section 4.2.1.3.2). The ethylene selectivity clearly deviates significantly to the negative side from the exponential curve of the olefins. This phenomenon is often observed for Fischer-Tropsch product spectrums and is generally ascribed to the high reactivity of ethylene for secondary reactions (*Van der Laan*, 1999). Lastly, it should be noted that the selectivity towards aromatics is almost negligible.

4.2.2 Bifunctional process - physical admixture of the two catalytic functions

4.2.2.1 Process operation

The baseline FT run was followed by three experimental runs where each of the HZSM-5 zeolites was physically admixed with the iron catalyst (see Table 4.6 for packing details). For these runs, the pressure drop over the catalyst bed increased more rapidly than for the baseline FT run, so that the runs were normally terminated after three to four days of synthesis (see Figure 4.8). It is known that coke is normally formed on zeolites during acid catalysed reactions of hydrocarbons, but that this

results in a serious loss of catalyst activity (*Horsley* et al., 1993). Since GC analysis of product samples indicated that the zeolites were still very active at the time that the bifunctional process runs were terminated, the more rapid increase in the pressure drop over the bed cannot be ascribed to coke formation on the HZSM-5.

The only feasible explanation for the more steep increase in the pressure drop over the catalyst bed for the case of the bifunctional process runs is that the addition of the fine HZSM-5 powder increased the packing density of the catalyst bed. Because of the lower initial void space, the packed bed would have had a much lower capacity for deposited carbon. Therefore, the amount of carbon formed by the iron catalyst over the first 40 hours of synthesis was already sufficient to notably restrict the flow of gas through the bed, resulting in a steep increase in the differential pressure early in the run. The differences in the pressure drop profiles over time on line for the three bifunctional process runs also suggest that the reactor was not packed exactly the same for each experiment. It thus seems as if a homogeneous mixture of the different particles (iron catalyst, HZSM-5 and carborundum) was not obtained during the loading of the reactor.

4.2.2.2 Conversion (reaction rate)

The CO and ($CO+CO_2$) conversions achieved for the bifunctional process runs are presented in Figures 4.9.1 and 4.9.2, along with that of the baseline FT run. For each of the bifunctional process runs, the conversion decreased sharply over the first few hours of synthesis, where after it seemed to level out at a fairly constant value for the remainder of the run. The stabilised conversion values differ quite significantly for the different runs, and all are notably lower than for the standard FT run.

It was previously stated that the pressure drop profiles over the bed for the various runs suggested an inhomogeneous mixture of material in the reactor. The presence of fine HZSM-5 powder would have affected the bed void space and a segregation of particles with different properties (density and particle size) probably occurred during the loading of the reactor. A variation in the packing density of the reactor would have caused channelling of gas through the bed. The differences in conversion for the various runs are therefore ascribed to a maldistribution of gas in the catalyst bed. The deposition of carbon in the bed may have enhanced the formation of channels and therefore aggravated the extent of gas bypassing.

4.2.2.3 Product distribution

4.2.2.3.1 Carbon mass balance

The sum of the hydrocarbon selectivities for the bifunctional process experiments are presented in Figure 10. As in the case of the baseline FT run, the carbon mass balance generally improved with time on line as the product spectrum became lighter. It is believed that this discrepancy in the carbon mass balance is due to similar reasons as discussed previously for the baseline FT run (see Section 4.2.1.3.3), but it should be noted that not all these reasons are valid for the case of the bifunctional process. For example, no oxygenates were identified in the product of the bifunctional process, so

that their omission from the product spectrum should not have any notable influence on the carbon balance. Furthermore, the expected increase in α value with increasing carbon number would not be a source of inaccuracy either, since the heavy end of the product from the bifunctional process was not estimated with the Schulz-Flory equation.

It is also evident from Figure 10 that the carbon balances for the bifunctional process runs are generally closer to 100 % than for the baseline FT run. This is ascribed to the fact the product spectrums of the bifunctional process runs were significantly lighter than for the case of the baseline FT run (this will subsequently be discussed in more detail). Furthermore, a highly active zeolite converts the gasoline range almost completely to aromatics, so that the total number of compounds in this fraction is reduced. Consequently, the GC-FID analysis is expected to be more accurate.

In order to ensure consistency in the processing of the data, the product spectrums of the bifunctional process runs were also normalised by scaling the C_{3+} selectivities in order to obtain a total selectivity of 100%.

4.2.2.3.2 Behaviour of FT catalyst function with time on line

The methane selectivities of the bifunctional process runs are compared to that of the baseline FT run in Figure 4.11.1. The addition of HZSM-5 to the HTFT process clearly resulted in a much higher methane selectivity. For each of the bifunctional process experiments, the methane selectivity also increased more extensively with time on line than for the baseline FT run. If the hydrogen / carbon ratio of the overall product spectrum (Figure 4.11.2) and of the C_{2+} fraction (Figure 4.11.3) is considered, the same trend is observed. Not only was the product from the bifunctional process more hydrogenated, but the increase in hydrogen content over synthesis time was also more extensive for the bifuncitonal process runs than for the standard FT run. This indicates that the presence of the zeolite caused the product spectrum to become more hydrogenated.

For the case of the baseline FT run, the increase in the methane selectivity and the hydrogen content of the overall product spectrum with time on line has been ascribed to the migration of alkali to carbon deposited on the catalyst. The enhancement of these effects upon the addition of HZSM-5 cannot be attributed to the catalytic properties of the zeolite per se, since the zeolite does not have a significant ability to activate the hydrogen molecule and thereby increase the hydrogen content of the overall product. It is therefore assumed that the addition of the zeolite had an indirect effect on the hydrogen content of the product by influencing the hydrogenation ability of the iron catalyst. The alkali promoters of the iron catalyst are very mobile under HTFT reduction and synthesis conditions (*Dry*, 1981) and contact between the catalytic functions is expected to results in a migration of alkali from the iron to the zeolite (*Butter* et al., 1981). It is thus evident that the physical admixture of the catalytic functions resulted in a depletion of the alkali content of the iron catalyst. Even though dilution of the catalyst bed with inert carborundum would have limited the contact between the two catalytic functions, alkali migration from the iron to the HZSM-5 was clearly not avoided.

4.2.2.3.3 Behaviour of the acid catalyst function with time on line

In general, zeolites may deactivate under typical HTFT operating conditions because of the following reasons (*Butter* et al., 1981; *Jothimurugesan* et al., 1998; *Udaya* et al., 1990):

- The abundance of olefins in the reactor can lead to the formation of large, unsaturated molecules that will eventually transform to coke. This coke will cover the surface and block the pores of the zeolite, restricting access to the acid sites.

- The presence of water (a product of the Fischer-Tropsch process) at the elevated operating temperatures may lead to dealumination of the zeolite, which will decrease the number of active sites.

- Migration of the alkali promoters from the iron catalyst to the zeolite will poison the acid sites (only applicable if the two catalytic functions are in contact with each other).

ZSM-5 has been the preferred choice of zeolite for use in the bifunctional process, because of its hydrothermal stability and resistance to coke formation (see Chapter 2). Notwithstanding, a significant decline in the activity of the HZSM-5 over the first day of synthesis has been reported by previous researchers (e.g. *Schulz* et al., 1991). Consequently, a deactivation of the HZSM-5 was also expected to occur during the current study on the bifunctional process.

The product distributions of the bifunctional process runs are presented for the various HZSM-5 zeolites at the beginning of the run (after two to three hours on line) and at the end of the run (after about 70 to 100 hours on line) in Figures 4.12 to 4.14. For all the runs, the selectivities of the aromatic and naphthenic compounds decreased with time on line. It should, however, be noted that the selectivities of the light paraffins (most notably methane and ethane) increased correspondingly. Considering Figures 4.11.1 to 4.11.3, it is clear that the product spectrum produced by the FT catalyst became lighter and more paraffinic over the course of the run. The lowering of the aromatics and naphthenes can therefore not be attributed exclusively to a zeolite deactivation effect, since the increasingly hydrogenated product spectrum produced by the FT catalyst would have provided the HZSM-5 with fewer reactive compounds (olefins and long chain paraffins) towards the end of the run. In fact, considering the fraction of aromatics in the C_{5+} fraction at the beginning and end of the runs (Table 4.10), it seems as if the zeolites deactivated only slightly over three days of synthesis.

Table 4.10: Aromatic content of C_5^+ fraction (carbon atom %) -
Bifunctional process, physical admixture of catalysts

	Time on line	
	3 hours (approx.)	**75 hours (approx.)**
"Low acidity" HZSM-5	13.1	11.7
"Medium acidity" HZSM-5	27.6	20.9
"High acidity" HZSM-5	33.1	27.1

It is not possible to quantify the extent of the HZSM-5 deactivation from the available data, because of the major changes in the Fischer-Tropsch product spectrum with time on line. However, because of the high aromatics content of the liquid fraction at the end of the run, it is clear that the zeolites were still very active after three days of synthesis. The low deactivation rate is attributed to the following:

- The partial pressure of hydrogen in the gas phase was in the order of 13 bar. Furthermore, the olefin content of the FT product spectrum was quite low and decreased further with time on line. Presumably, the high hydrogen content relative to the amount of olefins aided in limiting the formation of large molecules and their subsequent transformation to coke.

- The alkali level of the iron catalyst employed in this study is so low that a comprehensive poisoning of the acid catalyst by sodium would not have been possible. This statement was verified by calculating the number of aluminium atoms per gram of HZSM-5 for each of the zeolites. Under the assumption that each aluminium atom in the zeolite framework represents an acid site, the total molar amount of sodium in the iron catalyst could be expressed as a percentage of the calculated molar amount of acid sites on the various zeolites. The results are presented in Table 4.11 and a sample calculation is presented in Appendix III. This clearly indicates that there was not enough sodium available in the system to seriously affect the acidity of the HZSM-5, especially in the case of the two higher acidity zeolites. Therefore, alkali migration from the iron to the HZSM-5 would have affected the Fischer-Tropsch catalyst function far more seriously than the acid catalyst function.

Table 4.11: The ratio of the number of sodium atoms contained by the iron catalyst to the number of acid sites of each of the different HZSM-5 zeolites (See Appendix III for sample calculation)

	Sodium atoms / acid sites [%]
"Low acidity" HZSM-5	4.8
"Medium acidity" HZSM-5	12.4
"High acidity" HZSM-5	42.6

4.2.2.3.4 Effect of HZSM-5 addition on the product spectrum

From the foregoing discussions, it is clear that the results obtained are not adequate to make sound conclusions about the performance of the bifunctional process. Because of the serious influence that the HZSM-5 had on the selectivity of the iron catalyst via alkali migration, the product from the bifunctional process cannot be compared quantitatively to that of the baseline FT run. Furthermore, the performance of the iron catalyst deteriorated so severely that, towards the end of the run, there were very little hydrocarbons in the product spectrum that could potentially be converted by the zeolite. Therefore, the initial period of synthesis gives the most realistic indication (albeit far from perfect) of how the bifunctional process might perform if the reactor operating problems and alkali migration could be circumvented. In view of the

above, only product spectrums at the beginning of the runs (after a few hours of synthesis) will be considered further in order to illustrate qualitatively some differences in selectivity between the traditional HTFT process and the bifunctional process. A more quantitative comparison between the normal HTFT process and the bifunctional process will be presented in the next chapter, where the results of a follow-up experimental study (performed with a more appropriate choice of reactor) will be discussed thoroughly.

The overall carbon number distributions of the bifunctional process runs are compared to that of the baseline FT run in Figure 4.15. It is clear that the addition of HZSM-5 to the HTFT process changed the typical Schulz-Flory carbon number distribution of the Fischer-Tropsch reaction significantly. The differences in the methane selectivities have earlier been ascribed to the indirect effects of HZSM-5 on the process (see Section 4.2.2.3.2). The slight lowering of the C_2 fraction upon addition of the zeolite may indicate that some ethylene has reacted over the HZSM-5. However, because of the instability of primary carbenium ions, ethylene and ethane are not expected to be readily consumed or produced by the acid catalysed reactions. Therefore, the change in the C_2 selectivity can also be attributed to a shift in the product spectrum of the iron catalyst towards methane. On the other hand, the significant lowering of the C_3 selectivity is mainly ascribed to the high reactivity of propylene over an acidic zeolite. The product spectrum of the bifunctional process is further distinguished from the typical Schulz-Flory distribution by the occurrence of two clear humps. The first hump at C_4 corresponds to the distribution of olefins and paraffins, whereas the second hump at about C_8 corresponds to the favoured distribution of aromatics. There is also a fairly sharp cut-off in the product spectrum at around C_{10} to C_{11}. The reason for this is that long chain aliphatics are not stable at these temperatures in the presence of an acid catalyst, while aromatics higher than about C_{11} are too large to be formed readily inside the pores of HZSM-5.

Comparing Figures 4.12.1, 4.13.1 and 4.14.1 with Figure 4.7.1, it is clear that the HZSM-5 had a major influence on the types of components present in the product spectrum. Whereas the Fischer-Tropsch product contains negligible amounts of aromatics and naphthenes, the liquid fraction of the bifunctional process is very rich in these compounds. This represents an enormous increase in the octane value of the condensable hydrocarbons. It is also evident that the ratio of olefins to paraffins in the product of the bifunctional process is much lower than for the baseline FT run. Apart from the indirect influence that the HZSM-5 had on the selectivity of the FT catalyst via alkali migration, this decrease in olefin content is also a result of the formation of aromatic compounds over the acid catalyst. HZSM-5 does not have any significant ability to activate the hydrogen molecule and can therefore not affect the overall hydrogen / carbon ratio of the product. Since aromatic compounds are very lean in hydrogen, their formation is accompanied by the transfer of hydrogen to olefinic hydrocarbons. This transfer takes place via an ionic mechanism involving H^+ and H^- species, and not molecular hydrogen. The result is a transformation of olefins into paraffins.

A comparison between the C_{5+} product cuts of the different bifunctional process runs shows that an increase in the aluminium content of the HZSM-5 increased the total amount of cyclics in the liquid fraction (see Table 4.12). This was expected, since ring closure occurs faster over "higher acidity" zeolites than "lower acidity" zeolites.

Table 4.12: Aromatic and naphthenic content (carbon atom %) of C_{5+} fraction after about 3 hours of synthesis -

Bifunctional process, physical admixture of catalysts

	Benzene	BTXE aromatics	Total aromatics	Naphthenes	Aromatics and naphthenes
"Low acidity" HZSM-5	1.6	7.8	13.3	18.1	31.5
"Medium acidity" HZSM-5	1.9	16.7	24.4	17.6	42
"High acidity" HZSM-5	3.6	21.6	33	11.2	44.2

It is further evident that the ratio of aromatics to naphthenes was affected by the variation in the aluminium level of the zeolite, since an increase in the aluminium content resulted in a higher aromatic but lower naphthenic content. The reason for this is that the conversion of cyclic compounds to aromatics also occurs faster over "higher acidity" zeolites.

From the results of Table 4.12, it is thus clear that the composition of the liquid product from the bifunctional process can be tailored somewhat by changing the aluminium content of the HZSM-5. By using a "high acidity" HZSM-5, gasoline with a very high octane value can be produced. However, the aromatic content of such a gasoline, and in particular the amount of benzene, may not comply with future fuel specifications[iii]. If the aluminium level of the zeolite is lowered, the aromatic content will decrease with a corresponding increase in naphthenic compounds and branched aliphatics. Even though the octane value will be negatively affected, the composition of the gasoline might be more acceptable. Lastly, it should be noted that the fraction of BTXE aromatics in the liquid product exceeds 20% when the "high acidity" HZSM-5 is employed. Recovery of these compounds may have a positive influence on the economics of the bifunctional process, because of the chemical value of benzene, toluene and the respective xylenes. The bifunctional process can therefore be extended beyond mere fuel production.

4.2.3 Bifunctional process - catalytic functions in subsequent layers (dual bed arrangement)

4.2.3.1 Process operation

The bifunctional process was also operated in a mode where the two catalytic functions were contained in subsequent layers separated by inert carborundum, i.e. a "dual bed" arrangement (see Table 4.6 for packing details). For these runs, the pressure drop over the reactor bed also increased more rapidly than for the case of the baseline FT run (Figure 4.16). The top layer of the bifunctional process in the dual bed configuration consisted of a mixture of 1 g iron catalyst and 3 g carborundum,

[iii] Of all the aromatics, benzene poses by far the greatest health risk. It is therefore expected that, whereas other aromatics may be acceptable components of gasoline in the medium term future, harsh restrictions will be placed on benzene.

whereas 1 g of iron catalyst was diluted with 6 g of inert material for the case of the standard FT run. The more steep increase in the pressure drop observed for the bifunctional process runs are therefore ascribed to the small amount of diluent material used. The top layer of the dual bed arrangement had a low total void space, which meant that the deposition of carbon on the iron had a more severe restricting influence on the flow of gas through the bed. Furthermore, if there were significant temperature profiles along the length of the catalyst bed during the experiments, the peak temperatures for the bifunctional process runs would have been higher than for the case of the standard FT run, because of the higher concentration of iron catalyst. A higher peak temperature would have enhanced the rate of carbon formation on the catalyst. It is therefore clear that the lower capacity of the bed to accommodate deposited carbon and a possible higher peak temperature in the bed (leading to a higher rate of carbon formation) caused the more rapid increase in the pressure drop for the case of the bifunctional process runs in the dual bed arrangement.

4.2.3.2 Conversion (reaction rate)

The CO and ($CO+CO_2$) conversions for the bifunctional process runs with the catalytic functions in the dual bed arrangement are presented in Figures 17.1 and 17.2, respectively. The results are even more erratic than those obtained for the previous arrangement of the bifunctional process, and no clear trends are visible. The variations in conversion are once again ascribed to a maldistribution of gas in the catalyst bed due to plugging of the bed and resultant channelling of the gas. The non-ideal gas flow was possibly aggravated by the fact that the iron catalyst was not as well diluted with carborundum as for the foregoing experimental runs.

4.2.3.3 Product distribution

From the above discussions, it is evident that the dual bed configuration in the fixed bed reactor was not an optimal set-up of the bifunctional process either. Even though separation of the catalytic functions would have avoided the migration of alkali from the iron to the zeolite, the high concentration of FT catalyst in the top layer apparently aggravated the problems of gas channelling and temperature effects in the bed. Consequently, the results obtained with this set-up will be explained very briefly. In the next chapter, where the results of a follow-up study are reported, a more thorough discussion of the bifunctional process will be presented.

4.2.3.3.1 Carbon mass balance

For the bifunctional process experiments performed in the dual bed configuration, the selectivities again added up to values lower than 100%. Consequently, the selectivities were normalised as explained previously (see Sections 4.2.1.3.3 and 4.2.2.3.1 of this chapter).

4.2.3.3.2 Behaviour of FT catalyst function with time on line

The methane selectivities of the dual bed runs are presented in Figure 4.18, along with that of the baseline FT run. As was the case with the conversion, these data are somewhat erratic. However, it does seem as if the methane selectivities over time on line for the case of the dual bed runs are generally more or less in line with that of the baseline FT run. This indicates that the alkali content of the iron catalyst for all these runs (the bifunctional process in the dual bed arrangement and the baseline FT run) generally followed the same trend over the synthesis period. In the dual bed arrangement, the iron catalyst is separated from the zeolite by an inert layer, so that the two catalytic functions are not in direct contact. The migration of alkali from the iron to the acid catalyst, that caused excessive methane formation in the case of the bifunctional process with the catalytic functions in physical admixture, therefore seemed to be avoided for the dual bed configuration.

4.2.3.3.3 Behaviour of the acid catalyst function with time on line

The product distributions of the dual bed runs are presented for the various HZSM-5 zeolites at the beginning of the run (after two to four hours on line) and at the end of the run (after 75 to 80 hours on line) in Figures 4.19 to 4.21. For the case of the "high acidity" HZSM-5 (Figures 4.21.1 and 4.21.2), there was not only a marked decrease in the selectivity of the aromatic compounds over the synthesis period, but clearly also an increase in the ratio of naphthenes to aromatics. In addition, there was a notable increase in the amount of olefins relative to paraffins with time on line. Since olefins are consumed and paraffins produced during the acid catalysed formation of aromatics, these observations are indicative of significant zeolite deactivation over the three days of synthesis. For the zeolite with "intermediate acidity" (Figures 4.20.1 and 4.20.2), the increase in olefins with time on line may also point to a loss of activity, but the deactivation is not as clear as for the case of the "high acidity" HZSM-5. For the "low acidity" HZSM-5, there was also a substantial decrease in the selectivity of naphtenes and aromatics (Figures 4.19.1 and 4.19.2). However, for this experiment, the methane selectivity was more than 43 % at the end of the run (see Figure 4.18). The decrease in cyclic compounds is therefore mainly ascribed to a shift in the FT product spectrum towards the light end and no definite conclusions about acid catalyst deactivation can be made.

Even though acid catalyst deactivation is only clearly observed for the case of the "high acidity" HZSM-5, this is not surprising, since the coking tendency of a zeolite is expected to increase with increasing aluminium content (*Horsley* et al., 1993). The fact that zeolite deactivation occurred for an experiment conducted in the dual bed configuration, while no deactivation was evident when the two catalytic functions were in physical admixture, is ascribed to the amount of olefins present in the reactor. Since the selectivity of the iron catalyst did not deteriorate so severely for the case of the dual bed arrangement, the product spectrum was heavier and more olefinic. This implies a higher formation rate of molecules that are reactive over the zeolite, but also means a larger amount of compounds that can act as coke precursors.

4.2.3.3.4 Comparison of the two configurations of the bifunctional process

Previous researchers have reported a synergistic effect between the FT catalyst and the acid catalyst when the two catalytic functions were in close association (see, for example, *Jothimurugesan*, et al., 1998; *Varma* et al., 1986). Because of the detrimental influence that HZSM-5 had on the iron catalyst via alkali migration when the two catalysts were physically admixed, the synergistic effect was not observed for the current experiments. In fact, because of the much lower methane selectivity generally obtained for the case of the dual bed arrangement (compare Figures 4.11.1 and 4.18), this seems to be the preferred configuration of the bifunctional process. However, it must be noted that the preliminary investigation could have been conducted in a manner more suitable to study the bifunctional process. For instance, the use of more diluent material may have limited the contact between the iron and the zeolite to the extent that alkali migration would have been reduced significantly. Under such circumstances, the physical admixture of the catalysts may have compared favourably to the dual bed arrangement.

Despite the differences in methane selectivity, the composition of the C_{5+} fraction obtained with each of the two arrangements are very much alike (compare Tables 4.12 and 4.13). The effect of the zeolite aluminium content on the composition of the condensable product fraction is also similar for the two configurations (see discussion in Section 4.2.2.3.4).

Table 4.13: Aromatic and naphthenic content (carbon atom %) of C_{5+} fraction after about 3 hours of synthesis -

Bifunctional process, dual bed arrangement

	Benzene	BTXE aromatics	Total aromatics	Naphthenes	Aromatics and naphthenes
"Low acidity" HZSM-5	0.7	6.9	20.9	15.5	36.4
"Medium acidity" HZSM-5	1.3	12.1	21.5	17.1	38.6
"High acidity" HZSM-5	3.3	22.5	34.6	10.5	45.1

4.3 CONCLUSIONS AND RECOMMENDATIONS

4.3.1 Microreactor set-up

The fixed bed microreactor used for the preliminary investigation was clearly not an adequate set-up to study the addition of HZSM-5 to the HTFT process. For the baseline FT run, carbon deposition on the catalyst led to plugging of the packed bed. The run had to be shut down after about a week on line due to an increase in the pressure drop over the reactor. For temperature control purposes, the temperature was measured above the entrance to the bed (and not inside the bed itself). Due to the highly exothermic nature of the Fischer-Tropsch reaction, the temperature inside the bed might well have exceeded the set-point, which would have increased the rate of carbon deposition. The deposited carbon not only affected the operation of the process, but also had a serious influence on the product selectivity due to alkali

migration from the iron catalyst to the carbon. Consequently, the performance of the FT catalyst became consistent with that of a low alkali catalyst, producing a light, paraffinic product spectrum that would not be acceptable for a commercial process. The inadequacy of the fixed bed reactor set-up was even more pronounced when HZSM-5 powder was physically admixed with the iron catalyst. Presumably, the fine zeolite powder decreased the void space of the reactor bed, so that the deposition of carbon on the iron catalyst plugged the bed more quickly.

It is unlikely that the deposition of carbon on the iron catalyst occurred evenly across the catalyst bed. The formation of channels through the packed bed, with a resultant maldistribution of gas, was therefore a distinct possibility. This was the proposed reason for the observed variations in the CO conversion. The experimental data was especially inconsistent for the case of the bifunctional process in the dual bed arrangement. For this configuration, uneven carbon deposition and temperature effects may have been more severe, because the iron catalyst was less diluted than for the other configurations.

There are various ways in which the operation of the fixed bed microreactor might be improved for the purpose of studying the bifunctional process. For example, the catalyst bed can be diluted more by loading additional inert material or less catalyst, or the powdered catalysts can be pressed into pellets to obtain larger particles of a more uniform size so that the bed does not plug so easily. However, it is rather recommended that a Berty reactor be employed for further experimentation (see Chapter 5). Carbon deposition on the iron catalyst would not have a significant influence on the operation of this type of microreactor. Furthermore, the high internal recycle of the reactor will remove the reaction heat more effectively and thereby avoid the possibility of high peak temperatures inside the catalyst bed.

4.3.2 Effect of HZSM-5 on the product spectrum of the HTFT process

For both configurations studied (physical admixture of the catalytic functions and the dual bed arrangement), the addition of HZSM-5 to the HTFT process had the expected effect on the composition of the product. The condensable product fraction from the bifunctional process contained a large amount of naphthenes and aromatics. This represents a gasoline fraction with a much higher octane value than the predominantly linear hydrocarbons of the traditional Fischer-Tropsch product. It was also clear that the composition of the liquid fraction can be manipulated by changing the aluminium content of the HZSM-5. The higher the aluminium content of the zeolite, the more aromatics are produced and the higher the expected octane value of the product. On the other hand, a too large amount of aromatics in the gasoline might not be desirable because of environmental considerations. Lastly, it should be noted that the C_{5+} product fraction contains a substantial amount of BTXE aromatics, so that the combination process also has potential as a method to produce these chemicals directly from syngas.

Even though it was quite evident from the preliminary experimental study that the quality of the gasoline fraction can be vastly improved by the addition of an acid catalyst to the HTFT process, no final conclusions could be made regarding the gasoline selectivity. The main reason for this was the significant influence that the

packing arrangement of the reactor had on the operation of the process and the synthesis data obtained. For both configurations of the bifunctional process, the packing of the catalyst bed was clearly less optimal than for the case of the baseline FT run, so that a direct comparison between the processes would not be realistic. Furthermore, the FT catalyst produced a light product rich in paraffins, especially when HZSM-5 was also loaded into the reactor. This is neither acceptable for a commercial process, nor optimal for conversion over an acid catalyst. The physical mixture of HZSM-5 with the FT catalyst resulted in very high methane selectivities (presumably due to alkali migration from the iron to the zeolite) and therefore seems like an unfeasible option due to the low selectivity of desired (gasoline range) products. However, a more optimal configuration of the two catalytic functions may well bring about the expected increase in gasoline selectivity over the standard HTFT process.

4.3.3 Deactivation of the zeolite due to coke formation

In general, it would be expected that an acidic zeolite would deactivate in the HTFT environment due to coke formation (see, for example, *Schulz* et al., 1991). Such deactivation was not evident from the performance of the bifunctional process with the catalytic functions in physical admixture. This was ascribed to the low olefin selectivity of the iron catalyst for the case of these experiments. To the contrary, deactivation of the HZSM-5 was noted for the dual bed arrangement of the bifunctional process, especially for the case where the "high acidity" HZSM-5 was employed as the acidic co-catalyst. The deactivation was ascribed to the higher olefin selectivity of the FT catalyst in this arrangement, which increased the amount of coke precursors on the zeolite. In view of these findings, it is clear that the zeolite deactivation must be studied and quantified under more realistic HTFT operating conditions, which again implies the use of a Berty microreactor for further experiments.

4.3.4 Migration of the alkali promoter

In the literature, the problem of alkali migration from an iron FT catalyst to an acidic co-catalyst is discussed from the perspective that the alkali will poison the acid sites with resultant loss of acid catalyst activity, while little mention is made of the possible influence of alkali depletion on the behaviour of the iron catalyst (see, for example, *Butter* et al., 1981). For the current experiments performed with the two catalysts in physical admixture, the product became lighter with time on line, but the C_{5+} fraction was still rich in aromatics at the end of the run. Calculations confirmed that the total amount of alkali contained in the iron catalyst was not sufficient to significantly affect the acidity of any of the zeolites. It is therefore concluded that, if a low alkali iron catalyst is combined with a zeolite of reasonable acidity, alkali migration would have a more significant influence on the selectivity of the iron catalyst than on the activity of the zeolite. This implies that the use of a binder (such as alumina) to trap the alkali is not a solution to the problem of promoter migration for such a catalytic system, as the iron phase will still be depleted of alkali.

4.3.5 The effect of intimacy of contact between the two catalytic functions

One of the objectives of the preliminary study was to investigate the issue of intimacy of contact between the two catalytic functions. The experimental results indicated that the physical admixture of the two catalysts had an adverse effect on the performance of the iron catalyst. Any possible synergism between the two catalytic functions was clearly outweighed by the dramatic changes in the selectivity of the FT catalyst. Even though the adverse effects were probably mainly caused by alkali migration from the iron catalyst to the zeolite, it was clear that the operation of the fixed bed reactor was also negatively affected by the addition of the HZSM-5 powder; consequently, it is suggested that the issue of contact between the catalysts be investigated further with a more appropriate reactor set-up (i.e. a Berty microreactor).

Figure 4.1: Pressure drop over fixed bed microreactor as a function of time on line – *Baseline FT run*

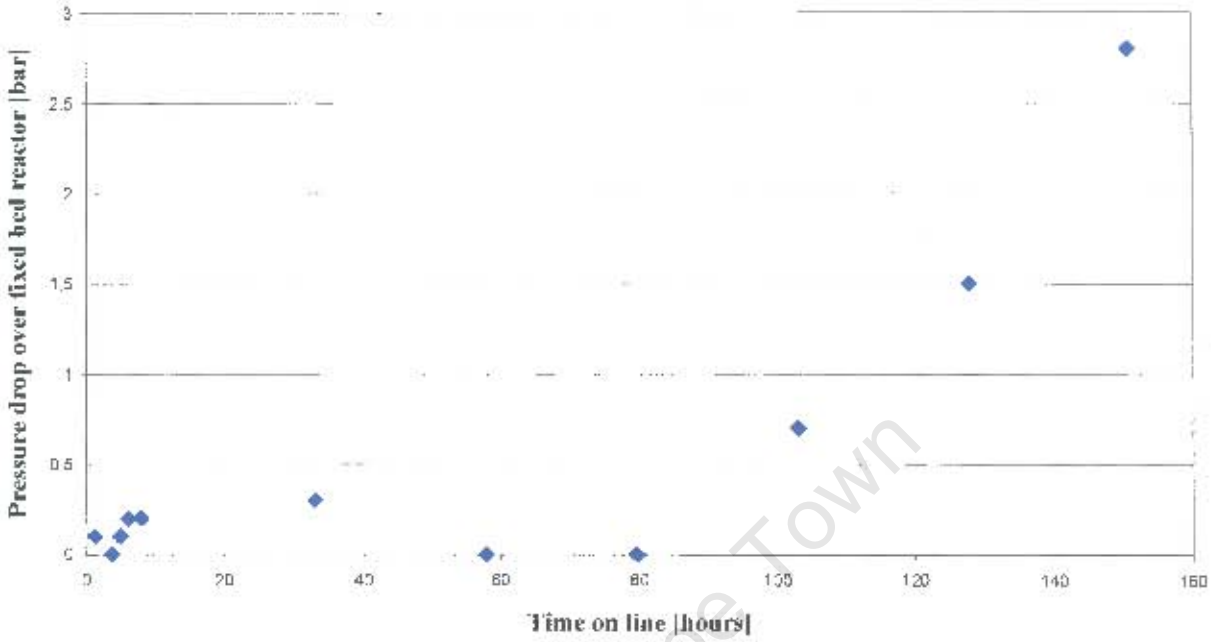


Figure 4.2: Conversion as a function of time on line – *Baseline FT run*

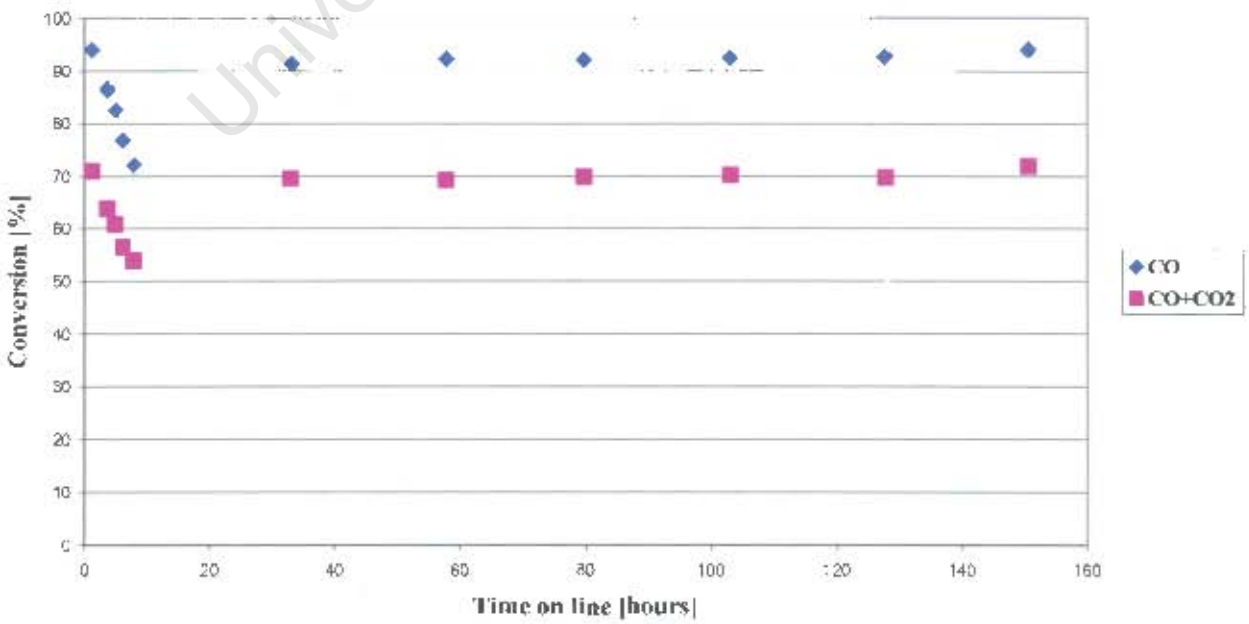


Figure 4.3.1: Methane selectivity as a function of time on line – *Baseline FT run*

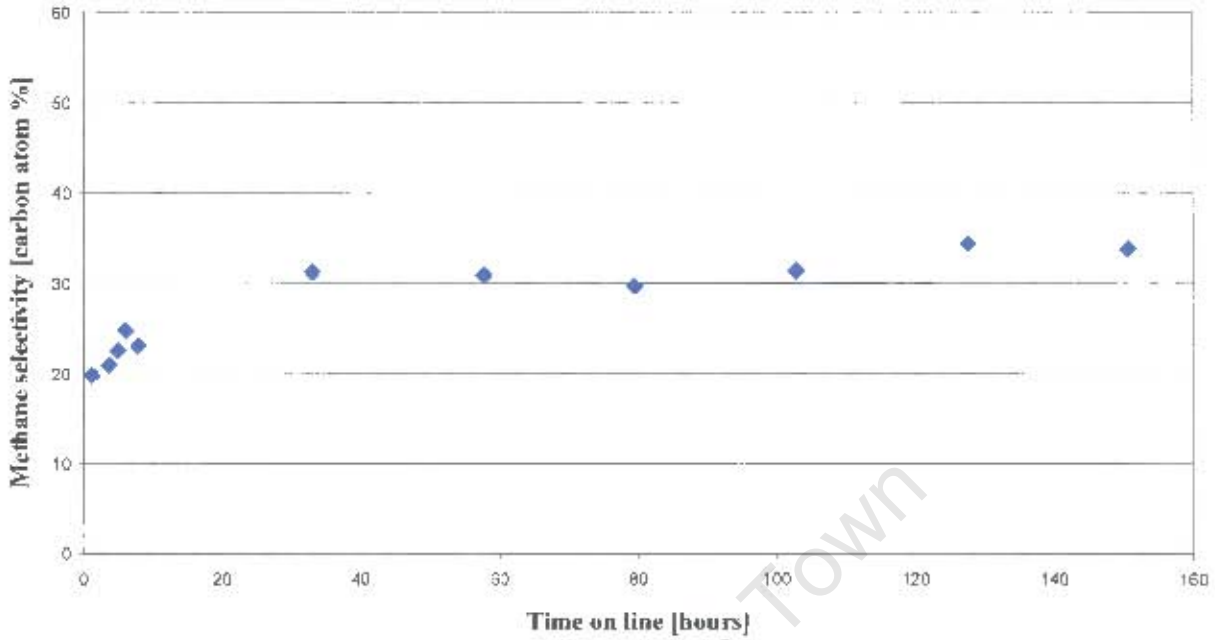


Figure 4.3.2: Olefin / paraffin ratios for the C_2 to C_4 range as a function of time on line – *Baseline FT run*

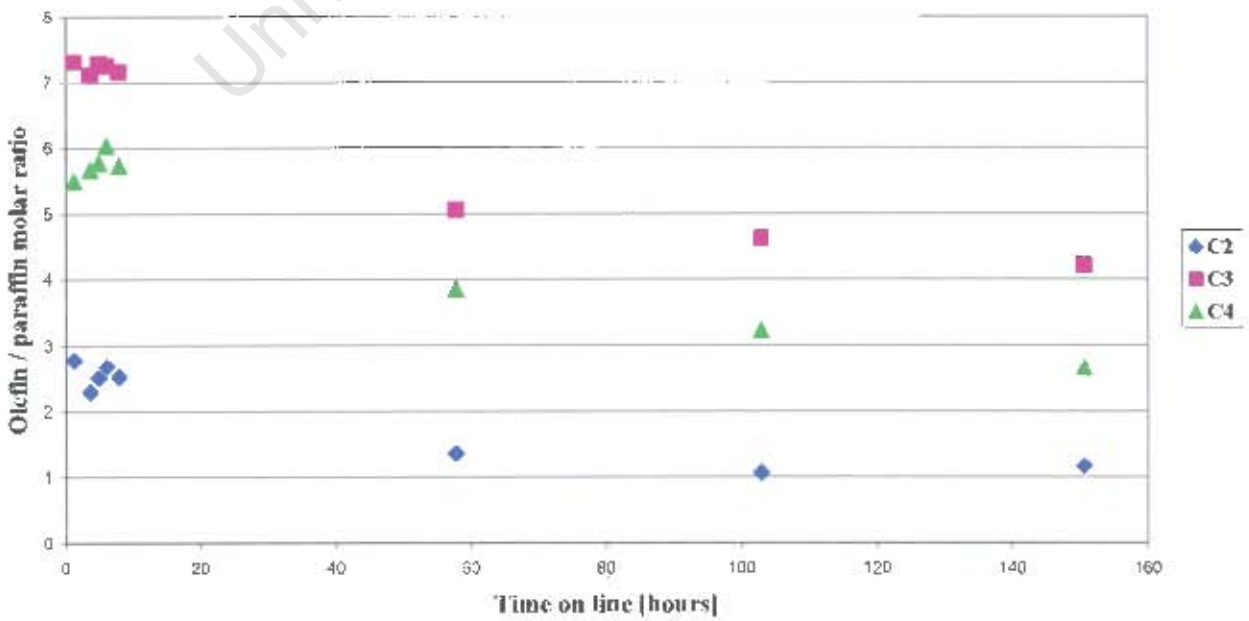


Figure 4.3.3: Hydrogen / carbon ratio of overall product spectrum as a function of time on line – *Baseline FT run*

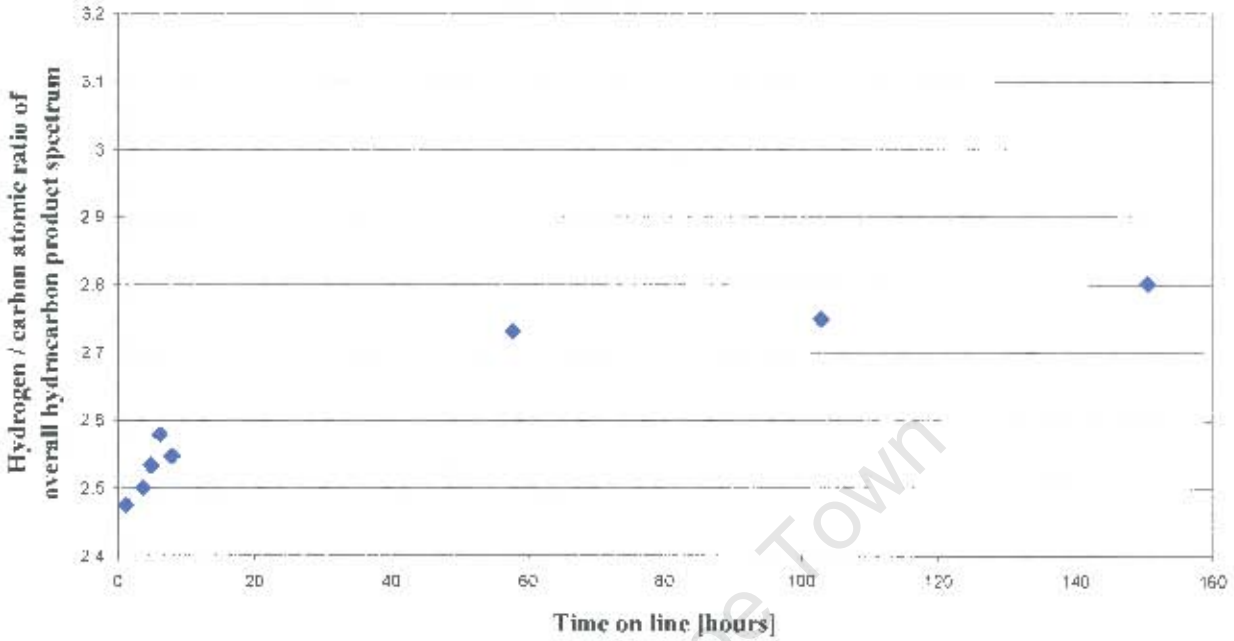


Figure 4.3.4: Hydrogen / carbon ratio of C_{2+} fraction of product spectrum as a function of time on line – *Baseline FT run*

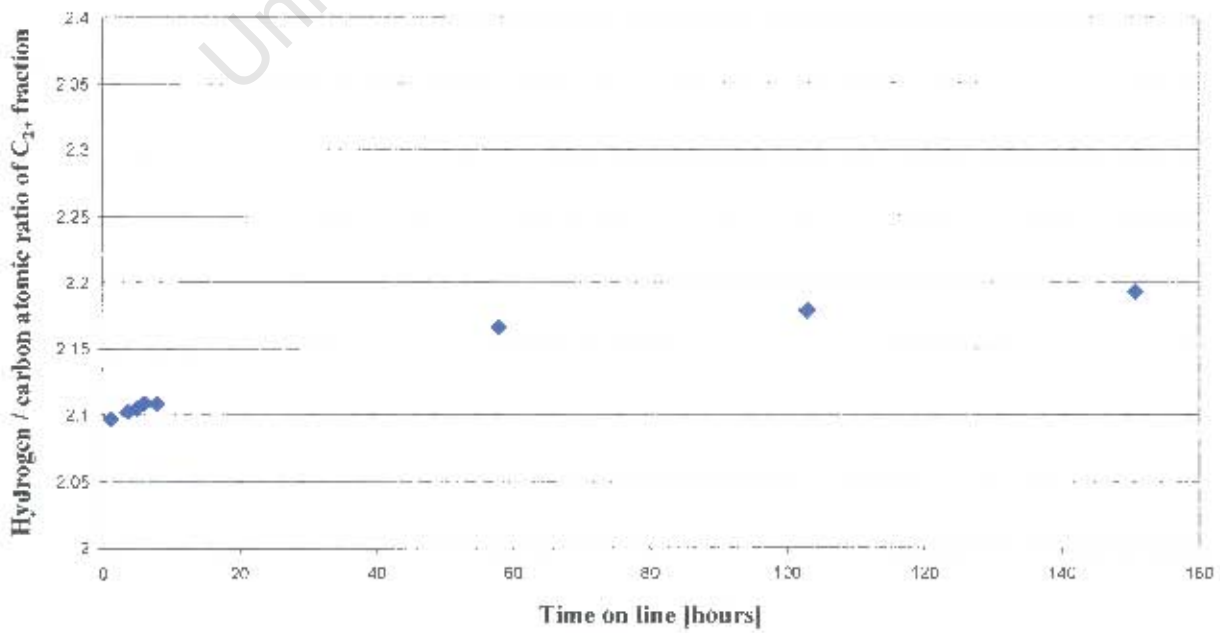


Figure 4.4.1: Schulz-Flory plot of hydrocarbon product distribution – *Baseline FT run, 8 hours on line*

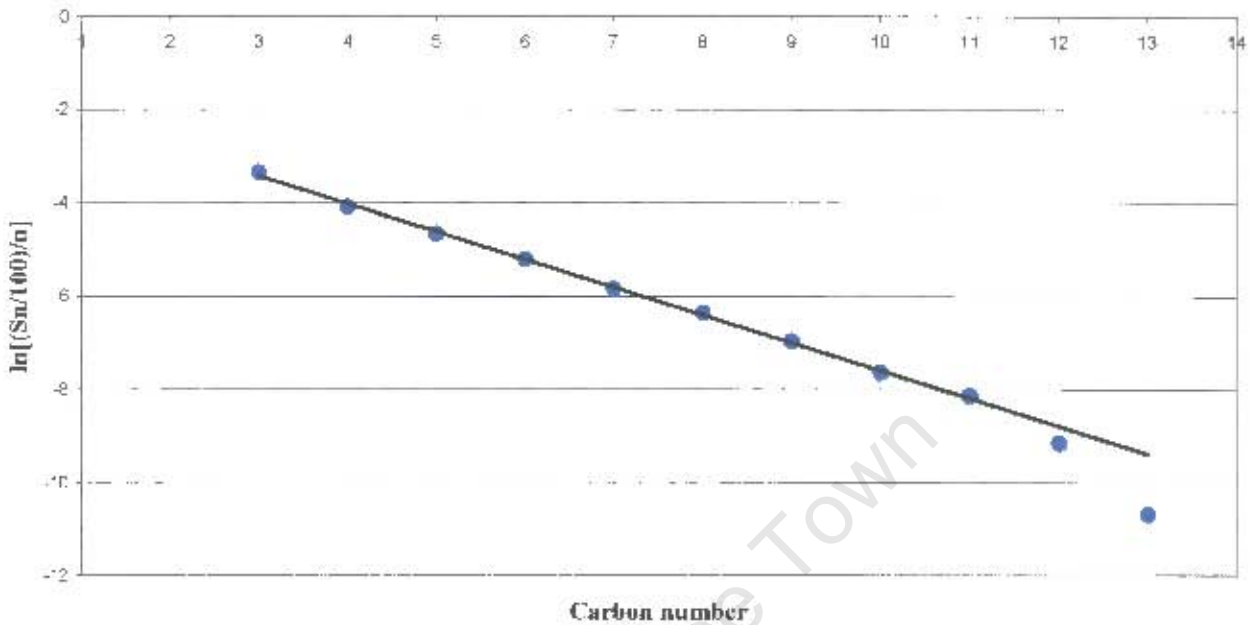


Figure 4.4.2: Schulz-Flory plot of hydrocarbon product distribution – *Baseline FT run, 58 hours on line*

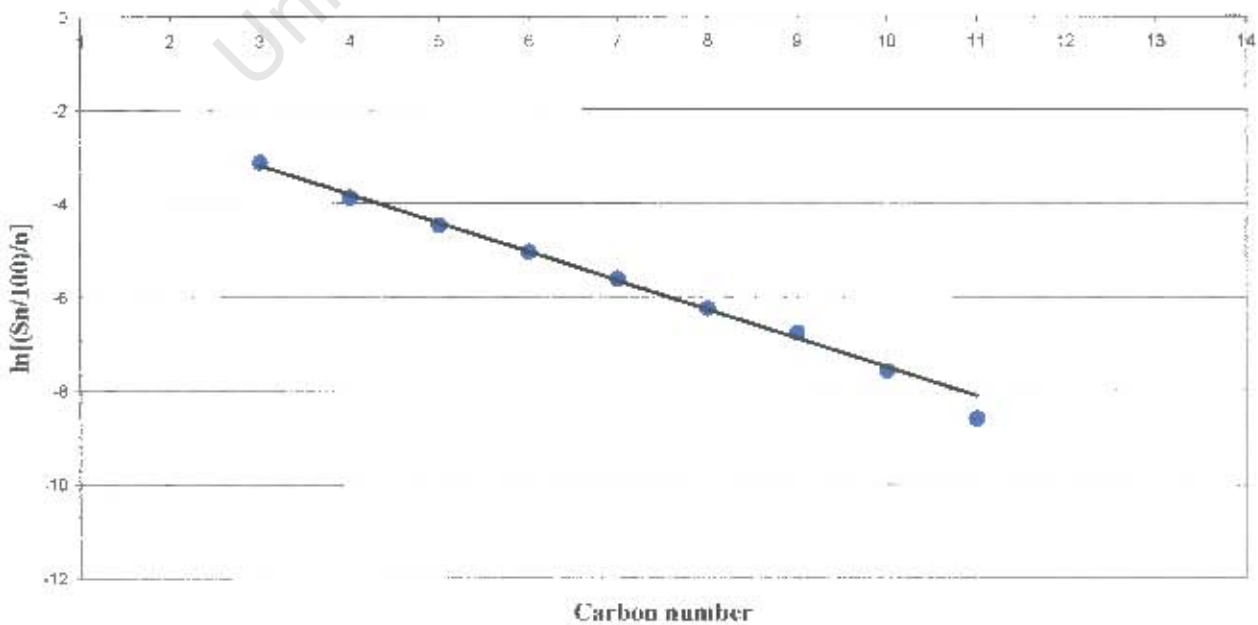


Figure 4.5: Variation in alpha value of hydrocarbon product distribution as a function of time on line – *Baseline FT run*

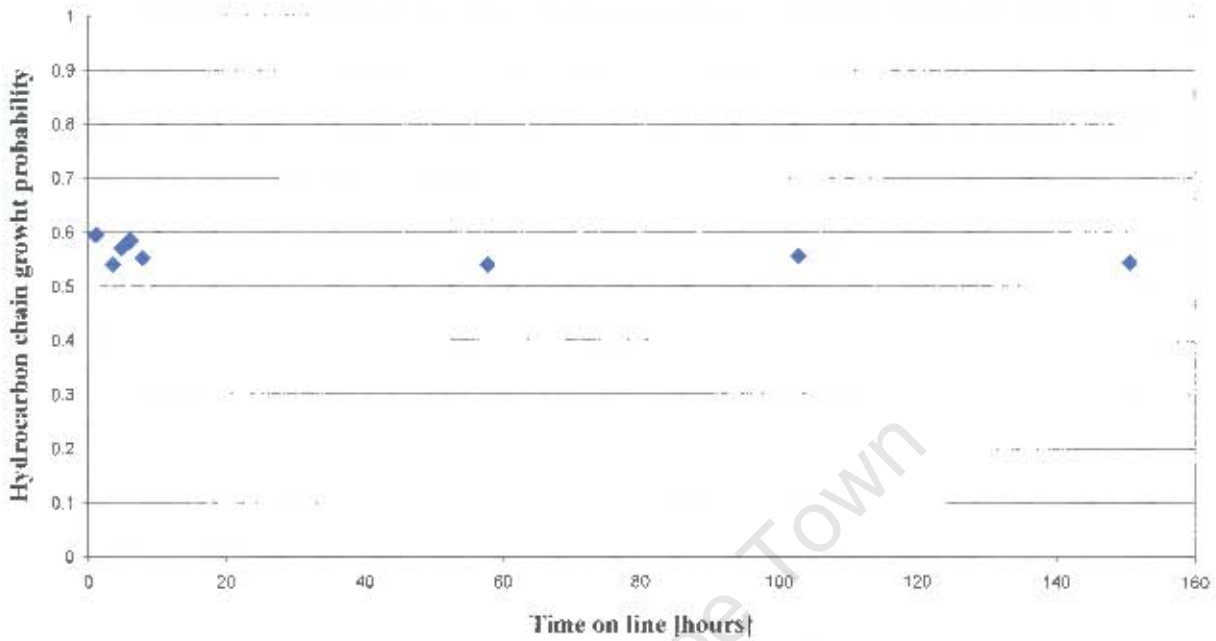


Figure 4.6: Variation in carbon mass balance as a function of time on line – *Baseline FT run*

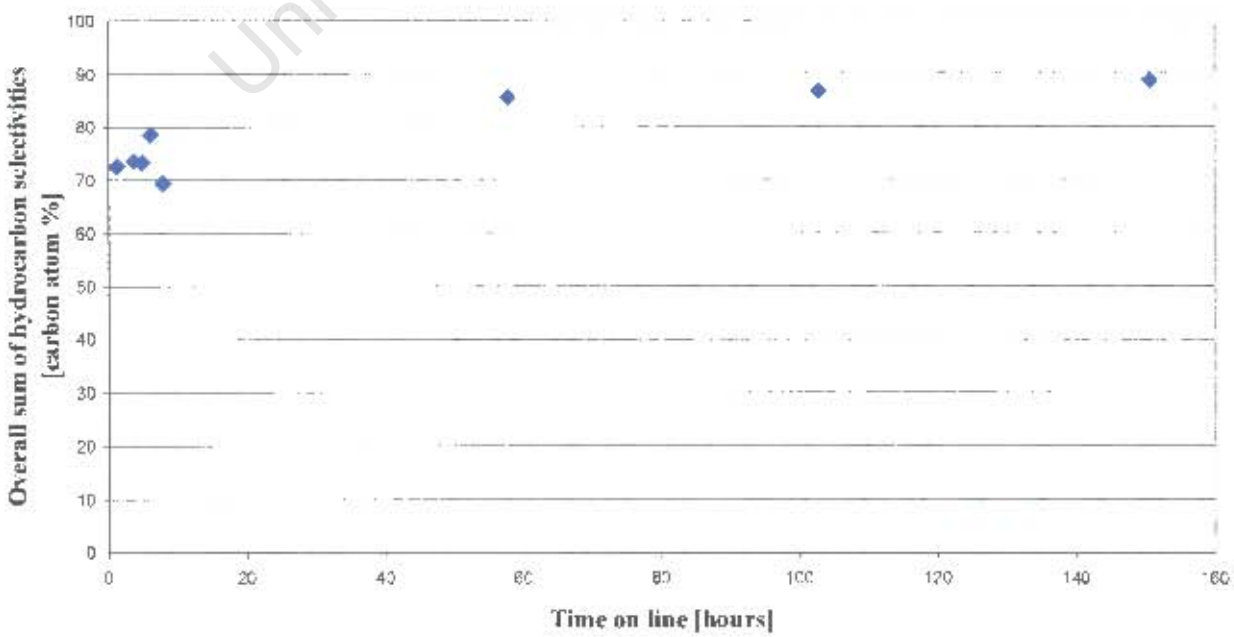


Figure 4.7.1: Hydrocarbon product distribution –
Baseline FT run, 3 hours on line

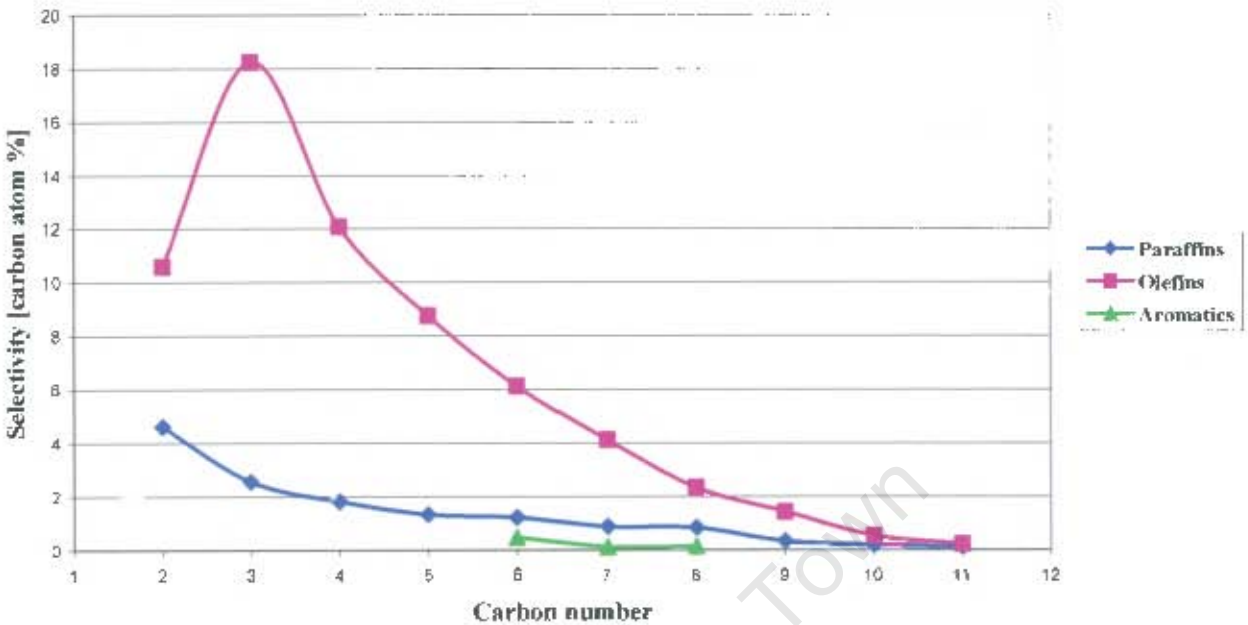


Figure 4.7.2: Hydrocarbon product distribution –
Baseline FT run, 58 hours on line

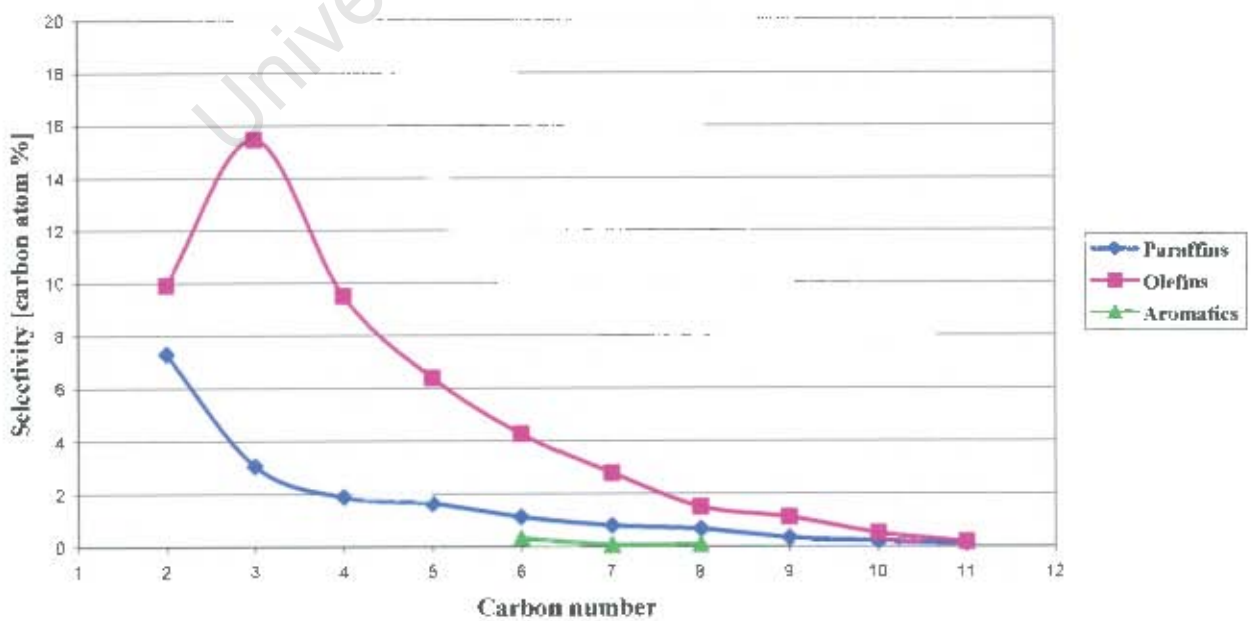


Figure 4.7.3: Hydrocarbon product distribution –
Baseline FT run, 151 hours on line

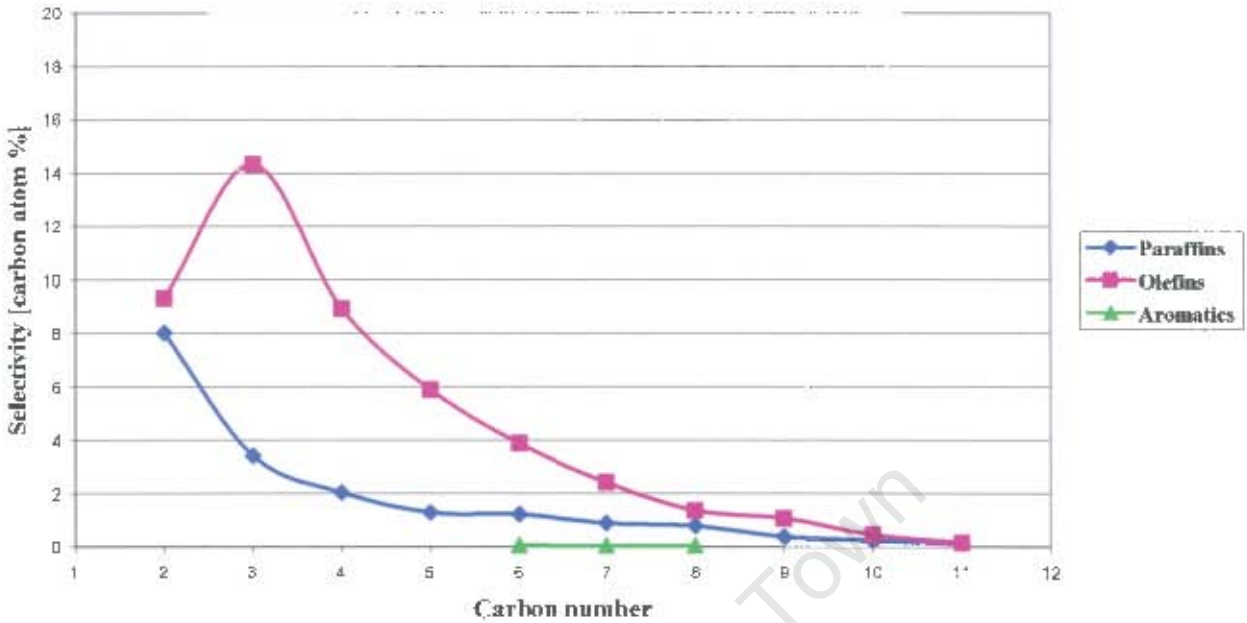


Figure 4.8: Pressure drop over fixed bed microreactor as a function of time on line –
Bifunctional process, physical admixture of catalysts

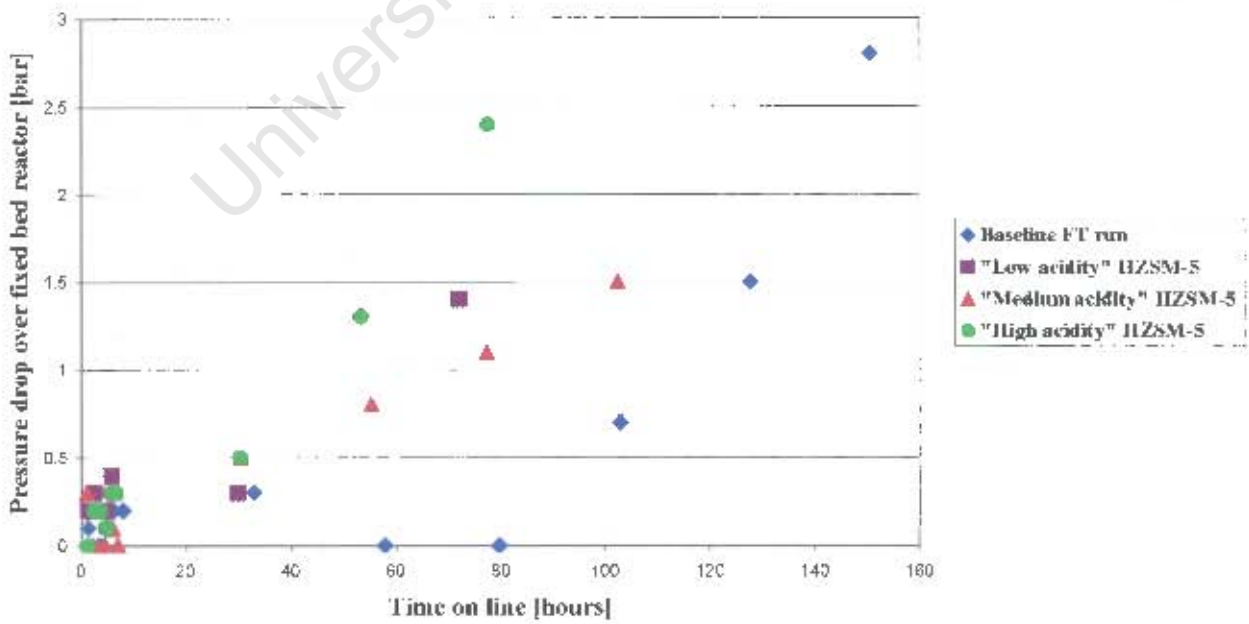


Figure 4.9.1: CO conversion as a function of time on line –
Bifunctional process, physical admixture of catalysts

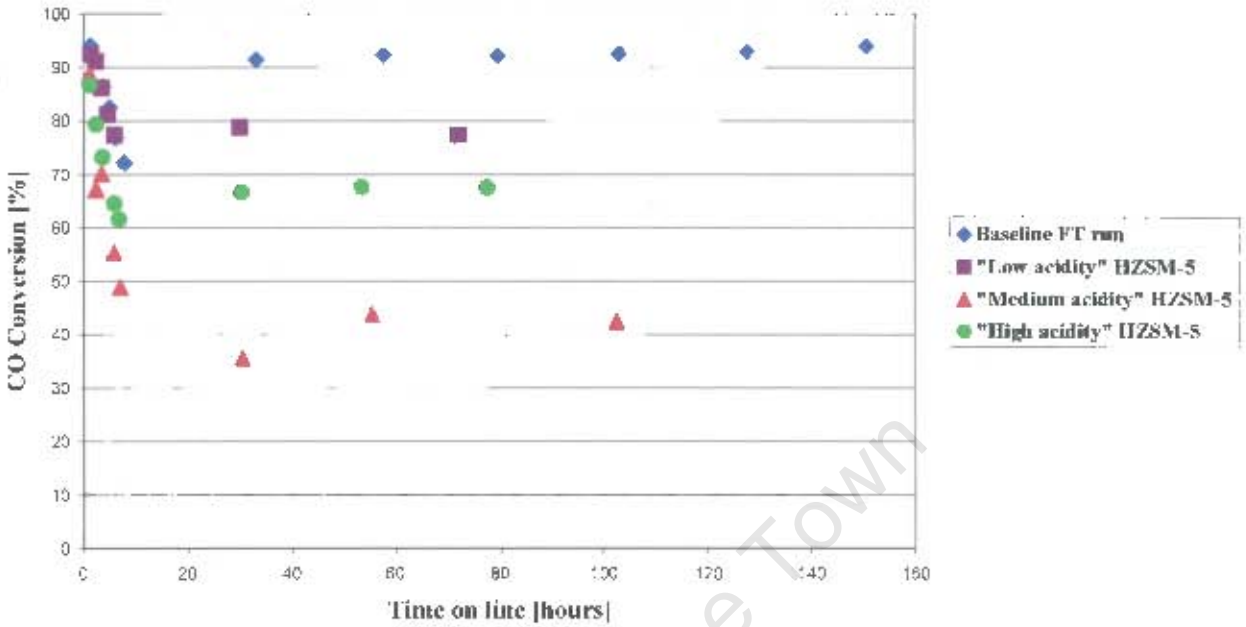


Figure 4.9.2: ($CO+CO_2$) conversion as a function of time on line –
Bifunctional process, physical admixture of catalysts

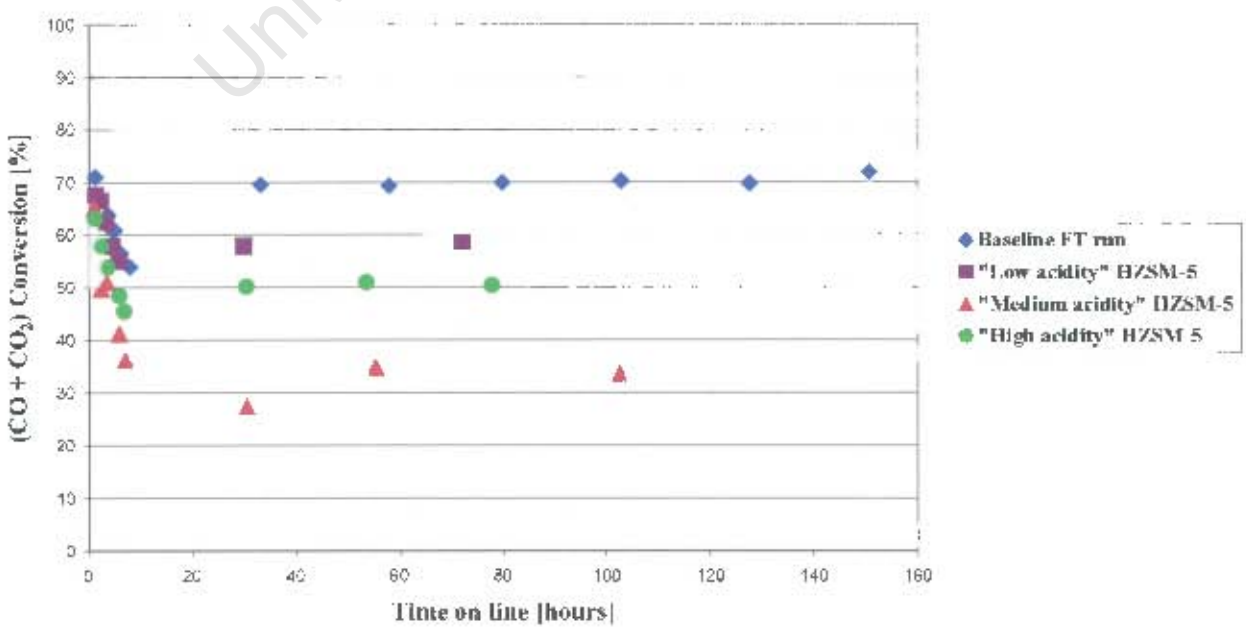


Figure 4.10: Variation in carbon mass balance as a function of time on line –
Bifunctional process, physical admixture of catalysts

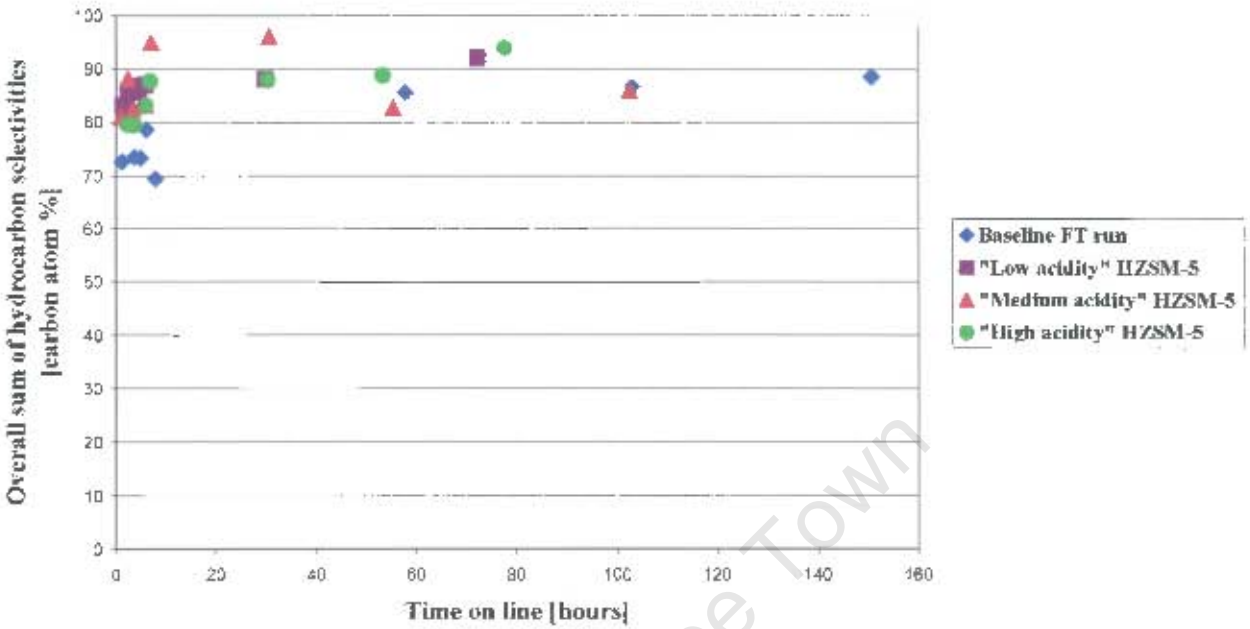


Figure 4.11.1: Methane selectivity as a function of time on line –
Bifunctional process, physical admixture of catalysts

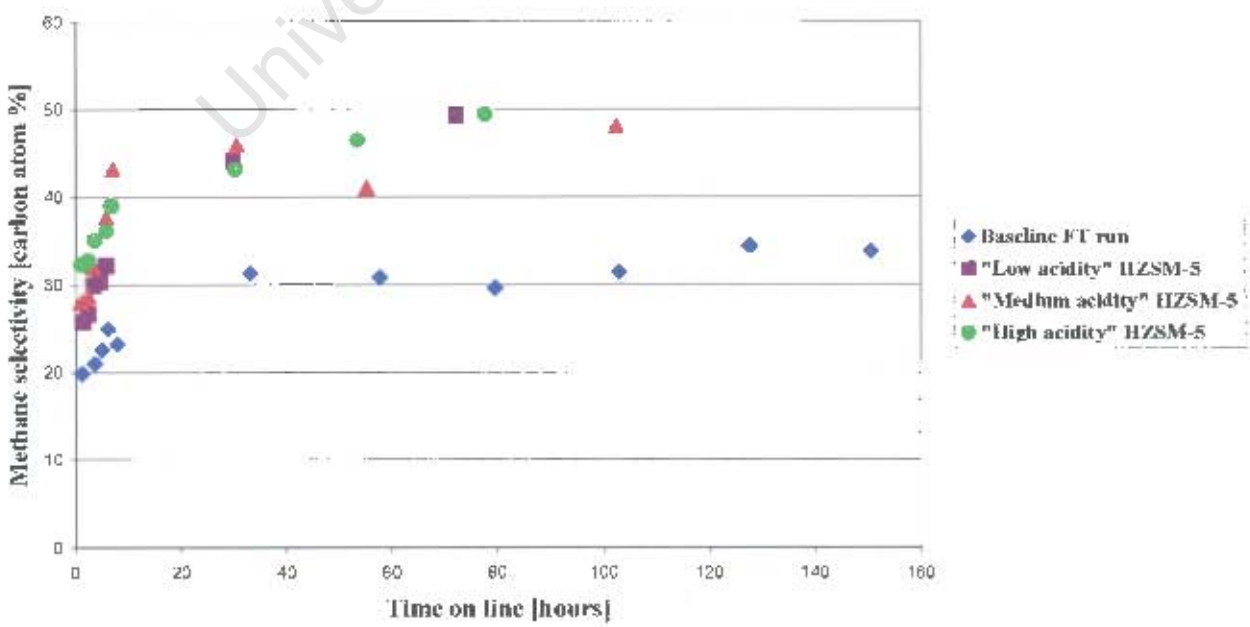


Figure 4.11.2: Hydrogen / carbon ratio of overall product spectrum as a function of time on line – *Bifunctional process, physical admixture of catalysts*

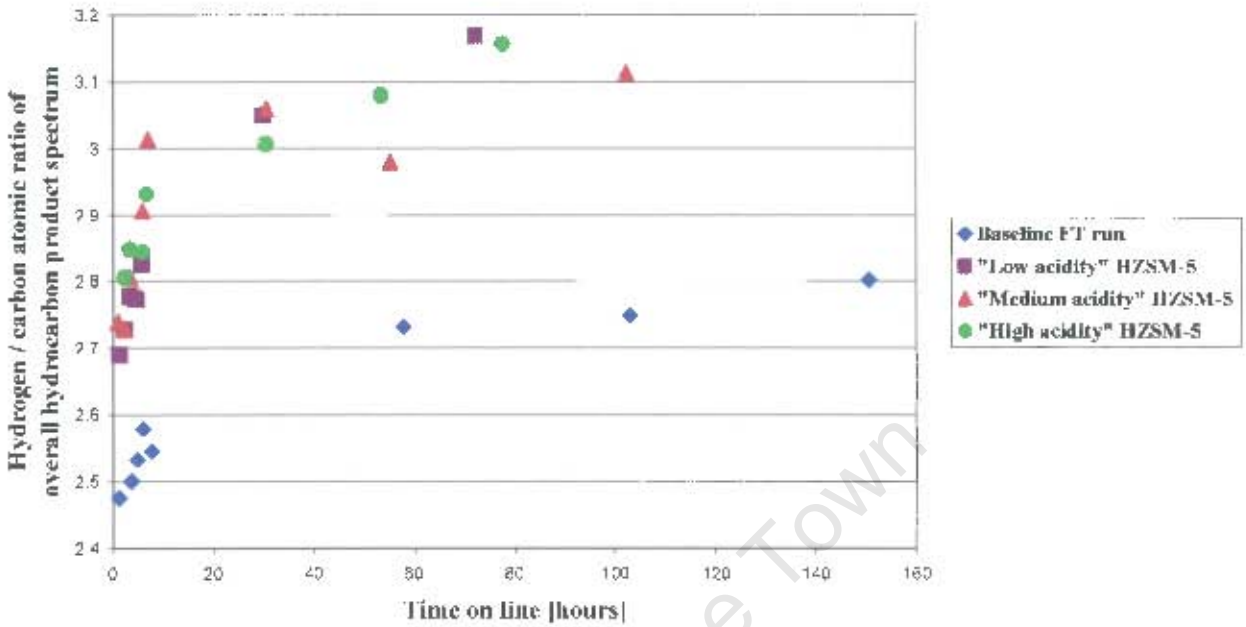


Figure 4.11.3: Hydrogen / carbon ratio of C_{2+} fraction of product spectrum as a function of time on line – *Bifunctional process, physical admixture of catalysts*

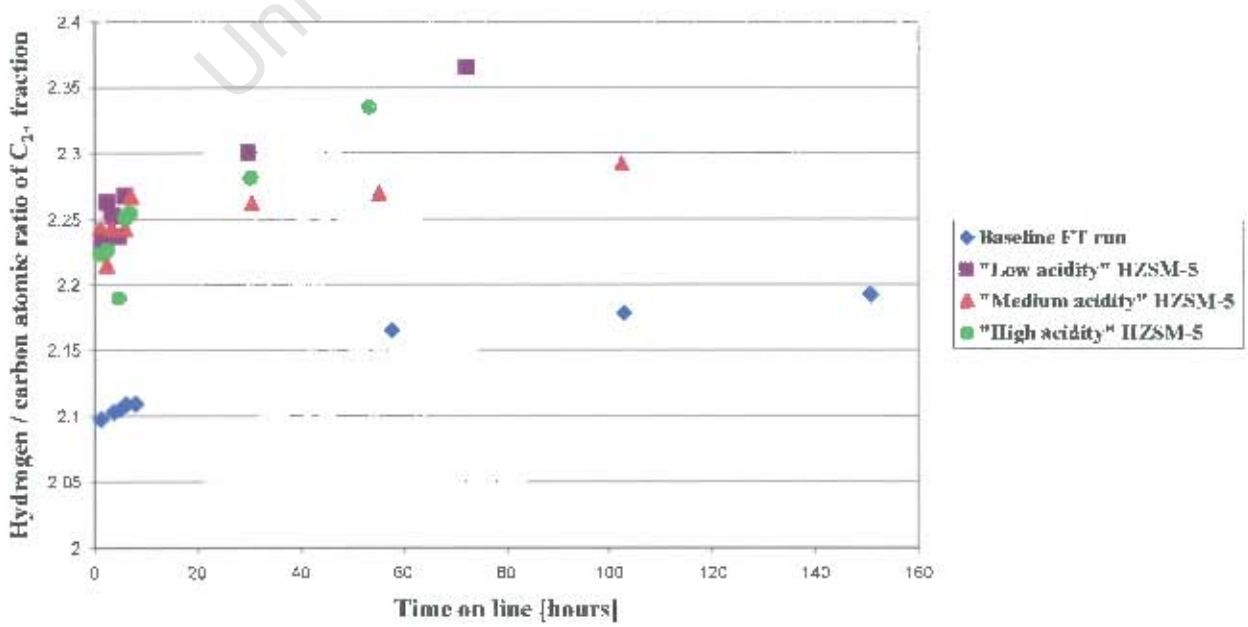


Figure 4.12.1: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZM-5, physical admixture of catalysts, 3 hours on line

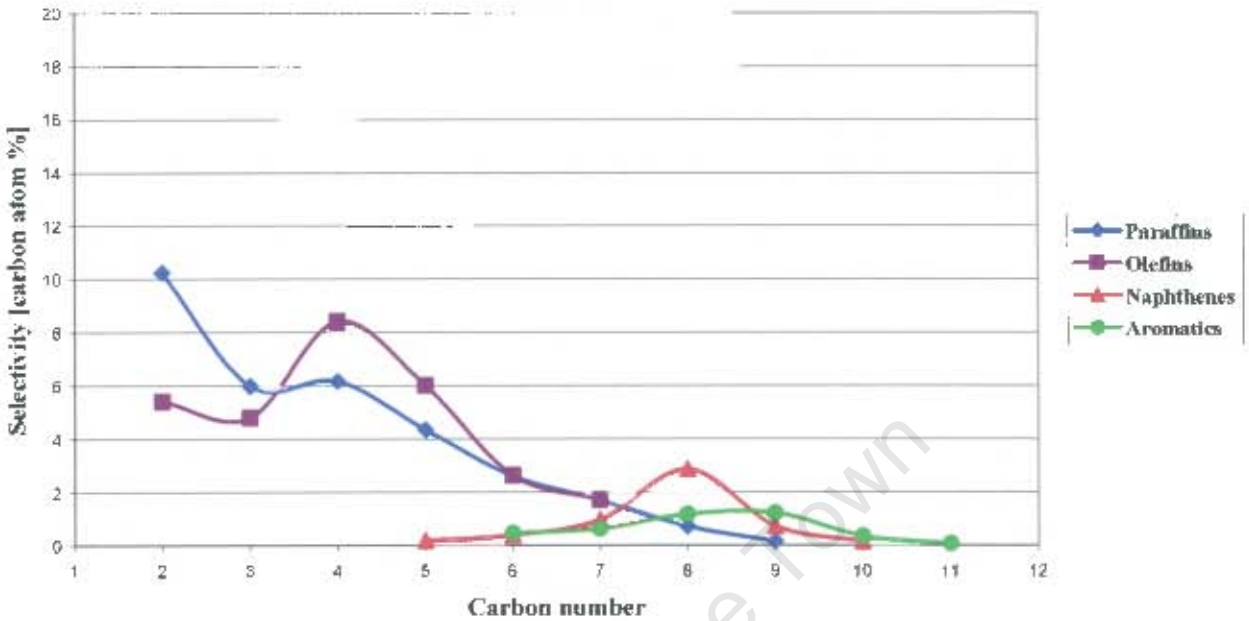


Figure 4.12.2: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZM-5, physical admixture of catalysts, 72 hours on line

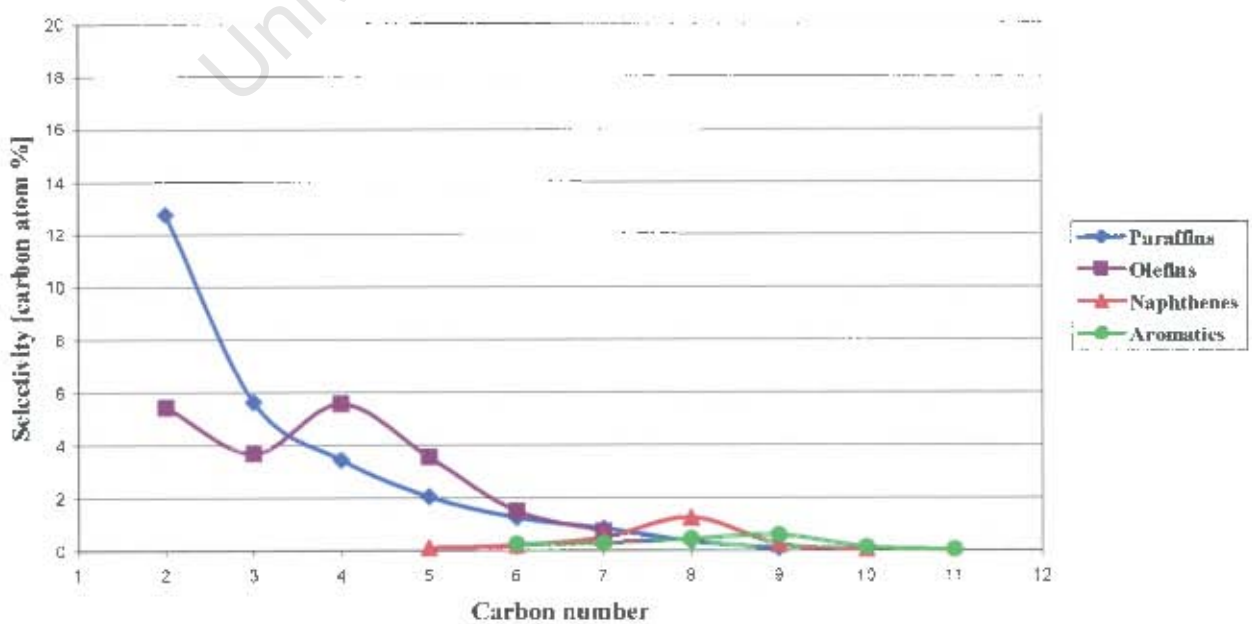


Figure 4.13.1: Hydrocarbon product distribution –
Bifunctional process, "medium acidity" HZM-5, physical admixture of catalysts, 3 hours on line

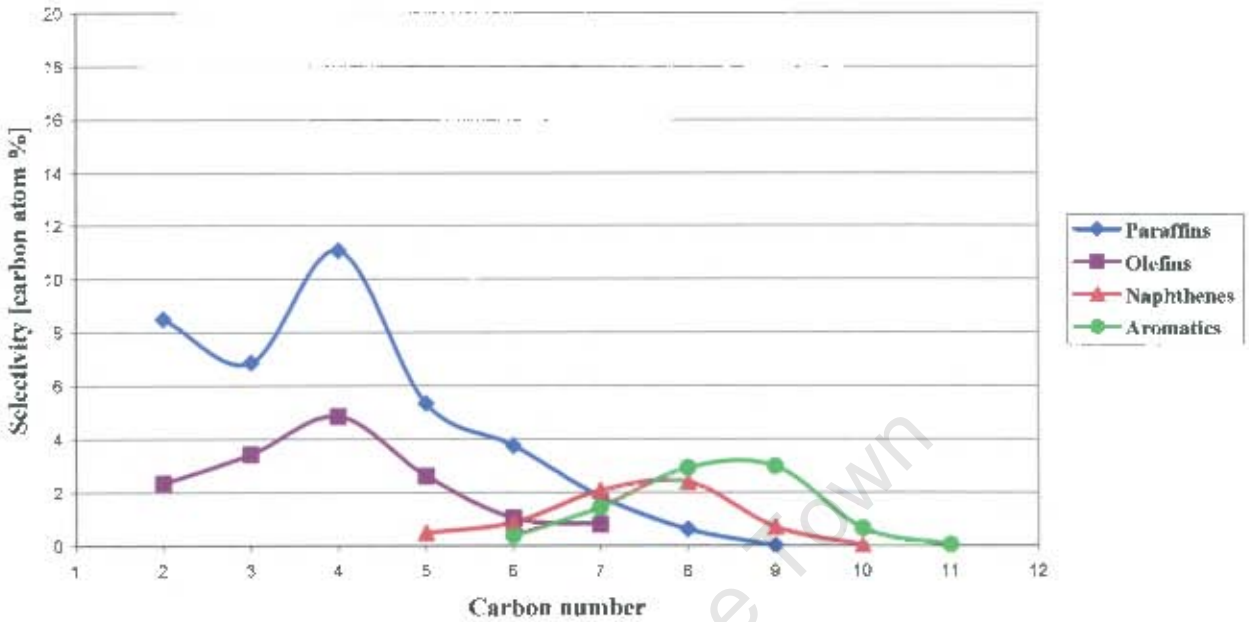


Figure 4.13.2: Hydrocarbon product distribution –
Bifunctional process, "medium acidity" HZM-5, physical admixture of catalysts, 102 hours on line

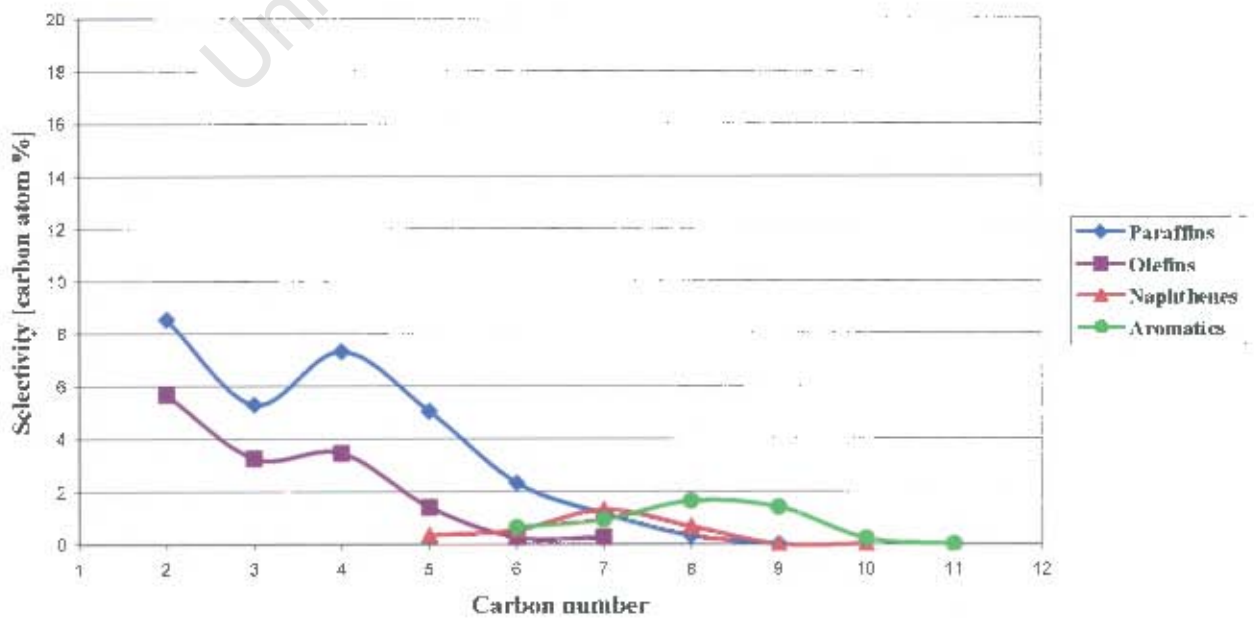


Figure 4.14.1: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZM-5, physical admixture of catalysts, 2 hours on line

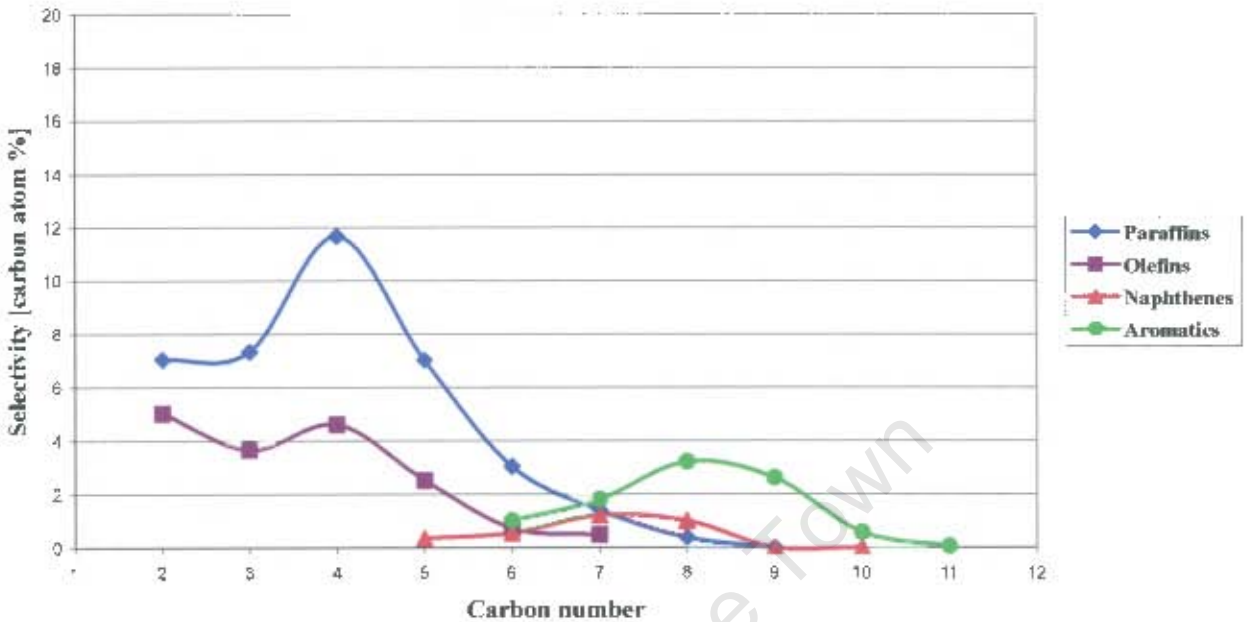


Figure 4.14.2: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZM-5, physical admixture of catalysts, 78 hours on line

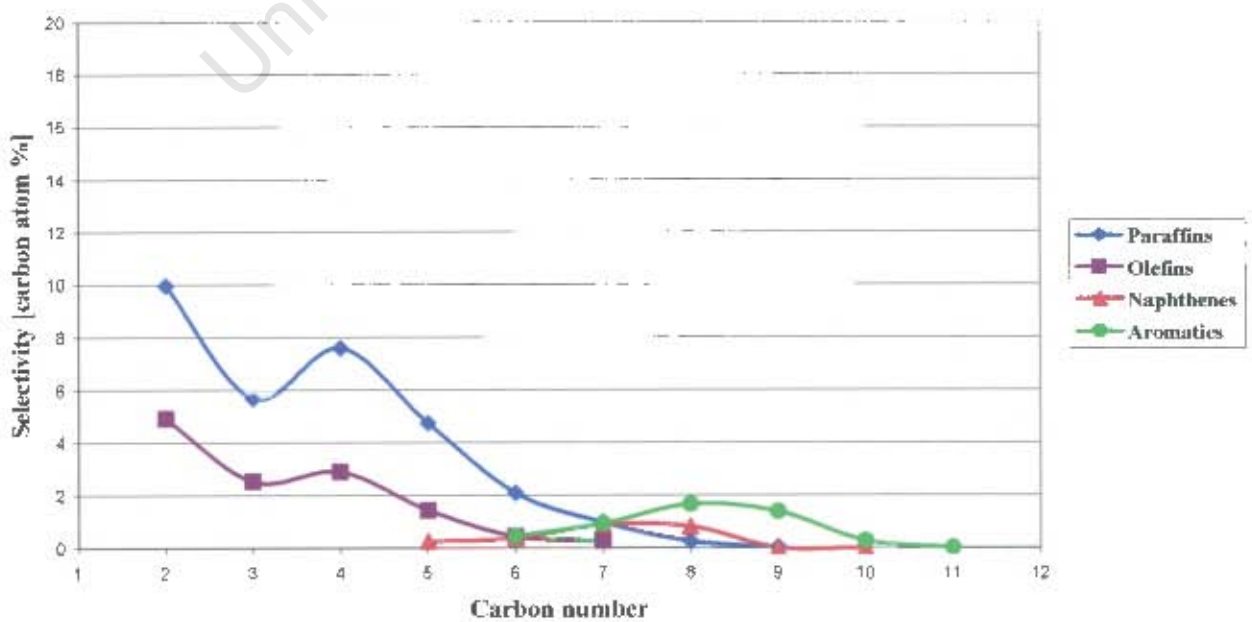


Figure 4.15: Overall carbon number distribution after 2 to 3 hours of synthesis – *Bifunctional process, physical admixture of catalysts*

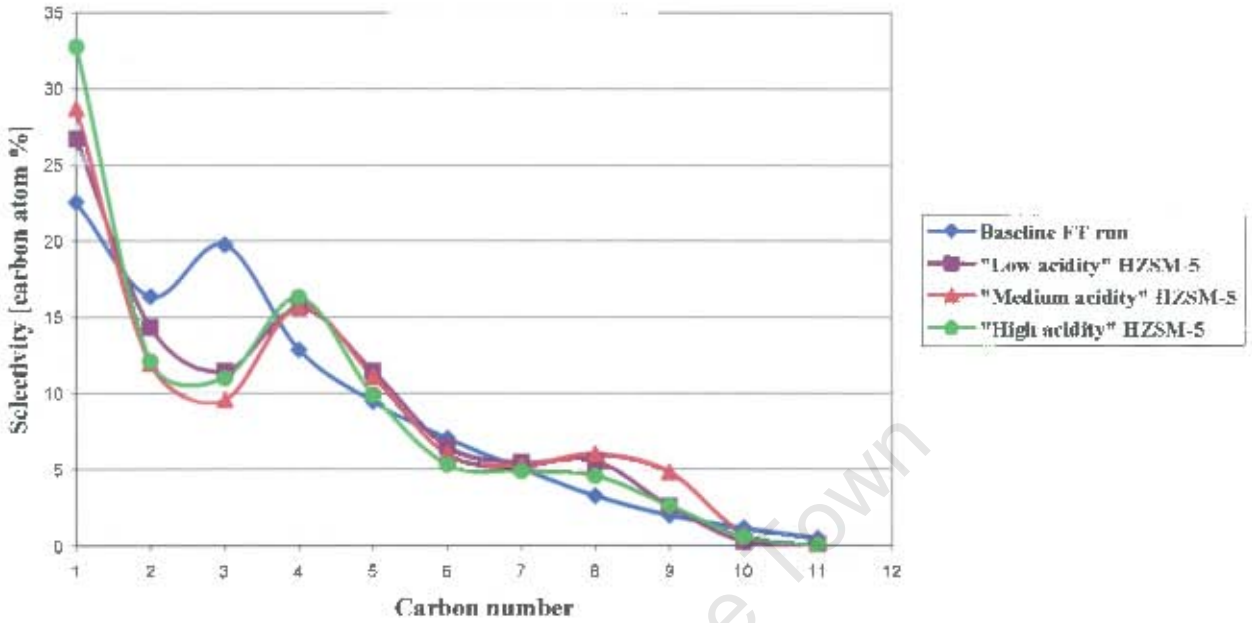


Figure 4.16: Pressure drop over fixed bed microreactor as a function of time on line – *Bifunctional process, dual bed arrangement*

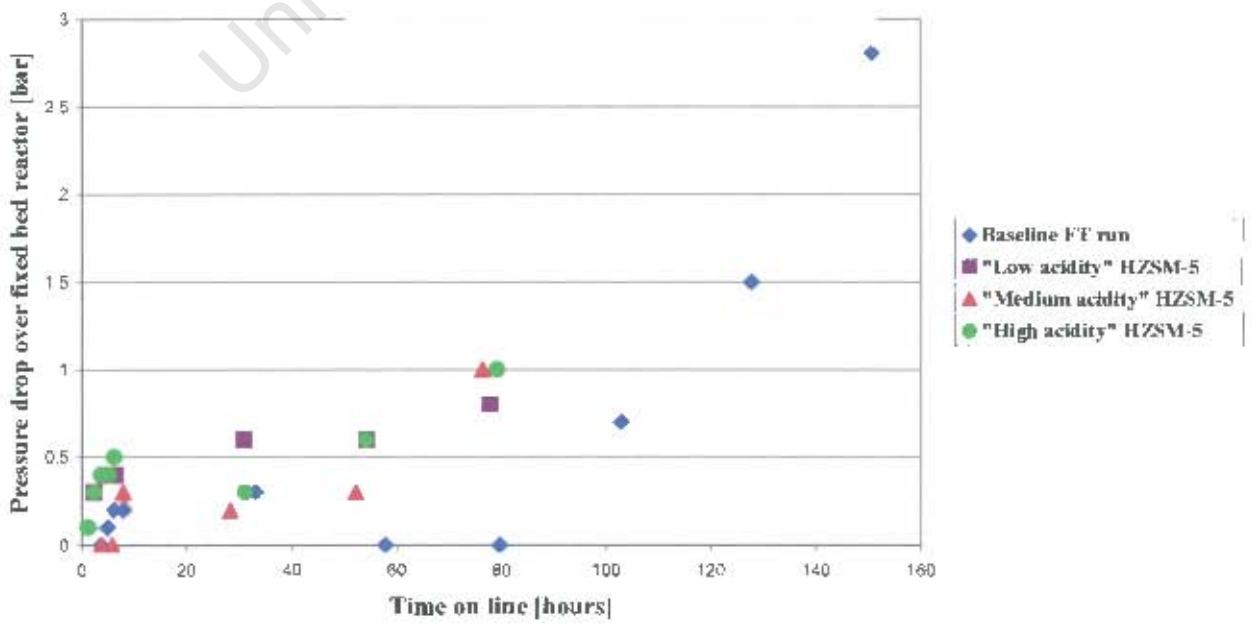


Figure 4.17.1: CO conversion as a function of time on line –
Bifunctional process, dual bed arrangement

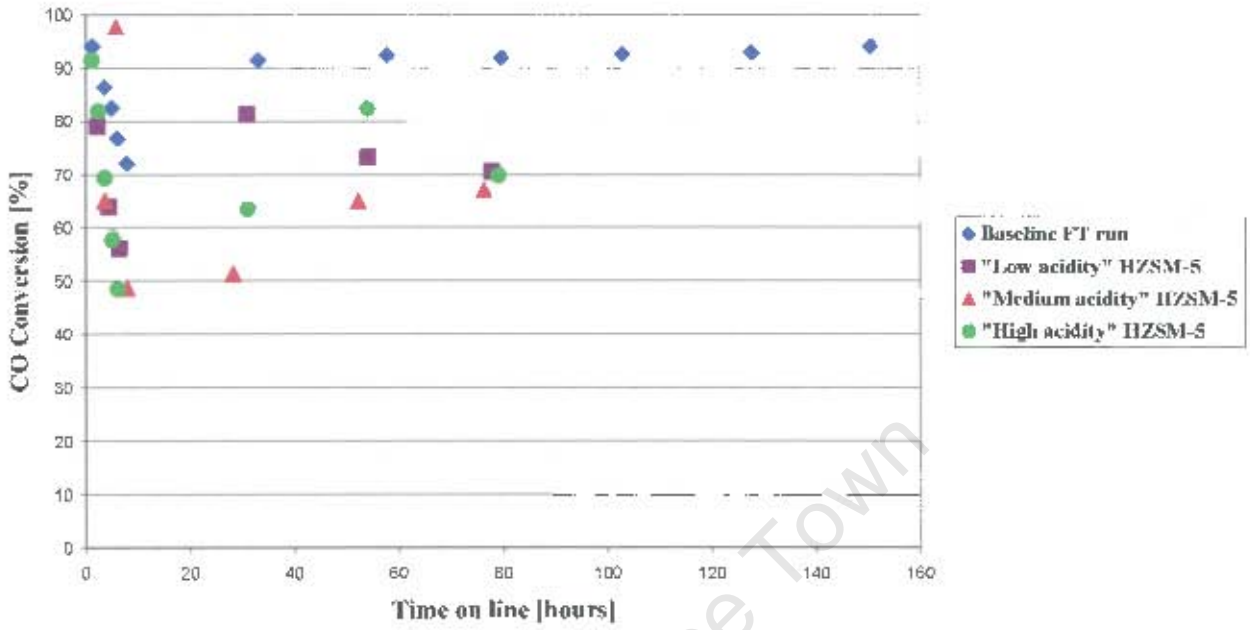


Figure 4.17.2: ($CO+CO_2$) conversion as a function of time on line –
Bifunctional process, dual bed arrangement

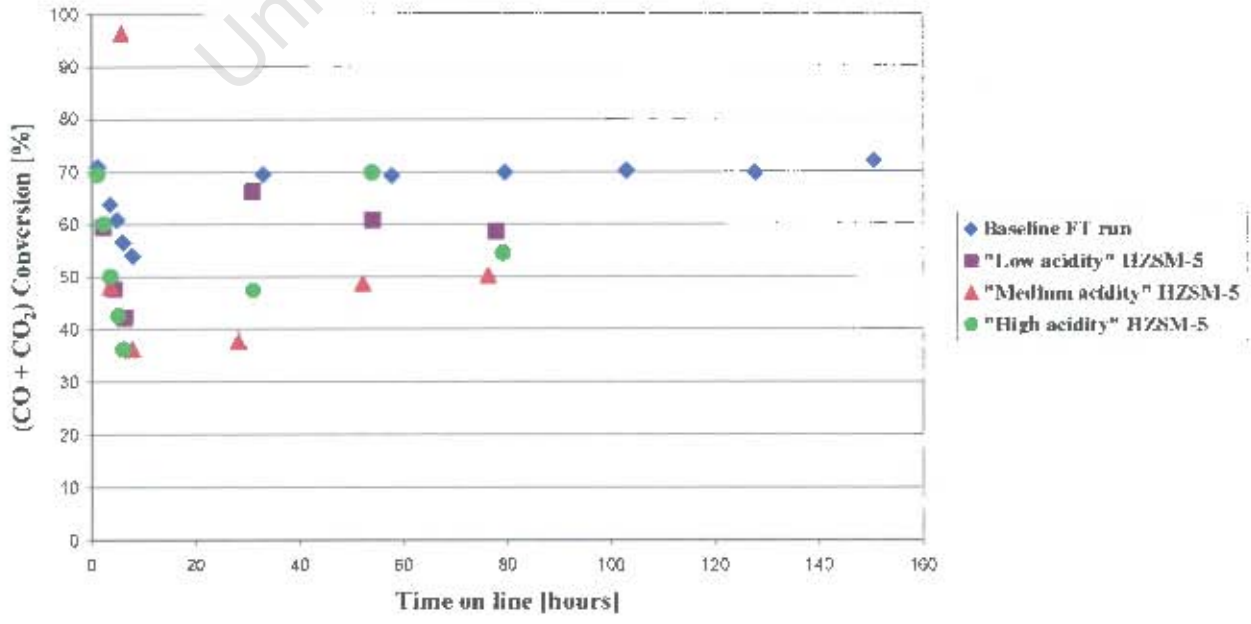


Figure 4.18: Methane selectivity as a function of time on line –
Bifunctional process, dual bed arrangement

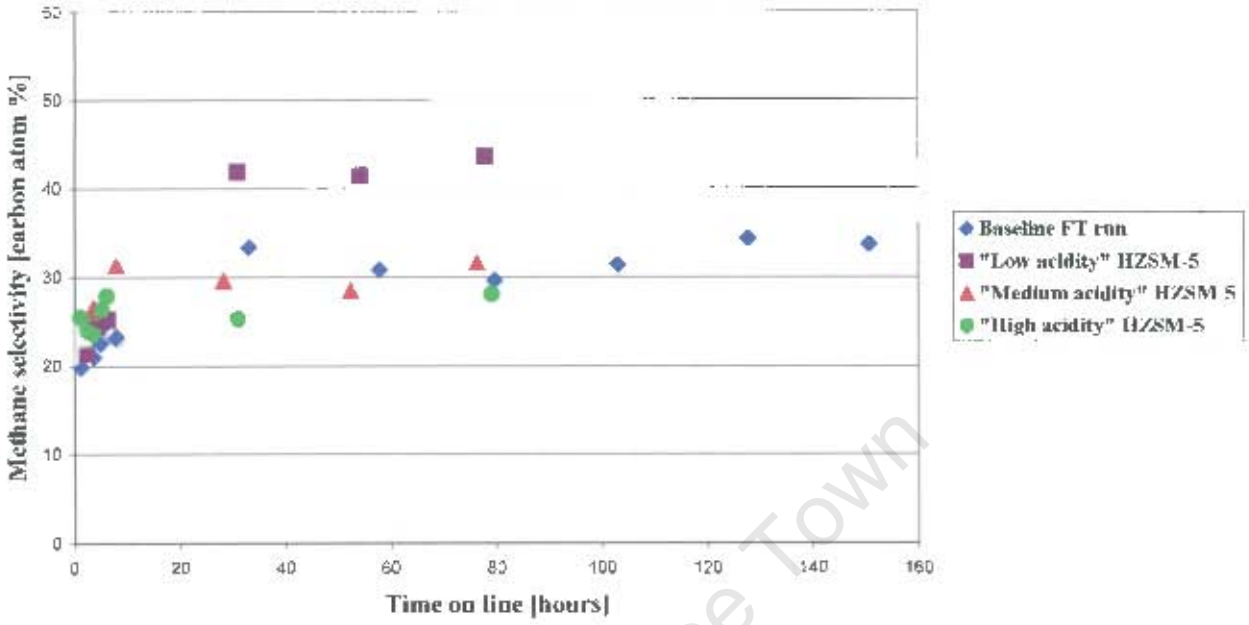


Figure 4.19.1: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZM-5,
dual bed arrangement, 4 hours on line

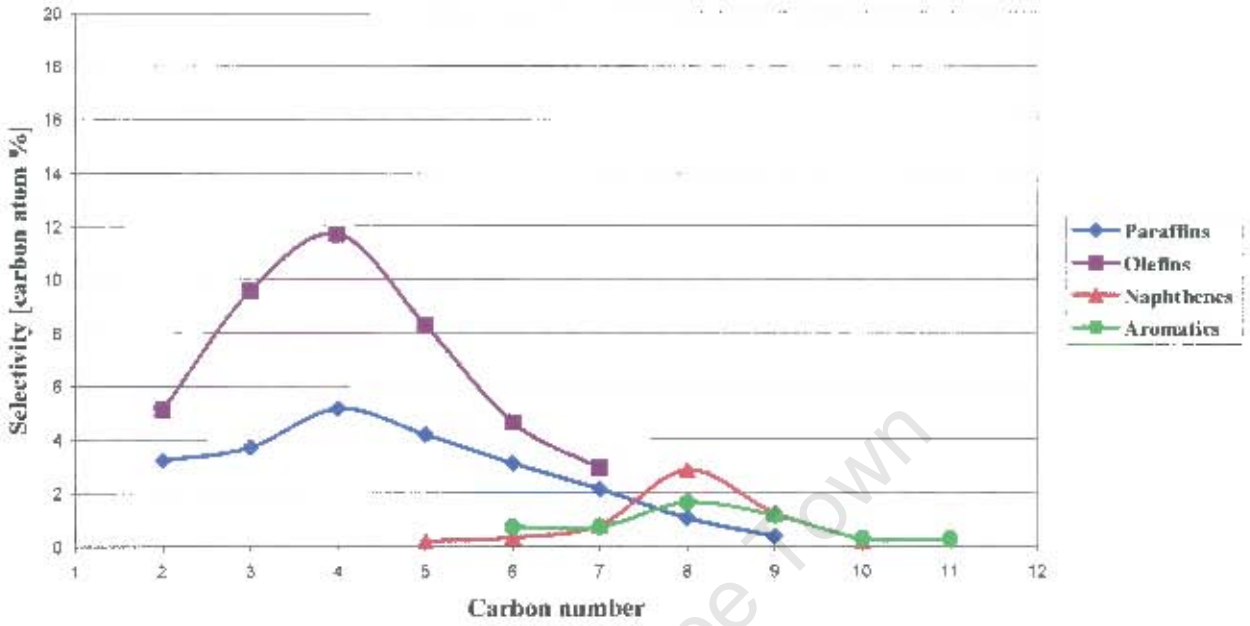


Figure 4.19.2: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZM-5,
dual bed arrangement, 78 hours on line

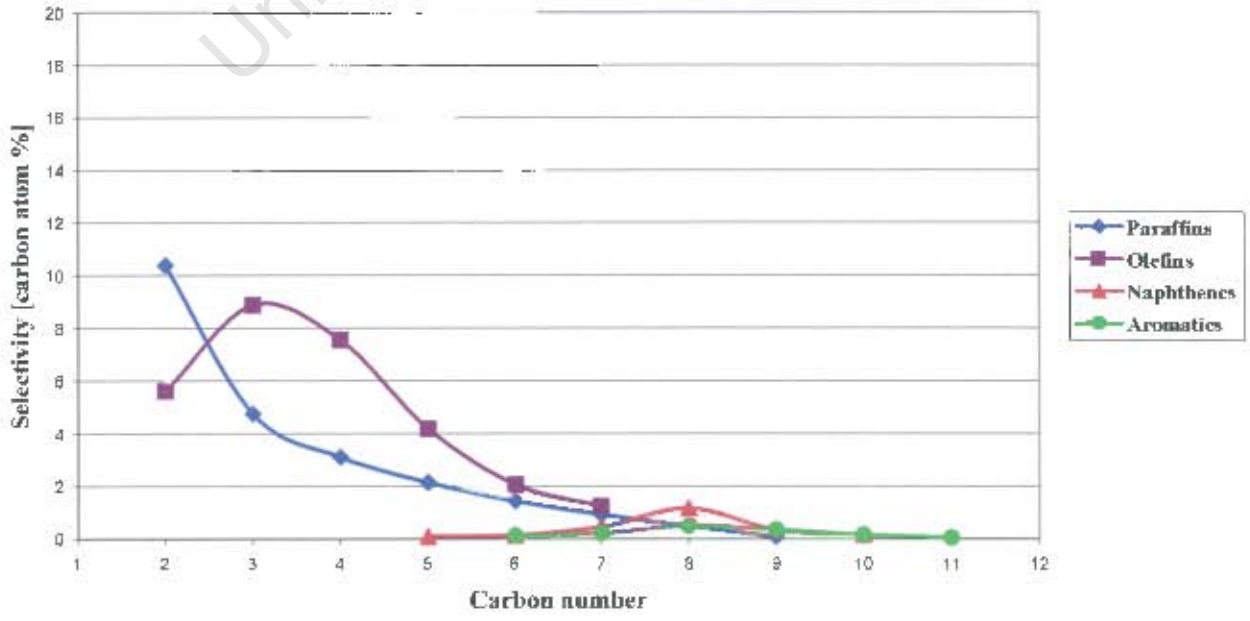


Figure 4.20.1: Hydrocarbon product distribution – *Bifunctional process, "medium acidity" HZM-5, dual bed arrangement, 4 hours on line*

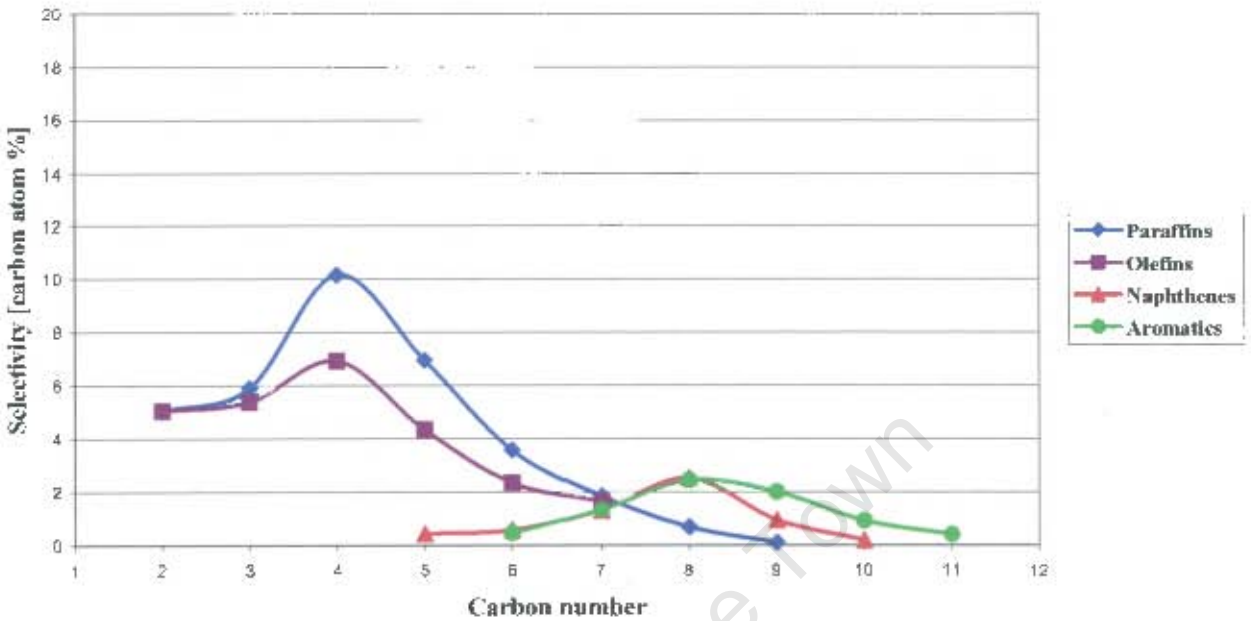


Figure 4.20.2: Hydrocarbon product distribution – *Bifunctional process, "medium acidity" HZM-5, dual bed arrangement, 76 hours on line*

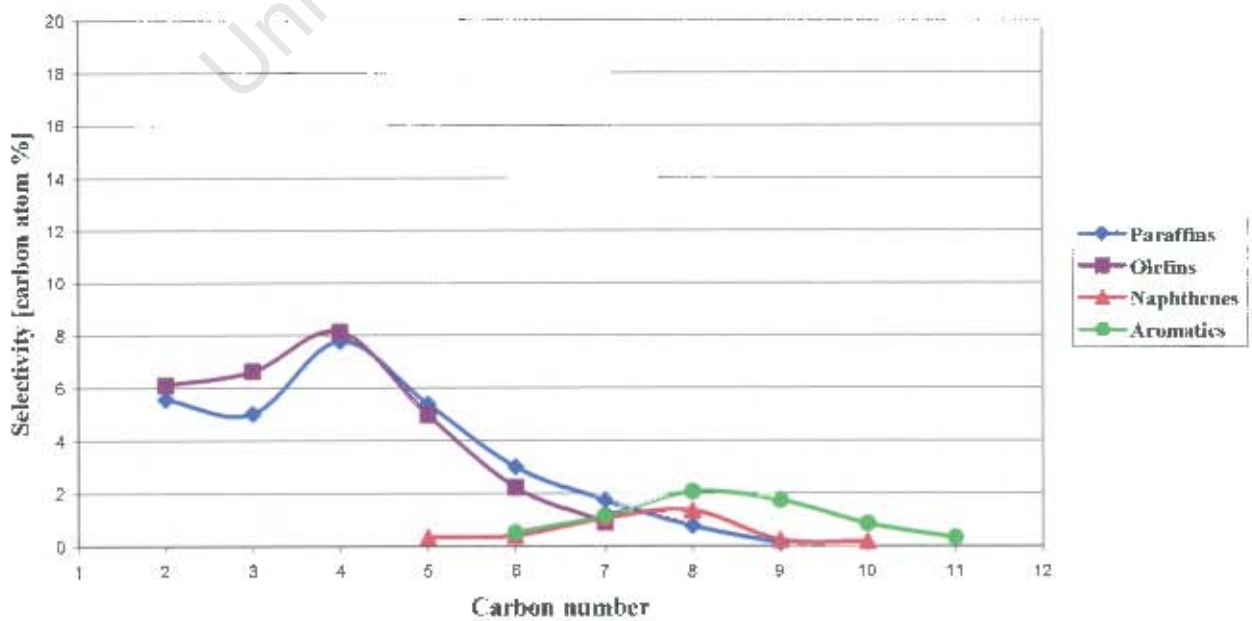


Figure 4.21.1: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZM-5,
dual bed arrangement, 2 hours on line

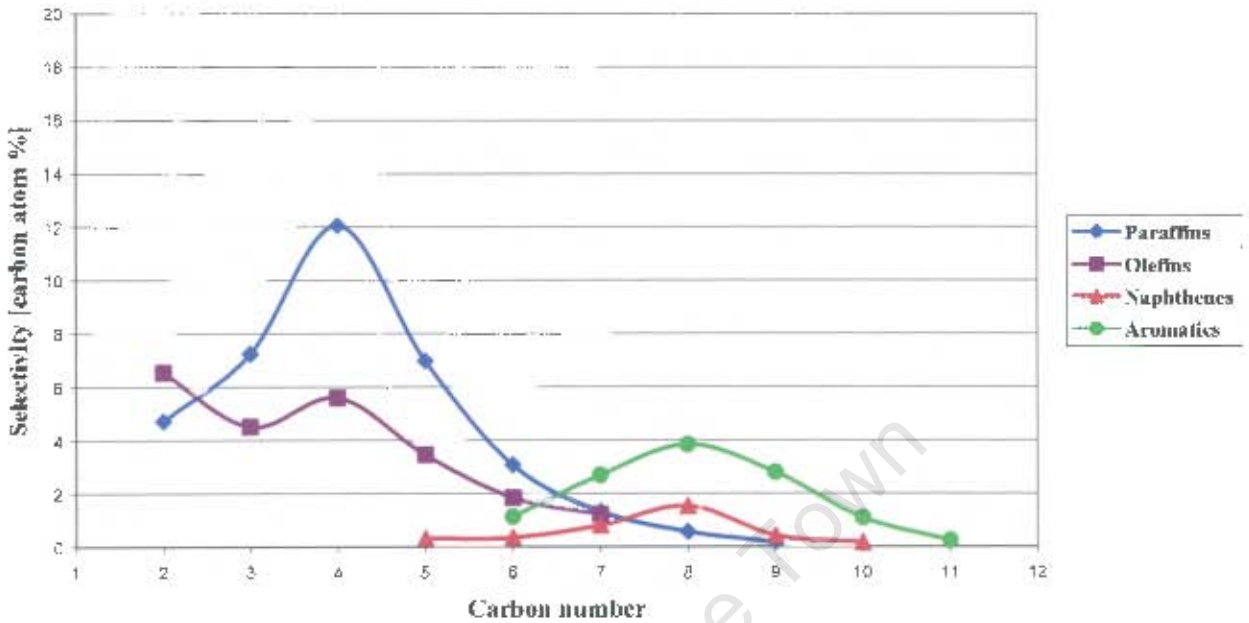
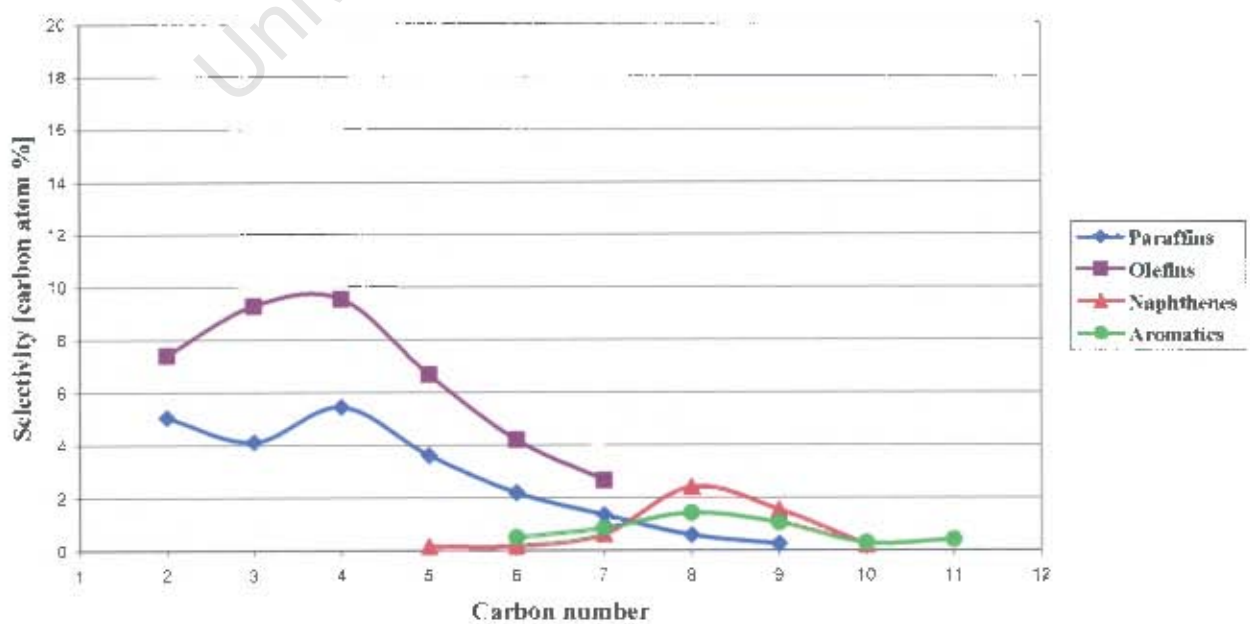


Figure 4.21.2: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZM-5,
dual bed arrangement, 79 hours on line



CHAPTER 5

FOLLOW-UP EXPERIMENTAL STUDY IN A BERTY MICROREACTOR

The fixed bed microreactor used for the preliminary experimental investigation was not an optimal reactor set-up. Carbon deposition in the iron catalyst bed caused operating problems and inadequate dissipation of the reaction heat may have contributed to the poor process performance. Consequently, quantitative information about HZSM-5 lifetime and the effect of zeolite addition on the HTFT product spectrum could not be obtained. It was therefore decided to rather study the bifunctional process further in a Berty microreactor, since carbon deposition on the iron catalyst would not impact as severely on the operation of this type of reactor. In addition, the high internal gas recycle rate of the Berty reactor ensures an even distribution of temperature in the catalyst bed.

By using a Berty microreactor, the process could be operated under more appropriate conditions, so that the selectivity of the iron catalyst was more acceptable for a commercial process. Meaningful results about the performance of the bifunctional process could therefore be obtained.

5.1 EXPERIMENTAL

5.1.1 Catalysts

A fused iron catalyst, which contained a low level of alkali, was employed as the syngas conversion function. The catalyst was obtained from Sasol, but since it falls within the proprietary technology of the company, the exact composition and additional information was not disclosed. A general description of the fused iron catalyst for the HTFT process is presented by *Dry* (1981).

The acid catalysts used for the Berty microreactor experiments were the same calcined HZSM-5 zeolites employed during the preliminary study (see Section 4.1.1.2 of Chapter 4 for details, in particular Tables 4.3 and 4.4). However, for the current study, only the "high acidity" zeolite (silica / alumina molar ratio of 30) and the "low acidity" zeolite (silica / alumina molar ratio of 280) were tested.

5.1.2 Reactor system

The Berty microreactor contains a metal cylinder with a height of 77 mm and an inner diameter of 70 mm. A wire mesh at the bottom of the cylindrical volume keeps the catalyst in place. The catalyst is spread out over the wire mesh to form a very thin, flat bed. Around the inner cylinder, there is a small annulus volume. A fan, situated below the wire mesh, circulates the gas inside the reactor downwards through the catalyst bed and up through the annulus volume at a very high rate. The reactor can therefore essentially be viewed as a short packed bed with an extremely high recycle ratio, and thus behaves approximately like a continuous stirred tank reactor (CSTR). A thermocouple, which runs along the centre axis of the inner cylinder, extends to a

point just above the catalyst bed. This thermocouple is used for temperature measurement and control inside the reactor. Since the high gas circulation rate through the catalyst ensures that there are no significant temperature or concentration profiles across the bed, the Berty microreactor is ideal for studying the highly exothermic HTFT reaction (*Bromfield*, 2001).

The main component of the feed to the microreactor was a commercial synthesis gas stream. Pure hydrogen and carbon dioxide were co-fed from bottles in order to obtain a total feed with the desired composition. In addition, bottled argon was fed to the reactor, which served as an internal standard. The flow rates of the four feed streams were controlled by Brooks mass flow controllers. The feed gas was sampled form a sampling point situated on the total feed line.

As was the case with the fixed bed microreactor set-up, the effluent from the Berty reactor was passed through a two-stage knock-out system. The temperature of the hot knock-out pot was 210°C, while the cold pot was kept at ambient temperature. A product gas sampling point was situated between the hot and cold knock-out pots. All uncondensed effluent passed through a back-pressure regulator (which maintained the pressure in the reactor system) into the vent system.

The main details of the reactor set-up are summarised in Table 5.1.

Table 5.1: Summarised information on Berty reactor system

Feed streams	
Argon (internal standard)	bottle
Syngas	commercial stream
Hydrogen	bottle
Carbon dioxide	bottle
Inner cylinder dimensions	
Internal diameter	70 mm
Height	77 mm
Temperature control	
Temperature measurement	thermocouple
Heat supply	heating mantle
Reactor effluent	
Hot knock-out temperature	210°C
Cold knock-out temperature	ambient

5.1.3 Loading of the reactor

At the start of the experimental investigation, a baseline HTFT run was performed with 5 g of iron catalyst (unreduced weight). Because of the adequate heat removal in a Berty reactor, it was not necessary to dilute the catalyst with inert material.

The bifunctional process runs were all performed with 5 g of iron catalyst (unreduced mass) and 5 g of HZSM-5. Two configurations of the process were tested, namely the physical admixture of the catalytic functions and a type of dual bed arrangement. For the former arrangement, the physical mixture of the two catalysts was spread out over the wire mesh at the bottom of the inner cylinder of the reactor. For the latter configuration, only the zeolite powder was spread over the wire mesh. A second wire mesh was then placed on top of the zeolite layer, upon which the iron catalyst was loaded. Since the two layers were separated by a fine wire mesh, contact between the catalysts was completely avoided. It should, however, be noted that this configuration is distinctly different from the dual bed arrangement in a fixed bed reactor where the syngas is first converted to linear hydrocarbons over an FT catalyst, after which the hydrocarbons are isomerised and aromatised by an acid catalyst. Since a Berty reactor approximates CSTR behaviour, the two catalysts are exposed to more or less the same gas composition. A summary of the packing configurations for the various experiments are presented in Table 5.2.

Table 5.2: Packing configurations of the Berty microreactor for the various experiments

Baseline FT run	
Number of layers	1
Iron catalyst (unreduced)	5 g
Bufunctional process - physical admixture of catalysts	
Number of layers	1
Iron catalyst (unreduced)	5 g
HZSM-5	5 g
Bifunctional process - separate catalyst layers	
Number of layers	2
Top layer: iron catalyst (unreduced)	5 g
Bottom layer: HZSM-5	5 g

It is envisaged that a commercial bifunctional process will be operated in fluidised bed reactors, since such reactors are currently employed for the commercial HTFT process (*Steynberg* et al., 1999). The reason for testing the two configurations of the bifunctional process in the Berty mixroreactor relates to the fact that the fluidised bed operation of the process cannot readily be simulated at laboratory scale. In a fluidised system, the catalyst particles will collide with each other and will therefore only be in contact for a fraction of the time. In this sense, physical admixture and dual layers

represent, respectively, the limiting cases of contact in a fluidised bed, namely continuous (intimate) contact and complete segregation.

5.1.4 Catalyst activation and synthesis

Before synthesis commenced, the iron catalyst was reduced at 420°C for 16 hours by feeding pure hydrogen to the reactor at a flow rate of 1000 ml/min. The HZSM-5, which did not require any additional activation, should not have been affected by the reduction procedure. Following the reduction, the reactor temperature was lowered to the synthesis temperature of 330°C under a combined feed of argon and hydrogen. After the temperature had stabilised, the various feed gas flow controllers were set to the desired values, which signalled the onset of synthesis. During reduction and synthesis, the total pressure of the reactor was kept at a value of 20 bar.

As was the case for the preliminary experimental investigation, it was decided to keep the synthesis conditions constant for all the Berty reactor runs. *Dry* (1981) published the partial pressures of the reagents at the entrance to a fluidised bed operated with a fused iron catalyst at 320°C for which reasonable methane selectivities and ethylene / ethane ratios were reported. The settings on the Brooks mass flow controllers of the Berty reactor system were therefore selected so that a similar total feed gas composition was obtained. The composition of the total feed to the reactor used for all the Berty experiments, as well as the other details of reduction and synthesis, is presented in Table 5.3.

5.1.5 Gas sampling and product analysis

The method of gas sampling, product analysis and data processing was exactly the same as for the preliminary experiments in the fixed bed reactor (see Sections 4.1.5 and 4.1.6 of Chapter 4 for a detailed description). However, it should be noted that the commercial synthesis gas stream, and thus the total feed to the reactor, contained a substantial amount of methane. In fact, the flow rate of methane into the reactor was normally around four times the amount that was produced by the Fischer-Tropsch reaction. Errors (for example caused by GC inaccuracies) in the methane inlet and outlet flow rates will be vastly amplified when these two large values are subtracted from each other in order to obtain the much lesser value of the methane production rate inside the reactor. The scatter in the calculated methane selectivity is thus expected to be fairly high for the set of Berty experiments.

As was the case for the preliminary study, GC-FID analysis was only performed on some of the samples due to the time consuming nature of this analysis. Therefore, whereas a full hydrocarbon product distribution was only obtained for some of the data points, the conversion and methane selectivity is reported for all samples taken.

Table 5.3: Reduction and synthesis conditions for all experiments performed in the Berty microreactor

Reduction conditions	
Reduction gas	hydrogen
Flow rate	1000 ml / min
Gas space velocity	200 ml / min / g unreduced iron cat
Temperature	420°C
Pressure	20 bar
Time	16 hours
Total feed gas composition during synthesis (volume %)	
H_2	58.0
CO	12.5
CO_2	12.0
CH_4	5.5
Ar	12.0
Synthesis conditions	
Total feed gas flow rate	1500 ml / min
Syngas (H_2+CO) flow rate	1057 ml / min
Syngas space velocity	211 ml / min / g unreduced iron cat
Temperature	330°C
Pressure	20 bar

5.2 RESULTS AND DISCUSSION

5.2.1 Baseline Fischer-Tropsch run

5.2.1.1 The stability of the iron catalyst over the period of synthesis

The CO and (CO+CO_2) conversions of the baseline FT run are presented as functions of the time on line in Figure 5.1. It is clear that the activity of the catalyst was quite stable over the more than two weeks of synthesis, since there was only a gradual decrease in the reaction rate over the course of the run. One possible explanation for the slight deactivation may be that some reoxidation of the iron catalyst occurred over the period of synthesis. The deposition of carbon on the catalyst, which is known to occur under typical HTFT operating conditions, may also have contributed to the slight decrease in the FT reaction rate (*Dry*, 1981; *Steynberg* et al., 1999).

It is well known that the methane selectivity of the HTFT process and the olefin / paraffin ratio of the product are quite sensitive to the alkali level of the iron catalyst (see *Dry*, 1981, as well as Chapter 4, Section 4.2.1.3.1 of this thesis). These parameters are therefore good indicators of the stability of the catalyst with respect to

product selectivity. Considering the methane selectivity[i] (Figure 5.2.1), as well as the olefin / paraffin ratios for the C_2 to C_4 carbon number range (Figure 5.2.2), merely a slight shift in the selectivity is observed over the course of the experiment. This indicates that the rate of carbon formation on the catalyst, with subsequent migration of alkali away from the active iron phase, was not excessive. The hydrogen / carbon ratio of the overall product spectrum (Figures 5.2.3) reflects both the scatter and the slight increase observed in the methane selectivity over the course of the run. On the other hand, the hydrogen / carbon ratio of the C_{2+} fraction (Figure 5.2.4) is much more constant over the whole period of synthesis, confirming that the olefin content of the product did not increase significantly. Figures 5.2.1 to 5.2.4 thus indicate that the alkalinity of the iron catalyst varied little during the full extent of the experiment. Since a very stable baseline FT run was obtained with which to compare the performance of the bifunctional process, it is clear that a Berty microreactor is indeed a very appropriate reactor set-up to study the addition of a co-catalyst to the HTFT process.

5.2.1.2 Carbon number distribution

A representative product distribution of the baseline FT run is presented in Figure 5.3 in the form of a Schulz-Flory plot. The positive and negative deviations of the C_1 and C_2 products, respectively, from the straight line relationship are typical of a real FT product spectrum and numerous explanations have been offered for these observations (*Dry*, 1981; *Van der Laan*, 1999). It is clear that the selectivities of hydrocarbons in the C_3 to C_{12} range follow the Schulz-Flory relationship quite well, which indicates that the chain growth probability (α value) in this carbon number fraction is constant. The deviation in the C_{13} to C_{15} range from the straight line points towards an underestimation of the selectivities of these products rather than an actual decrease in the α value. There are a few aspects that may have contributed to the underestimation of the heavier end. If condensation occurred during product sampling, the heavier hydrocarbons would have condensed preferentially because of their higher boiling points; consequently, some of the heavy product may not have been contained in the glass ampoule. Furthermore, the selectivity towards the heavy fraction is low and, additionally, a large number of products is contained in this range. It seems as if the GC-FID does not detect and accurately integrate the areas of all the components in the heavy end because of the small amounts of some of the compounds present.

The α values obtained from the linear part of the Schulz-Flory plots (typically the C_3 to C_{12} range) are presented in Figure 5.4 as a function of time on line. It appears as though there was only a very slight decrease in the chain growth probability during the course of the run, which once again testifies to the stability of the iron catalyst in the Berty microreactor. It should further be noted that the FT product spectrum obtained for the Berty reactor experiments is much heavier than that achieved during the preliminary study (compare Figures 4.5 and 5.4). Since a heavy, highly olefinic product spectrum is desired for the purpose of the bifunctional process, the current experimental set-up (reactor system and choice of FT catalyst) is much more

[i] The scatter in the methane selectivity with time on line is ascribed to the relatively large amount of methane in the reactor feed in comparison to the amount that is produced by the FT reaction, as was explained earlier in Section 5.1.5 of this chapter.

appropriate to study the addition of an acid catalyst to the HTFT process than the set-up used during the preliminary investigation.

5.2.1.3 Discrepancy in carbon mass balance

The overall sum of the hydrocarbon selectivities for the baseline FT run is presented in Figure 5.5 as a function of time on line. The trend in the accuracy of the mass balance is much less apparent than for the case of the fixed bed reactor experiments (compare Figures 4.6 and 5.5), mainly for two reasons. Firstly, as a consequence of the stability of the iron catalyst in the Berty reactor, the shift in the product spectrum towards the light end is much less pronounced than was the case during the preliminary experiments. Secondly, the extensive scatter in the calculated methane selectivitiy for the case of the Berty reactor experiments introduced a random scatter in the sum of the selectivities, which partly obscures the slight trend in the accuracy of the mass balance. Despite the lack of a clear trend, it is evident that the discrepancy in the carbon mass balance is (as previously) a systematic error rather than merely random scatter, since the deviation from 100 % is generally towards the negative side. This systematic error is attributed to similar reasons as stated before (see Chapter 4, Section 4.2.1.3.3). For the sake of consistency, the product spectrum was normalised in the same manner as described in Chapter 4, i.e. the selectivities of the C_{3+} components were scaled by a certain factor so that the selectivities of all hydrocarbon products (from methane onwards) summed up to 100 %. This ensured that a perfect carbon mass balance was obtained while the Schulz-Flory product relationship for the case of the baseline FT run was retained.

5.2.1.4 Product distributions

Overall product distributions, obtained at the beginning and at the end of the baseline FT run, are presented in Figures 5.6.1 and 5.6.2, respectively. These graphs also indicate that there was not a significant change in the product spectrum over the synthesis period of 16 days. Some of the small differences that are observed may reflect the slight increase in methane selectivity during the course of the experiment. This is in line with earlier findings that the iron catalyst was quite stable with respect to product selectivity. Clearly, the product spectrum was very rich in olefins (mainly linear 1-olefins), which makes it ideal for conversion over an acidic co-catalyst. Merely a small amount of aromatics was present in the C_6 to C_8 fraction, while the light end contained an appreciable amount of oxygenates (most notably ethanol).

5.2.1.5 Improvements in the experimental set-up

From the foregoing discussion, it is clear that the current experimental set-up is vastly superior to that of the preliminary investigation for the purpose of this study. The fixed bed reactor could never be operated for longer than one week due to an increase in the pressure drop over the catalyst bed. To the contrary, a two week long synthesis run was performed in the Berty reactor without any operational problems. Furthermore, whereas the performance of the FT catalyst in the fixed bed reactor

deteriorated extensively during the one week of synthesis, the iron catalyst in the Berty reactor was remarkably stable for a period of two weeks.

The selectivity of the FT catalyst as operated in the Berty reactor was also much improved over that achieved during the preliminary experimental investigation, since a heavy, highly olefinic FT product spectrum is required for optimal performance of the bifunctional process. For the baseline FT run in the fixed bed reactor, the methane selectivity quickly increased from 20 % to above 30 % (Figure 4.3.1), and α values of around 0.55 were reported (Figure 4.5). On the other hand, the methane selectivity and hydrocarbon chain growth probability for the baseline FT run in the Berty reactor assumed values of about 18 % (Figure 5.2.1) and 0.65 (Figure 5.4), respectively. The olefin content of the product spectrum was also much higher for the case of the Berty reactor. For example, the propylene / propane ratio of the Berty experiments was always above 10 (Figure 5.2.2), while this ratio decreased from about 7.5 to 4 during the fixed bed reactor run (Figure 4.3.2). The hydrogen / carbon ratio of the C_{2+} fraction also indicates that the FT product was more saturated during the fixed bed reactor experiments than for the case of the Berty runs. During the preliminary experimental program, the hydrogen / carbon ratio increased from 2.1 to 2.2 (Figure 4.3.4), but a fairly constant value of around 2.07 was achieved during the Berty FT experiment (Figure 5.2.4).

The superiority of the Berty experimental set-up can probably be ascribed to both the characteristics of the microreactor and the type of iron catalyst used. The thin catalyst bed and the high internal gas recycle rate ensure that the reaction heat generated by the highly exothermic FT reaction is dissipated effectively. Thereby, hot spots in the catalyst layer and excessive carbon deposition on the iron catalyst are avoided. Furthermore, the fused iron catalyst obtained from Sasol for the Berty experimental program was prepared in a similar way to the commercial HTFT catalyst. The consistency in the product selectivity during the course of the run was probably in part due to the inherent stability of this type of catalyst.

5.2.2 Bifunctional process – physical admixture of catalysts

Only the "high acidity" HZSM-5 was tested in this configuration (see Table 5.2 for packing details).

5.2.2.1 Time on line behaviour of the FT catalyst

The methane selectivity of the bifunctional process run is compared to that of the baseline FT run in Figure 5.7.1. The bifunctional process not only had a substantially higher methane selectivity than the HTFT run, but the increase over the first 200 hours of synthesis also seems to be more pronounced. The same trends are observed when the hydrogen / carbon ratio of the overall product spectrum (Figure 5.7.2) and of the C_{2+} fraction (Figure 5.7.3) are considered. The increase in the hydrogen content is especially notable on the graph of the C_{2+} fraction (Figure 5.7.3), since these data are not affected by the scatter in the methane selectivity. The product from the bifunctional process clearly had a very high hydrogen content that increased further

over time on line. On the other hand, the standard FT product of the baseline run had a lower hydrogen content that was much more constant over the synthesis period.

Since HZSM-5 does not have a significant ability to activate molecular hydrogen, the increases in the methane selectivity and hydrogen content of the product are ascribed to changes in the behaviour of the iron catalyst (as was the case for the fixed bed reactor runs). Because of the stable selectivities observed during the baseline FT run, it does not seem as if the migration of alkali from the iron catalyst to deposited carbon was responsible for the dramatic increase in the hydrogenation ability of the FT catalyst. It thus appears as though alkali migration from the iron to the HZSM-5 during reduction and synthesis caused the severe deterioration in the selectivity of the FT catalyst.

In Figures 5.8.1 and 5.8.2, the CO and ($CO+CO_2$) conversions of the bifunctional process run are presented, along with that of the baseline FT run. From these graphs, it seems as if the conversions of the two experimental runs were very similar at the onset of synthesis. However, for the case of the bifunctional process run, there was a much more significant drop in the FT reaction rate over time on line than was observed for the baseline FT run. As a result of this more rapid decline, the difference in conversion between the two runs is quite obvious after 400 hours of synthesis. From data presented by *Dry* (1981) for the HTFT process, it is clear that a decrease in the alkali content of the iron catalyst leads to a decrease in conversion, but that the product selectivities are more notably affected by a change in the alkali level. This is precisely what has been observed for the bifunctional process run, namely an extensive shift in the product selectivity and a less substantial decrease in syngas conversion. Therefore, the decline in the FT reaction rate for the bifunctional process run is also ascribed to the lowering of the alkali content of the iron catalyst due to alkali migration from the FT catalyst to the zeolite.

It should be noted that an extensive increase in the hydrogenation ability of the FT catalyst was also observed during the preliminary investigation in the fixed bed reactor when the two catalysts were in physical admixture (see, for example, the discussion in Section 4.2.2.3.2 of Chapter 4, as well as Figures 4.11.1 and 4.11.3). During the discussion of those results, the shift in the product selectivity was also ascribed to the migration of alkali from the iron catalyst to the HZSM-5. However, because of the severe operating problems experience with the fixed bed reactor (especially when the zeolite was physically mixed with the FT catalyst), no conclusions regarding the effect on the FT activity could be made.

5.2.2.2 Feasibility of the bifunctional process in the physically admixed configuration

Typical product distributions of the bifunctional process, obtained at the beginning and end of the run, are presented in Figures 5.9.1 and 5.9.2, respectively. As previously, the methane selectivity is not included in these figures, as it would unnecessarily increase the scale of the graphs and distract from the observations regarding the rest of the product spectrum. From the graphs, it is clear that the condensable fraction of the product spectrum is rich in aromatics and naphthenes, indicating a vast improvement in the octane number (quality) of the gasoline cut in

comparison to the standard HTFT process. However, the overall selectivity of the condensable fraction seems quite low. Considering Figures 5.10.1 and 5.10.2, it is confirmed that the bifunctional process has a very high selectivity towards C_1 to C_4 paraffins (low value products), with a correspondingly low selectivity of the C_5 to C_{11} fraction (desirable product). This is mainly ascribed to the progressive shift in the product spectrum of the FT catalyst towards lighter and more paraffinic compounds as the alkali migrated from the iron catalyst to the zeolite. Because of the excessive production of light paraffins, it does not seem as if the bifunctional process would be commercially viable if there is an intimate contact between the catalytic functions. For this reason, no further experiments were performed with the catalysts in physical admixture.

5.2.3 Bifunctional process – catalysts in separate layers

Since physical contact between the two catalytic functions is not an option for a commercial process, it was thought more appropriate to separate the catalysts with a wire mesh for the purpose of further studying the selectivity of the bifunctional process and the deactivation behaviour of the HZSM-5 (see Table 5.2 for packing details). As indicated before, this represents the best case scenario for a fluidised bed reactor as far as alkali migration is concerned. The instantaneous contact between particles during collisions in a fluidised system means that the particles will be in contact for a certain fraction of the time.

5.2.3.1 Time on line behaviour of FT catalyst function

5.2.3.1.1 Hydrogenation ability of the iron catalyst

The methane selectivities of the bifunctional process runs are compared to that of the baseline FT run in Figure 5.11.1. Within the experimental scatter of the data, no differences are visible between the various runs. The hydrogen / carbon ratio of the overall product spectrum and of the C_{2+} fraction are presented in Figures 5.11.2 and 5.11.3, respectively, for the different experiments. From this data, it appears as though the addition of an acidic co-catalyst has lowered the hydrogen content of the product. Even though HZSM-5 does not have a significant ability to activate molecular hydrogen (and therefore cannot readily extract hydrogen from the FT product in molecular form), it can be argued that the dehydration of oxygenates (e.g. alcohols) over the acid catalyst can remove hydrogen from the product spectrum in the form of water. The increase in the hydrogen / carbon ratio with time on line, which is especially evident for the case of the C_{2+} fraction (Figure 5.11.3), can then be explained in terms of a zeolite deactivation effect (a decrease in the ability of the zeolite to dehydrate the alcohols). It should, however, be noted that the method of interpreting the GC-FID trace of the product from the bifunctional process would have lowered the calculated hydrogen / carbon ratio of the product artificially. For example, it is basically assumed that all the unidentified components in the C_{8+} fraction are naphthenes or aromatics, while in actual fact there may still be aliphatic molecules (including paraffins) present in this part of the product spectrum. Since cyclic compounds (especially aromatics) have a low hydrogen / carbon ratio, the hydrogen content of the product will be underestimated. Despite the uncertainty in

the actual hydrogen / carbon ratio of the product, it is clear from Figures 5.11.1 to 5.11.3 that there was not a serious increase in the hydrogenation ability of the FT catalyst upon addition of HZSM-5 in a separate layer. The wire mesh between the two layers therefore effectively avoided significant alkali migration from the iron catalyst to the zeolite.

5.2.3.1.2 Fischer-Tropsch reaction rate

In Figures 5.12.1 and 5.12.2, the bifunctional process runs are compared to the baseline FT run with respect to the CO and ($CO+CO_2$) conversions over time on line. For all runs, the conversion was fairly constant during the period of synthesis. This means that the syngas conversion function (i.e. the iron catalyst) had a very stable activity during the course of each run. However, it seems as if the addition of HZSM-5 to the process resulted in a lowering of the FT reaction rate. Furthermore, it may be argued that the extent of the decrease in FT activity is dependent on the number of acid sites present in the reactor, since the decrease in CO conversion was more severe for the "high acidity" HZSM-5 than for the "low acidity" HZSM-5. The same trend appears to be present in the data of the fixed bed reactor experiments. For both configurations of the bifunctional process in that reactor, the FT reaction rate was always lower than for the case of the baseline FT run (see Figures 4.9.1 and 4.9.2, as well as Figures 4.17.1 and 4.17.2). In addition, there seems to be some correlation (albeit far from perfect) between the acidity of the zeolite and the drop in the syngas conversion. Unfortunately, the erratic variations in the data cast some doubt over the integrity of the results obtained with the fixed bed reactor.

Returning to the Berty results, it is highly unlikely that the FT catalyst was poisoned by some volatile compound (e.g. ammonia) contained in HZSM-5. Any compound in the zeolite that survived the 16 hours of calcination at 500°C would surely have been stable at the reduction and synthesis temperatures (420°C and 330°C, respectively) as well. If the iron catalyst was affected by a poison contained in the feed gas, one would expect a continuous decrease in CO conversion over the synthesis period rather than the observed stable activity. The effect of HZSM-5 addition on the activity of the FT catalyst is clearly not a result of alkali migration either, since a loss of alkali from the iron catalyst would have reflected more notably in the hydrogenation ability of the iron catalyst (methane selectivity and hydrogen / carbon ratio of the product) than in the CO conversion. Temperature effects can be ruled out as well, because the exothermic acid-catalysed reactions would rather tend to increase the temperature with a consequent increase in reaction rate.

Consideration was also given to the possibility that the HZSM-5 may have affected the FT catalyst activity by changing the concentrations of components in the gas phase. If the zeolites lowered the concentration of a reactive component by means of adsorption, one would expect a temporary effect on the conversion, since the small amount of zeolite would only have a limited capacity for such a substance. If a reactive compound or inhibitor is consumed or produced by a chemical reaction catalysed by the HZSM-5, one would expect a continuous change in the FT activity over time as the zeolite deactivated. In fact, zeolite deactivation was so extensive that the performance of the "high acidity" HZSM-5 became similar to that of the "low acidity" HZSM-5 towards the end of the run. Notwithstanding, the CO conversions

for the respective experimental runs were substantially different over the whole period of synthesis.

Another explanation for the observations regarding the CO conversion is that the second wire mesh, which was installed to separate the two catalysts, altered the hydrodynamics inside the Berty reactor, which affected the gas flow rate through the iron catalyst layer. This hypothesis can be tested by performing a baseline FT run with the second wire mesh in place in order to simulate the hydrodynamics of the bifunctional process experiments. The hydrodynamic explanation seems to be supported by the results of the bifunctional process run with the two catalysts in physical admixture. For this run, the second wire mesh was not installed. Even though the "high acidity" HZSM-5 was present in the reactor, the CO and ($CO+CO_2$) conversions was initially comparable to that of the baseline FT run. The continuous decrease in the conversion during the course of the run was ascribed to the extensive alkali migration from the iron catalyst to the zeolite (see Section 5.2.2.1 of this chapter, as well as Figures 5.8.1 and 5.8.2). This drop in conversion noted for the physical admixed configuration is thus apparently unrelated to the lower FT reaction rate observed for the case of the "dual layer" arrangement.

In view of the foregoing discussion, it is clear that the effect of an acidic zeolite on the syngas conversion rate in the bifunctional process is still an unresolved issue that warrants further investigation.

5.2.3.2 Deactivation of the acid catalyst function

The change in the selectivity and composition of the C_3 fraction upon HZSM-5 addition to the HTFT process provides some indication of the activity of the acid catalyst function. Over HZSM-5, additional propane is mainly produced as the hydrogen-rich byproduct of the aromatisation of olefins, but can also form via the cracking of longer chain aliphatics. Although additional propylene can be produced by the zeolite through cracking, propylene from the FT reaction is mostly consumed by the acid catalyst during the aromatisation and oligomerisation reactions. A high propane and low propylene selectivity is therefore indicative of a highly active zeolite.

The propane and propylene selectivities are presented in Figures 5.13.1 and 5.13.2, respectively, as a function of the time on line for the different experimental runs. From the data presented for the baseline FT run, it is clear the C_3 fraction produced by the iron catalyst was highly olefinic. The product of the bifunctional process generally contained much more propane and much less propylene than the standard FT product. At the beginning of the run, the "high acidity" HZSM-5 clearly increased the propane selectivity enormously, while the propylene was consumed almost completely. This is indicative of a very high initial acid catalyst activity for this zeolite. However, there was a dramatic change in the selectivities of the C_3 components with synthesis time, indicating a rapid decrease in the initial high activity of the acidic co-catalyst. From the graphs, it is also clear that the "low acidity" HZSM-5 had a substantially lower initial activity, but a much more stable performance over the course of the run.

The linearity of the C_6 paraffin and olefin fractions are presented in Figures 5.14.1 and 5.14.2, respectively, in order to indicate the variations in the isomerisation activity of the acidic co-catalysts. The graphs clearly show that the product of the baseline FT run is highly linear, as would be expected (*Dry*, 1981). On the other hand, the product from the bifunctional process is generally much more branched due to the isomerisation ability of the acid catalyst function. For the case of the "high acidity" commercial HZSM-5, the C_6 fraction initially contained mainly branched molecules, but the linearity increased steeply with time on line as a result of the rapid deactivation of this type of zeolite. The "low acidity" commercial HZSM-5 had a lower initial isomerisation activity, but the deactivation was much less severe, since the linearity of the C_6 fraction increased only slightly over the course of the synthesis run.

The observations concerning the zeolite activity are confirmed if the aromatic content of the C_8 carbon number fraction is considered (Figure 5.15). Initially, the "high acidity" HZSM-5 had a high selectivity towards ethylbenzene and the xylenes, but this decreased rapidly as the zeolite deactivated. The "low acidity" zeolite had a lower but more constant C_8 aromatic selectivity. In fact, considering Figures 5.13 to 5.15, it seems as if the deactivation of the "high acidity" HZSM-5 was so severe that its activity dropped below that of the "low acidity" HZSM-5 after about 150 hours on line. It is also appears as if the aromatisation ability of the "high acidity" zeolite was more notably affected by the deactivation than its isomerisation ability. The reason for this is that aromatisation is the slowest of the acid catalysed reactions and is therefore highly dependent on the activity of the catalyst.

5.2.3.3 The effect of HZSM-5 addition on the HTFT product spectrum

5.2.3.3.1 Product distributions

Typical product distributions of the bifunctional process runs are presented for the two HZSM-5 zeolites at the beginning and at the end of each run (Figures 5.16 to 5.17). From these figures it is evident that a "highly acidic", highly active zeolite produces a product spectrum rich in aromatics (Figure 5.17.1). Since olefins are consumed and paraffins produced during the formation of aromatics, the light end of the product spectrum is almost completely paraffinic. Because of the severe deactivation of the "high acidity" HZSM-5, there was a significant lowering in the aromatic selectivity corresponding to an enormous increase in the olefin content of the light fraction towards the end of the run (compare Figures 5.17.1 and 5.17.2). Similar trends are observed for the case of the "low acidity" HZSM-5 (compare Figures 5.16.1 and 5.16.2), albeit to a much lesser extent. Since the "low acidity" zeolite has a lower initial activity and a less rapid deactivation rate, the changes in the product spectrum are not so dramatic as for the case of the "high acidity" zeolite. It should also be noted that merely small amounts of alcohols and aldehydes were detected in the product spectrum of the bifunctional process. It therefore seems as if the oxygenates present in the HTFT product spectrum is very easily converted over the acidic co-catalyst.

5.2.3.3.2 Overall carbon number distribution

The overall carbon number distributions obtained for the two bifunctional process runs at the beginning of synthesis are compared to the HTFT carbon number distribution in Figure 5.18.1. It is clear that the addition of a zeolite effected significant changes to the product distribution of the traditional HTFT process. The notable lowering in the selectivities of the C_2 and C_3 carbon number fractions indicate that both ethylene and propylene were converted over the acidic co-catalyst. However, due to the higher stability of secondary carbenium ions compared to primary carbenium ions, propylene has a higher reactivity for acid catalysed reactions than ethylene. Furthermore, in the FT product spectrum, the C_3 fraction is more olefinic than the C_2 fraction (see, for example, Figures 5.2.2 and 5.6.1). These aspects explain the more substantial lowering in the selectivity of the C_3 fraction than in the C_2 fraction upon zeolite addition to the HTFT process.

The overall carbon number distribution of the bifunctional process product is mainly distinguished from the Schulz-Flory distribution of the traditional HTFT product by the occurrence of two clear humps. The first hump at around C_4 corresponds to the favoured distribution of olefins and paraffins. The reason for this hump is that, at the prevailing conditions, longer aliphatic molecules are not stable in the presence of an active acid catalyst and are readily cracked down to lighter olefins and paraffins. The C_4-olefins and –paraffins seems to be the preferred products of these cracking reactions due to the high stability of the tertiary carbenium ion. (Note that, for the case of a C_3 carbenium ion, there is no tertiary position for the positive charge; consequently, the formation of C_4 species is kinetically favoured over C_3 species during the cracking of heavier olefins and paraffins.) The second hump in the carbon number distribution occurs at about C_8 and corresponds to the favoured distribution of aromatics. There is also a fairly sharp cut-off in the product spectrum at around C_{10} to C_{11}. The reason for this is that long chain aliphatics are not stable at these temperatures in the presence of an acid catalyst, while aromatics higher than about C_{11} are too large to be formed readily inside the pores of HZSM-5.

Due to zeolite deactivation over the course of synthesis, the carbon number distribution of the bifunctional process product started to approach that of the baseline FT run towards the end of the run (Figure 5.18.2). It is interesting to note that, after about 270 hours of synthesis, the "low acidity" HZSM-5 seemed to have a more significant effect on the overall carbon number distribution than the "high acidity" HZSM-5. The lowering in the selectivities of the C_2 and C_3 fractions is more notable, and the aromatic hump at C_8 is more clearly visible. This supports the notion that the activity of the "high acidity" zeolite dropped below that of the "low acidity" zeolite towards the end of the run due to the more rapid deactivation of the former.

5.2.3.3.3 Gasoline selectivity

The gasoline selectivities[ii] of the different experimental runs are presented in Figure 5.19 as a function of time on line. For the baseline FT run, the gasoline selectivity decreased steadily over the course of the experiment as there was a slight shift in the

[ii] The gasoline fraction is defined as the C_5 to C_{11} carbon number range.

product spectrum towards the lighter end. The decline in gasoline selectivity towards the end of the bifunctional process runs can thus not solely be ascribed to the deactivation of the acid catalyst function, since the amount of compounds that are reactive over a zeolite would have decreased as the selectivity of the FT catalyst shifted towards lighter and more paraffinic hydrocarbons.

Figure 5.19 indicates that the addition of the "low acidity" HZSM-5 to the HTFT process resulted in a substantial improvement in the selectivity of the C_5 to C_{11} fraction throughout the course of the experiment, probably mainly due to oligomerisation and cyclisation of light olefins. To the contrary, the "high acidity" HZSM-5 did not significantly improve the gasoline selectivity of the HTFT process during the early stages of the run. The proposed reason for this is the vast amount of aromatics produced by such a highly active zeolite, which is accompanied by the formation of light paraffins that fall outside the petrol range. The deactivation of this zeolite had a more serious negative effect on the aromatisation reaction than on the oligomerisation reaction. Consequently, since the oligomerisation of olefins into the gasoline range started to dominate over the aromatisation reaction as the activity of the acid catalyst declined, the gasoline selectivity increased and approached that of the "low acidity" zeolite. However, towards the end of the run it seemed as if the gasoline selectivity for the case of the "high acidity" HZSM-5 dropped more sharply than for the other zeolite, possibly because the very rapid deactivation rate started to impact more significantly on the oligomerisation of light olefins.

From Figure 5.19, it is evident that the gasoline selectivity of the bifunctional process is in general substantially higher than that of the traditional HTFT process. For the case of the "low acidity" HZSM-5, the increase in C_5 to C_{11} selectivity over the baseline FT run was between 25% and 35% throughout the run. It was also seen that, in order to optimise the amount of petrol produced, a zeolite with a lower aluminium content is preferable. For a highly active, "highly acidic" zeolite, a large amount of light paraffins are initially produced along with the formation of aromatics. Such a zeolite also deactivates quite rapidly, which eventually starts to impact negatively on the gasoline selectivity.

5.2.3.3.4 Gasoline quality

The benzene content of the C_5 to C_{11} carbon number fraction is presented in Figure 5.20.1 for the various experimental runs. From this graph, it seems as if the benzene production rate during the baseline FT run may have been higher than for the bifunctional process runs. However, it should be noted that the gas chromatograph used for the product analysis did not achieve a good separation between benzene and n-butanol (another compound present in the HTFT product spectrum). The overlap in the peaks of these two components on the GC-FID trace might well have caused an overestimation in the amount of benzene for the case of the baseline FT run. To the contrary, n-butanol is not present in the product spectrum of the bifunctional process. Since the benzene peak on the GC-FID trace does not overlap with any other peaks in this case, it is probably integrated more accurately. The extensive scatter in the benzene content of the gasoline for the case of the baseline FT run compared to that of the bifunctional process runs is in line with the notion that benzene may have been analysed inaccurately in the former case.

The possible inaccuracy in the benzene measurement for the case of the baseline FT run is not of serious concern. The benzene content of the gasoline from the bifunctional process is generally quite low (around 1%), so clearly there wasn't excessive formation of benzene over the acidic co-catalyst. The only exception is for the "high acidity" HZSM-5 at the beginning of the run, when the benzene content was above 5%. However, this value dropped steeply due to the rapid deactivation of the zeolite. The constant amount of benzene in the petrol produced by the "low acidity" zeolite is a result of its more stable activity over the period of the run.

Similar trends are observed if the fraction of BTXE-aromatics in the gasoline is considered (Figure 5.20.2). The fairly high BTXE-selectivity of the standard HTFT process may be incorrect because of the possible inaccuracy in the benzene measurement. For the "high acidity" zeolite, the level of BTXE-aromatics was initially very high, but this decreased sharply over the course of the run. In fact, the activity decline was so severe that the BTXE content of the gasoline dropped below that of the "low acidity" HZSM-5 after about 150 hours of synthesis. For the "low acidity" zeolite, the BTXE-content of the C_5 to C_{11} fraction also decreased from its original value of 15%, but was still around 7% at the end of the run. Because of the substantial amount of these aromatic compounds in the condensable product fraction of the bifunctional process, it may be economically viable to recover them as chemicals from the liquid hydrocarbon fraction.

The amounts of aromatics and total cyclic compounds in the gasoline fraction are presented in Figures 5.20.3 and 5.20.4, respectively[iii]. Clearly, the product of the bifunctional process is generally very rich in these high octane compounds. The olefins and paraffins in the gasoline range are also mostly branched, as was evident from Figures 5.14.1 and 5.14.2. These aspects show that the octane number of the gasoline fraction from the traditional HTFT process was vastly improved by the addition of an acidic zeolite. It was also found that the very high aromatisation and isomerisation activity initially achieved with the "high acidity" HZSM-5 could not be sustained and after about 150 hours of synthesis the product from the "low acidity" zeolite seemed to be superior. The "low acidity" HZSM-5 would probably be the preferred choice of acid catalyst for the bifunctional process, because of its more stable performance over an extended period of synthesis.

5.3 Conclusions and Recommendations

5.3.1 The experimental set-up for bifunctional process experiments

The preliminary study on the bifunctional process, performed in a fixed bed microreactor, was not very successful. Carbon deposition on the iron catalyst led to plugging of the bed that caused operational difficulties. Furthermore, the light, paraffinic product spectrum of the iron catalyst was neither acceptable for a commercial HTFT process, nor optimal for conversion over an acidic co-catalyst.

[iii] Note that the reported amounts of aromatics and naphthenes are based on certain assumptions made about the unidentified peaks on the chromatogram. Initially, when the zeolites are still active, these assumptions should be fairly accurate. However, the assumptions become less valid as the acid catalyst deactivates.

Addition of the zeolites indirectly affected the performance of the iron catalyst in a negative way via the process operation, which made it unrealistic to compare the bifunctional process runs directly with the baseline FT run. Even though the choice of iron catalyst, the particle sizes of the various catalysts and inert materials, and the process conditions may have been optimised to improve the operation of the fixed bed reactor, it was decided to rather perform the subsequent experimental investigation in another reactor system.

The Berty microreactor was operated with a fused iron catalyst, which is the same type of catalyst used for Sasol's commercial HTFT operation. The operating conditions were chosen to be similar to that published by *Dry* (1981), for which acceptable methane selectivities and olefin / paraffin ratios were obtained. For the Berty experimental set-up, a baseline FT run was performed for which the conversion, the methane selectivity and the olefin content of the product spectrum was fairly constant over two weeks of synthesis. Even though the FT reaction rate was affected when the zeolites were added in a separate layer, the selectivity of the iron catalyst per se did not seem to be influenced. The data obtained could therefore provide for a realistic comparison between the bifunctional process and the standard HTFT process. The stability of the iron catalyst with respect to activity and selectivity therefore showed that this experimental set-up was quite appropriate to study the traditional HTFT process, as well as the addition of an acidic co-catalyst to the process.

The success obtained with the Berty experimental set-up can probably be ascribed to both the characteristics of the microreactor and the type of iron catalyst used. The thin catalyst bed and the high internal gas recycle rate ensure that the reaction heat generated by the highly exothermic FT reaction is dissipated effectively. Thereby, hot spots in the catalyst layer and excessive carbon deposition on the iron catalyst are avoided. Furthermore, the fused iron catalyst obtained from Sasol for the Berty experimental program was prepared in a similar way to the commercial HTFT catalyst. The consistency in the product selectivity during the course of the run was probably in part due to the inherent stability of this type of catalyst.

5.3.2 The effect of contact between the catalytic functions

The findings of the preliminary experimental investigation regarding the physical mixing of the two catalytic functions were verified by the Berty experimental results. It was clear that an intimate contact between the catalysts resulted in extensive alkali migration from the iron catalyst to the zeolite. The result was a severe shift in the selectivity of the FT catalyst towards light paraffins that cannot be converted to higher value products by the zeolite. The selectivity of these low value paraffins was so high that the commercial viability of a bifunctional process in this mode is doubtful. The prospect of having both catalytic functions on one particle is therefore also not feasible when an alkali-promoted iron catalyst is to be combined with an acidic co-catalyst in the same reactor.

In a fluidised bed reactor, alkali transfer between separate iron catalyst and zeolite particles is also expected to occur during collisions between the particles. The extent of this migration would be dependent on the overall time of contact between the

particles. It has been found that the one extreme (continuous contact) is not a commercially viable process. The Berty experiments performed in the "dual layer" configuration (catalysts separated by a wire mesh) was quite successful, but this represents the best case scenario of the bifunctional process performed in a fluidised bed reactor. Even so, the two layer set-up in a Berty microreactor is currently the most realistic way to investigate the process on laboratory scale.

5.3.3 Deactivation of the acid catalyst function

During the preliminary experimental investigation in the fixed bed microreactor, little deactivation of the acid catalyst function was noted. The proposed reason was that the non-optimal experimental set-up caused a severe shift in the selectivity of the FT catalyst to the extent that little olefins and long chain paraffins (the compounds that can readily be converted over an acid catalyst) were produced. Under such conditions, deactivation of the acid catalyst would not have been apparent, because even a low acid activity would have been adequate to convert the available hydrocarbons. Furthermore, since the amount of hydrocarbons converted by the zeolite was low, the deactivation rate was presumably also low.

For the case of the Berty microreactor, the selectivity of the iron catalyst was more in line with what would be expected from commercial HTFT operation. Because of the heavier and more olefinic product spectrum, more hydrocarbons were available to react over the zeolite. Any decrease in acid catalyst activity would therefore have reflected quite notably in the composition of the product spectrum of the bifunctional process. Furthermore, the highly olefinic nature of the FT product and the large amount of hydrocarbons converted by the zeolite were presumably the reasons for the significant deactivation of the acid catalyst function. As expected, the deactivation rate was related to the aluminium content of the zeolite, with the "high acidity" zeolite deactivating more rapidly. In fact, the deactivation of the "high acidity" HZSM-5 was so severe that it converted less propylene than the "low acidity" HZSM-5 after about 150 hours of synthesis.

Due to the extensive zeolite deactivation, the product spectrum of the bifunctional process with the "high acidity" HZSM-5 changed dramatically over the first week of synthesis. During the initial hours on line, the liquid fraction of the product contained almost 80% aromatics. The aromatic content was, however, halved after about two days and continued decreasing over the remainder of the run (Figure 5.20.3). Such variation in the product spectrum is not desirable for a commercial process. The more stable activity throughout the run and the enhanced performance during the latter stages of the run probably makes the "low acidity" HZSM-5 a more preferred choice as the acid catalyst function of the bifunctional process.

5.3.4 The gasoline selectivity and quality of the bifunctional process

The experimental results have shown that the use of a "highly acidic" zeolite in the bifunctional process does not significantly improve the gasoline selectivity of the HTFT process. At the beginning of the run, when the activity of the zeolite is high, the liquid fraction of the product is almost completely transformed into aromatics.

However, the production of aromatics is accompanied by the formation of light paraffins that fall outside the petrol range and therefore has a negative impact on the gasoline selectivity. As the zeolite deactivates, the gasoline production initially increases as the oligomerisation of light olefins to petrol range compounds becomes more predominant than the aromatisation reactions, but drops steeply in the latter part of the run due to the rapid deactivation of the "highly acidic" zeolite. It was thus found that, in order to optimise the gasoline production, a lower aluminium content zeolite should rather be employed, since the excessive formation of light paraffins is avoided and the catalyst also has a more stable activity. In fact, for the case of the "low acidity" HZSM-5 in the current set of experiments on the bifunctional process, the gasoline selectivity was around 25% to 35% higher than for the baseline FT case throughout the course of the run.

It was also seen that the liquid fraction from the bifunctional process was rich in aromatics, naphthenes and branched aliphatics. This product will therefore have a much higher octane number than the predominantly linear aliphatic compounds produced by the traditional HTFT process. Benzene, which is by far the most dangerous aromatic compound from an environmental point of view, was produced in fairly small amounts (it comprised only about 1 % of the gasoline fraction). The "low acidity" HZSM-5 again seemed to be the preferred choice of acid catalyst for the bifunctional process, because there was less variation in the product composition over the course of the synthesis run than for the "high acidity" zeolite.

It should also be noted that the yield of high octane gasoline from the bifunctional process can be increased further by additional product work-up. Isobutane is formed in reasonable amounts by the bifunctional process. The alkylation of this isobutane with light olefins (also present in the product spectrum) to highly branched paraffins (e.g. isooctane) will convert light compounds to gasoline range components with a high octane number.

5.3.5 Feasibility of the bifunctional process as a method to produce gasoline on commercial scale

From the experiments, it is clear that significant alkali migration from the iron FT catalyst to the zeolite can make this combination of catalysts unfeasible. However, in a fluidised bed reactor, particles will only be in contact during collisions. This might limit the extent of alkali migration to the point where the process is commercially viable. It also seems that, because of the rapid deactivation rate of the "high acidity" zeolite, a low aluminium content zeolite is the preferred choice for the bifunctional process. For the "low acidity" HZSM-5 used in this study, the acid catalyst improved both the gasoline selectivity and quality substantially and still had a reasonable activity after 11 days of synthesis under realistic HTFT conditions.

Figure 5.1: Conversion as a function of time on line – *Baseline FT run*

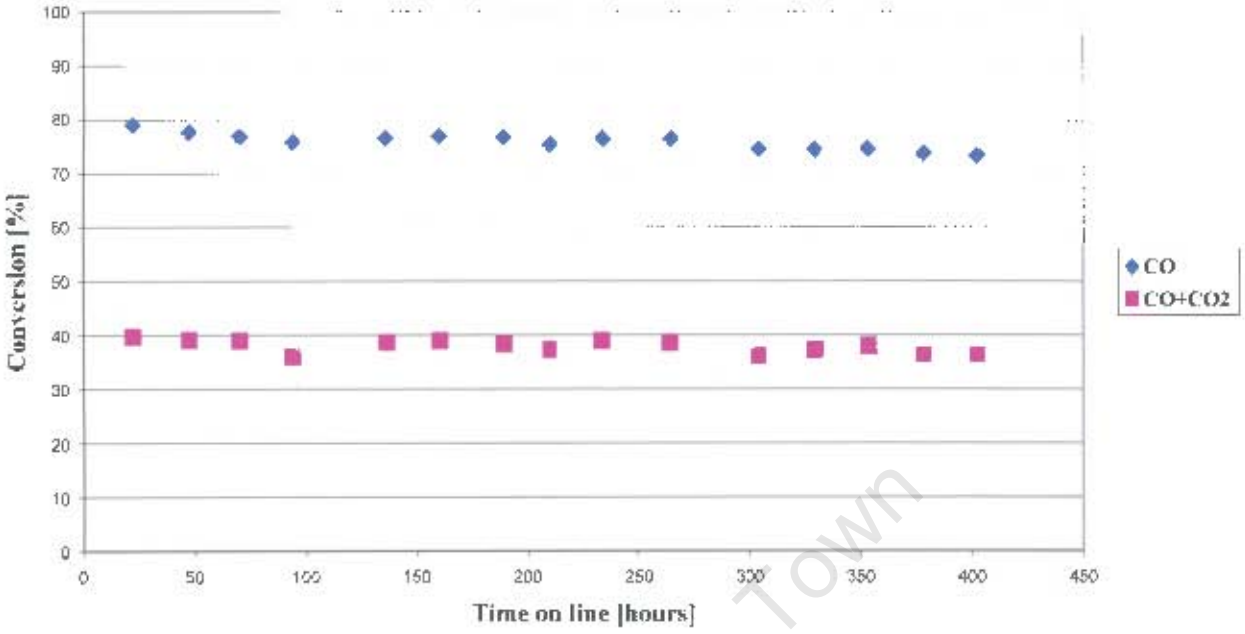


Figure 5.2.1: Methane selectivity as a function of time on line – *Baseline FT run*

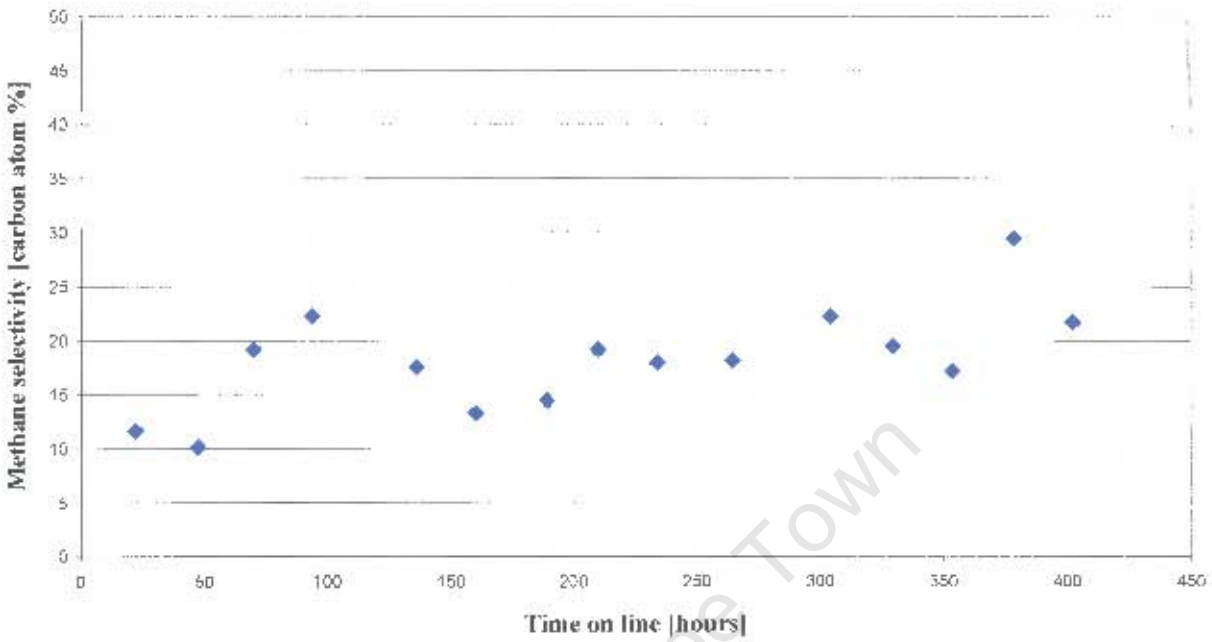


Figure 5.2.2: Olefin / paraffin ratios for C_2 to C_4 range as a function of time on line – *Baseline FT run*

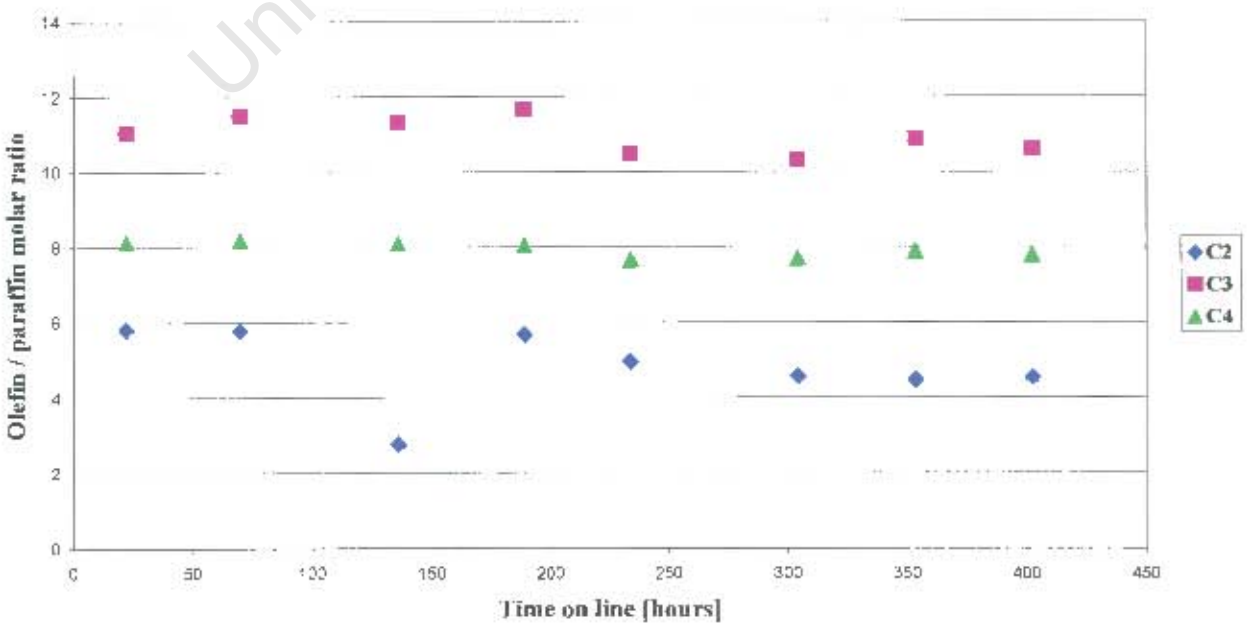


Figure 5.2.3: Hydrogen / carbon ratio of overall hydrocarbon product spectrum as a function of time on line – *Baseline FT run*

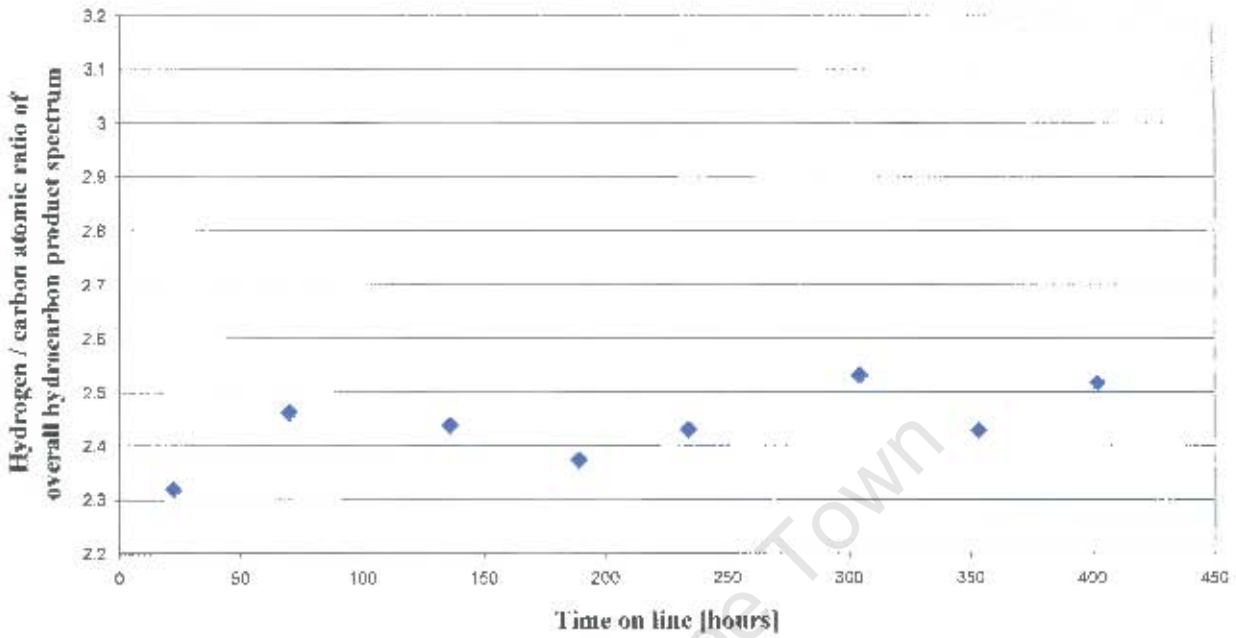


Figure 5.2.4: Hydrogen / carbon ratio of C_{2+} fraction of product spectrum as a function of time on line – *Baseline FT run*

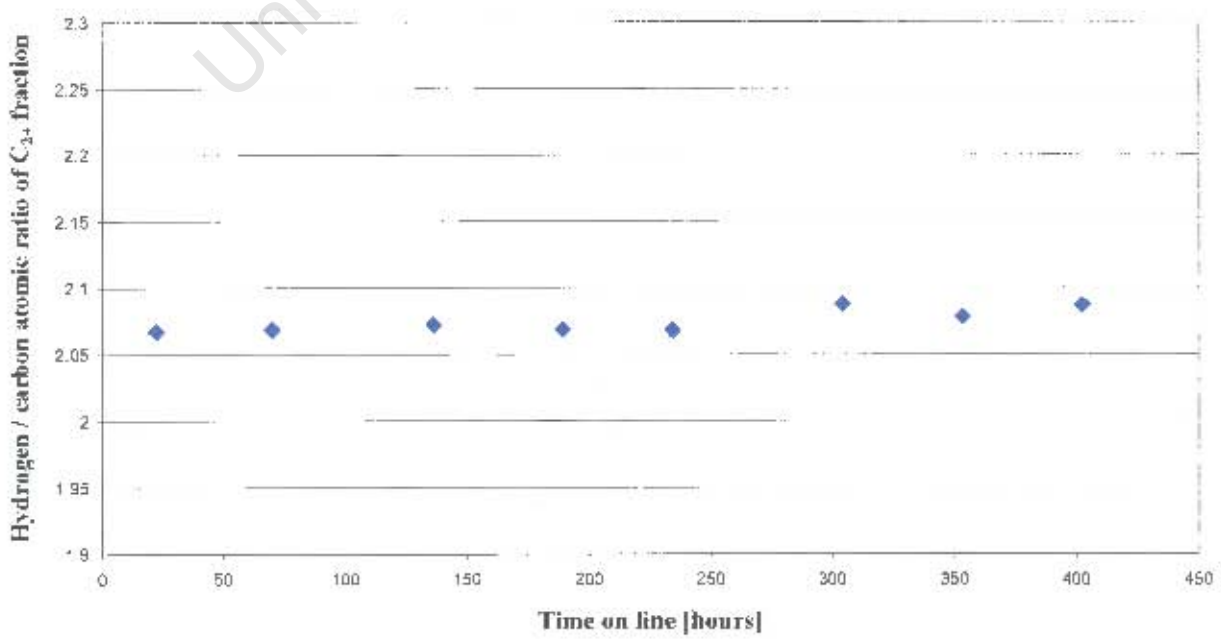


Figure 5.3: Schulz-Flory plot of representative hydrocarbon product distribution – ***Baseline FT run, 136 hours on line***

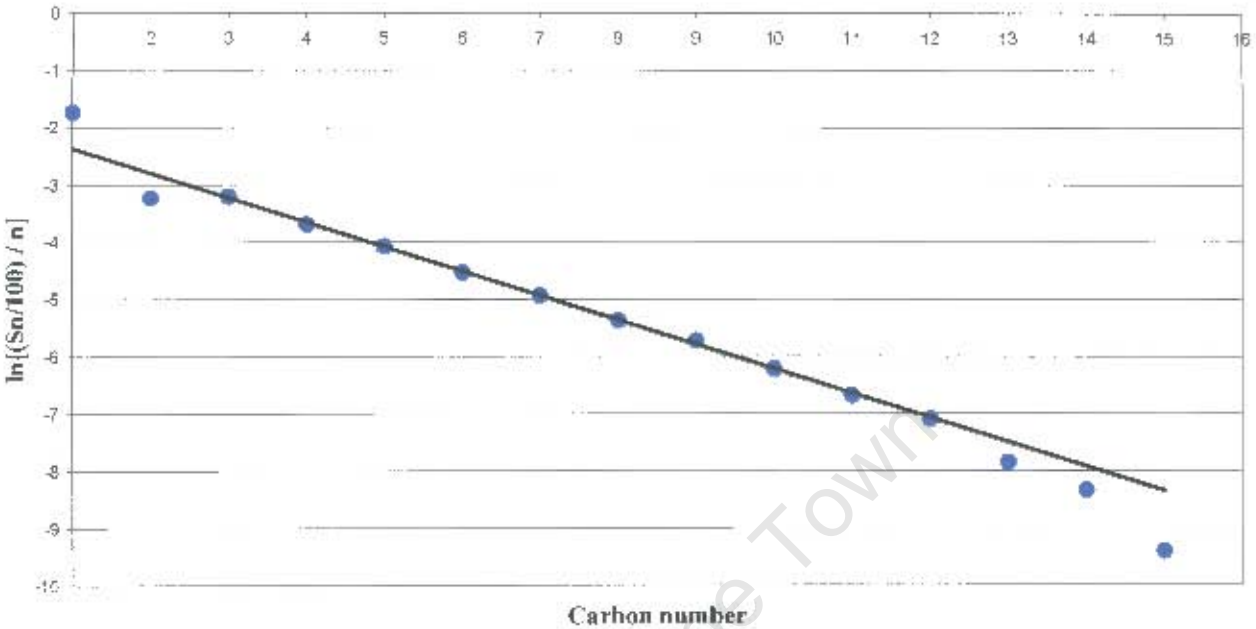


Figure 5.4: Variation in alpha value of hydrocarbon product distribution as a function of time on line – ***Baseline FT run***

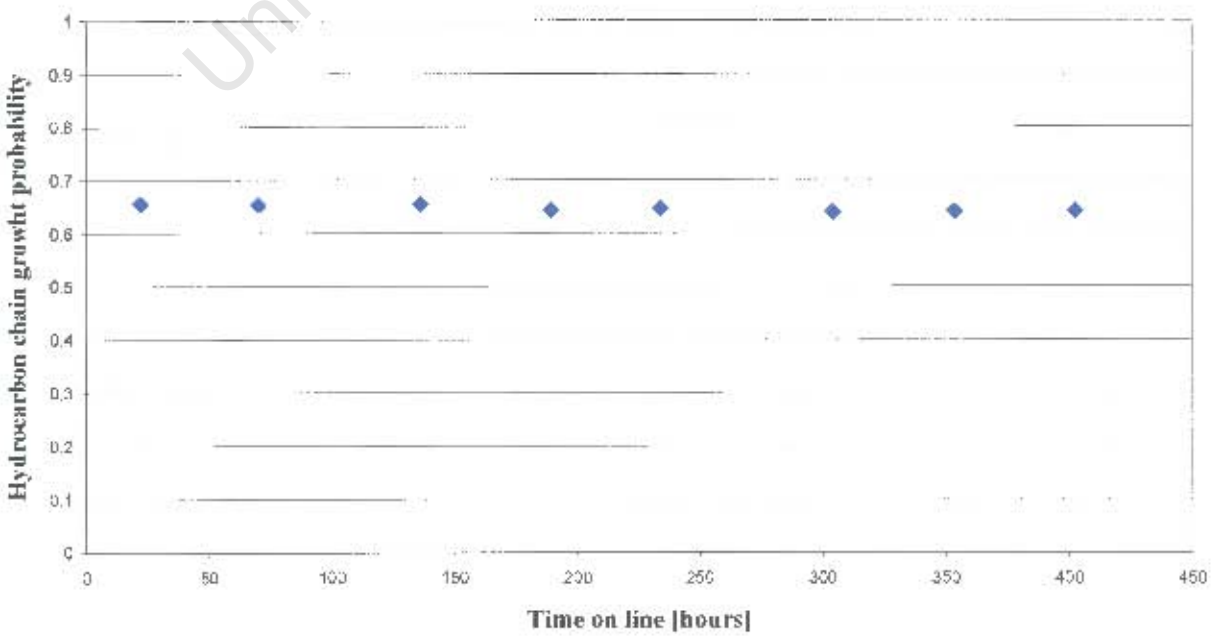


Figure 5.5: Variation in carbon mass balance as a function of time on line – *Baseline FT run*

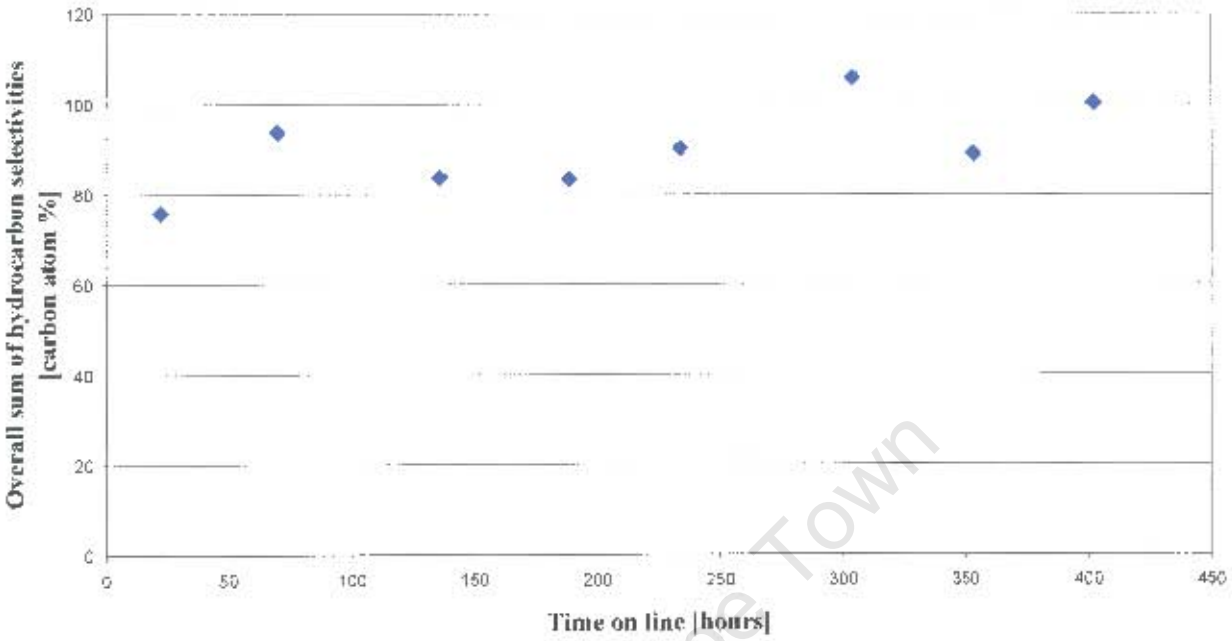


Figure 5.6.1: Hydrocarbon product distribution –
Baseline FT run, 22 hours on line

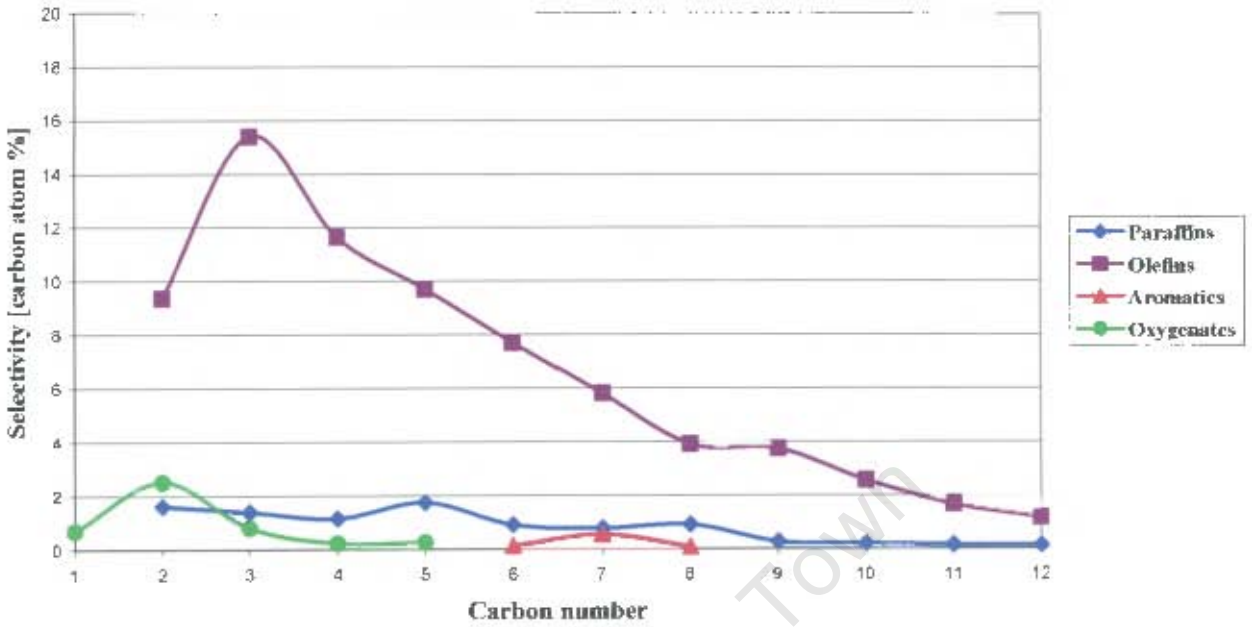


Figure 5.6.2: Hydrocarbon product distribution –
Baseline FT run, 402 hours on line

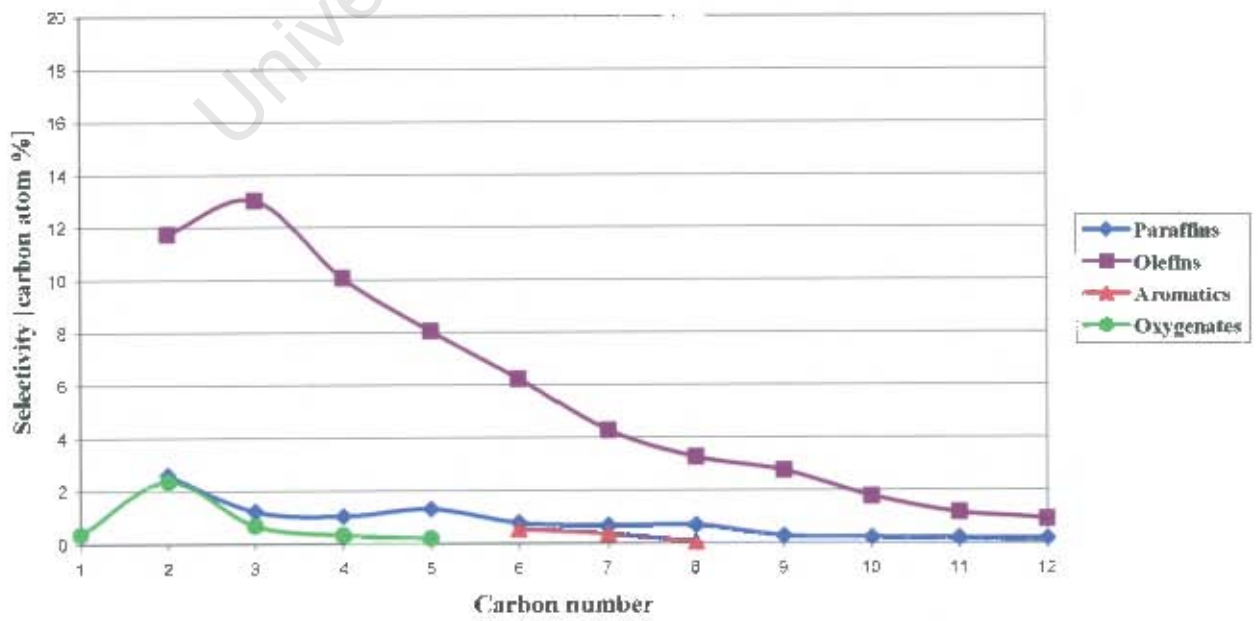


Figure 5.7.1: Methane selectivity as a function of time on line –
Bifunctional process, physical admixture of catalysts

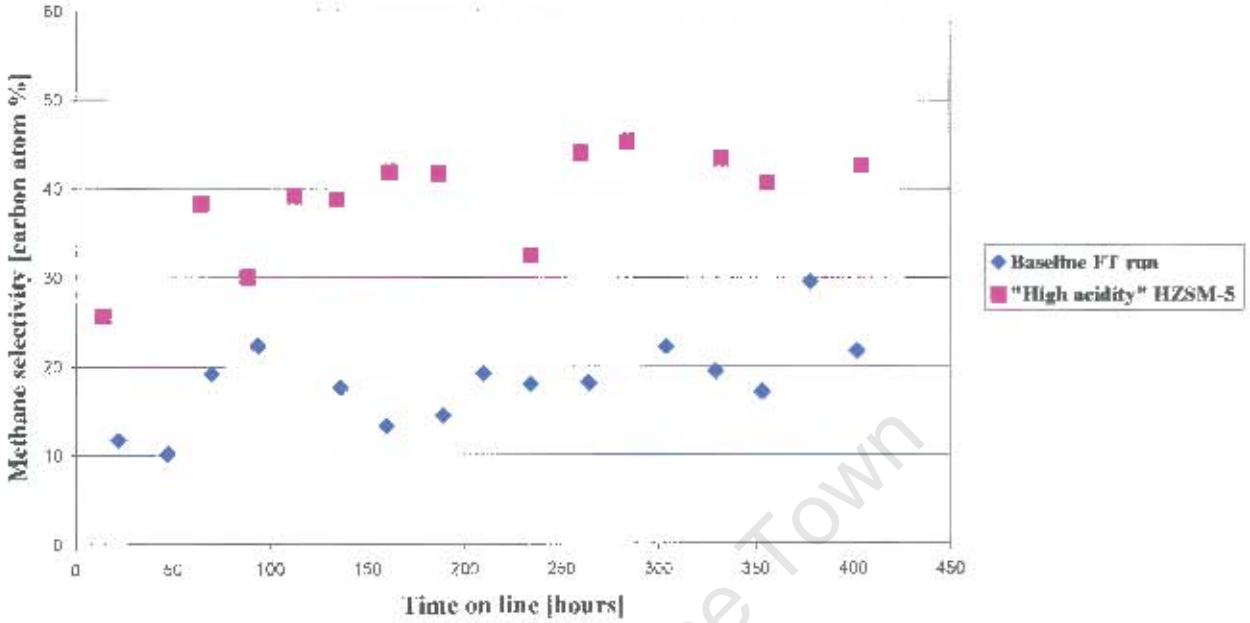


Figure 5.7.2: Hydrogen / carbon ratio of overall hydrocarbon product spectrum as a function of time on line –
Bifunctional process, physical admixture of catalysts

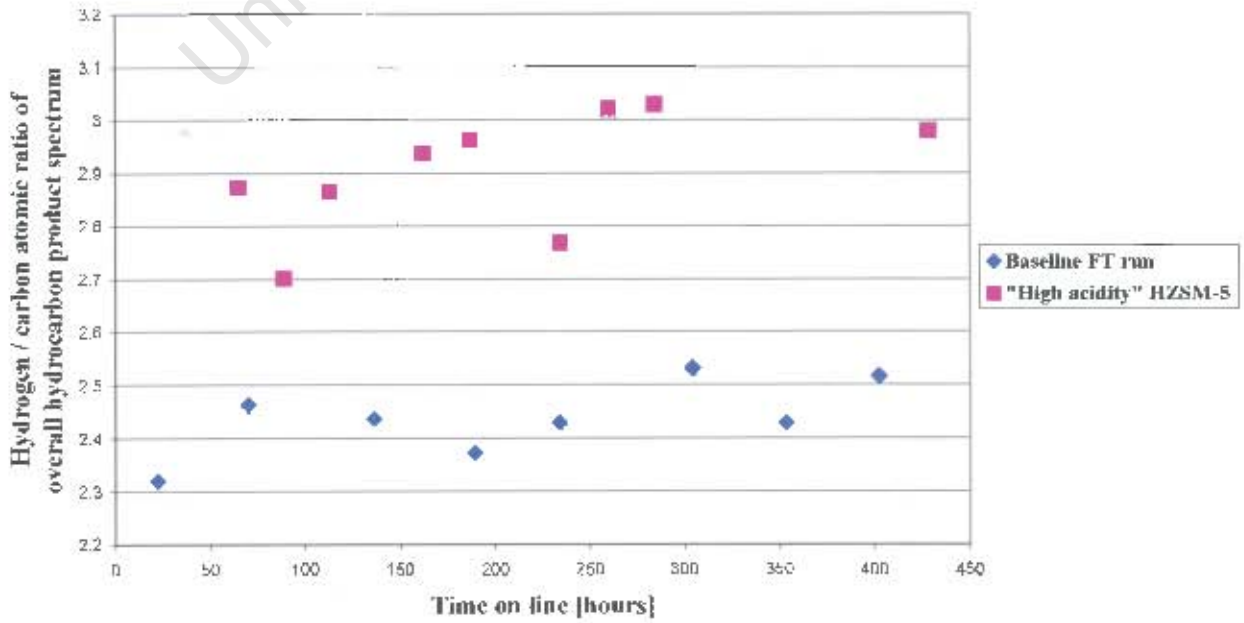


Figure 5.7.3: Hydrogen / carbon ratio of C_{2+} fraction of product spectrum as a function of time on line –
Bifunctional process, physical admixture of catalysts

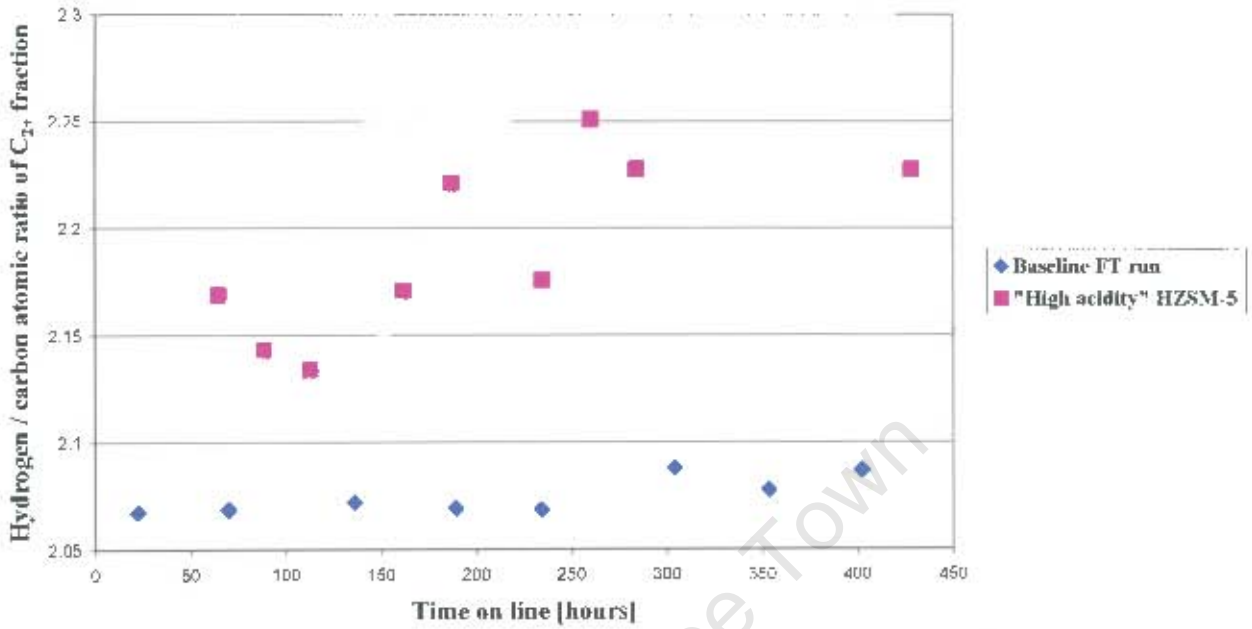


Figure 5.8.1: CO conversion as a function of time on line –
Bifunctional process, physical admixture of catalysts

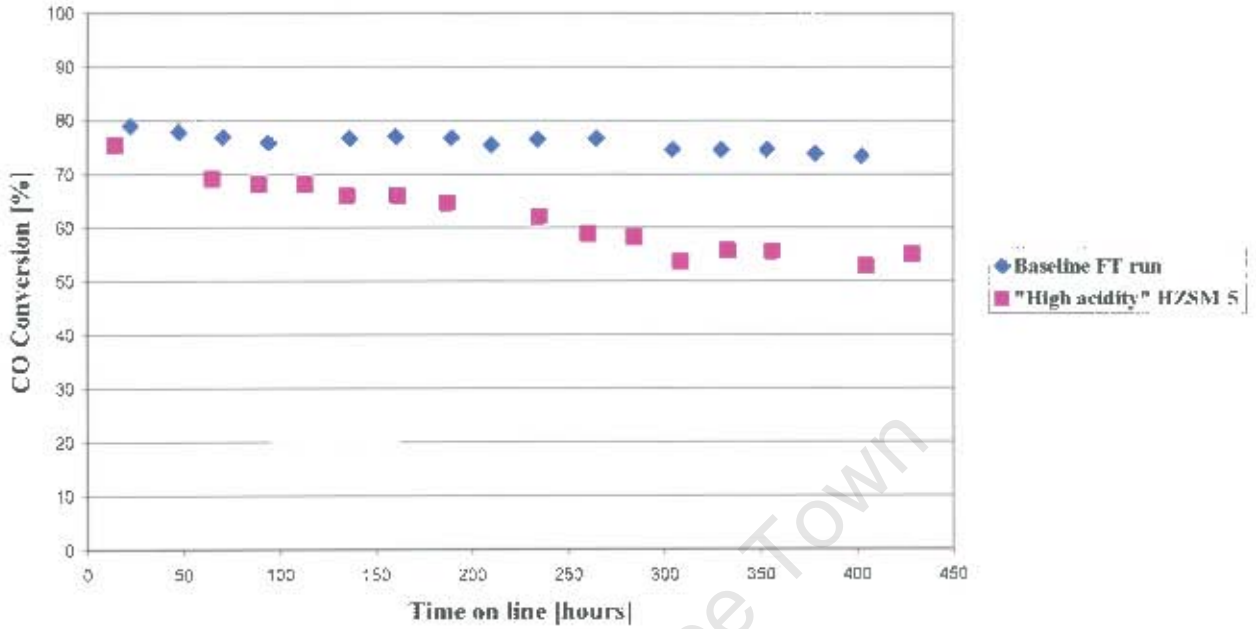


Figure 5.8.2: ($CO+CO_2$) conversion as a function of time on line –
Bifunctional process, physical admixture of catalysts

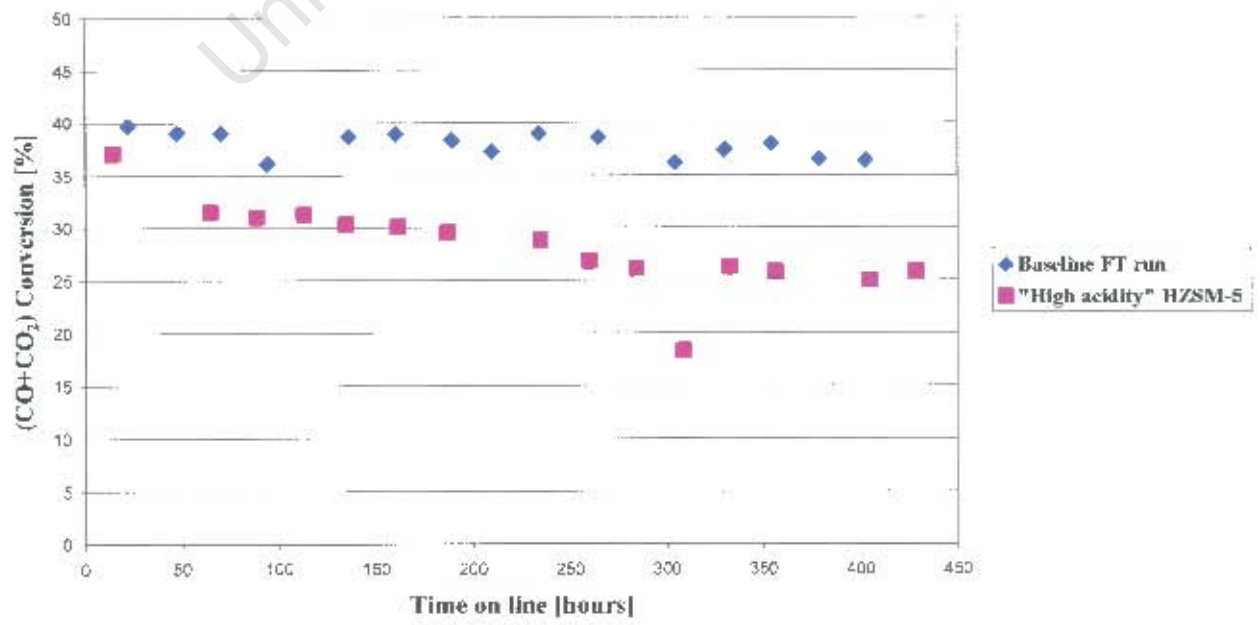


Figure 5.9.1: Hydrocarbon product distribution – *Bifunctional process, "high acidity" HZSM-5, physical admixture of catalysts, 65 hours on line*

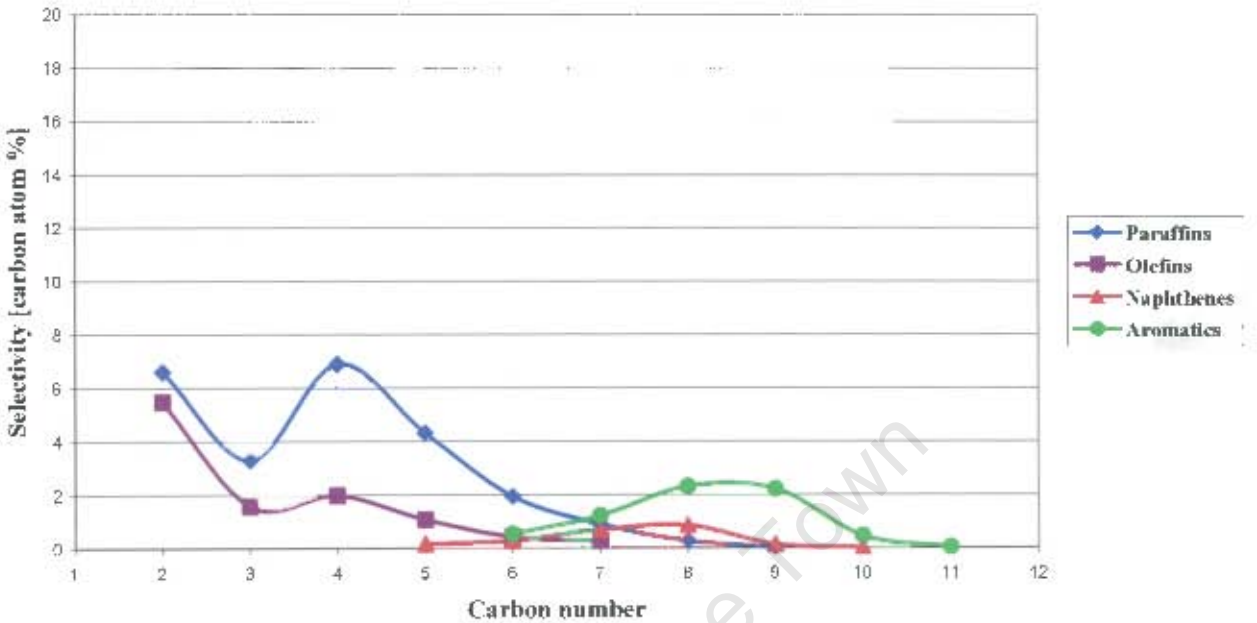


Figure 5.9.2: Hydrocarbon product distribution – *Bifunctional process, "high acidity" HZSM-5, physical admixture of catalysts, 428 hours on line*

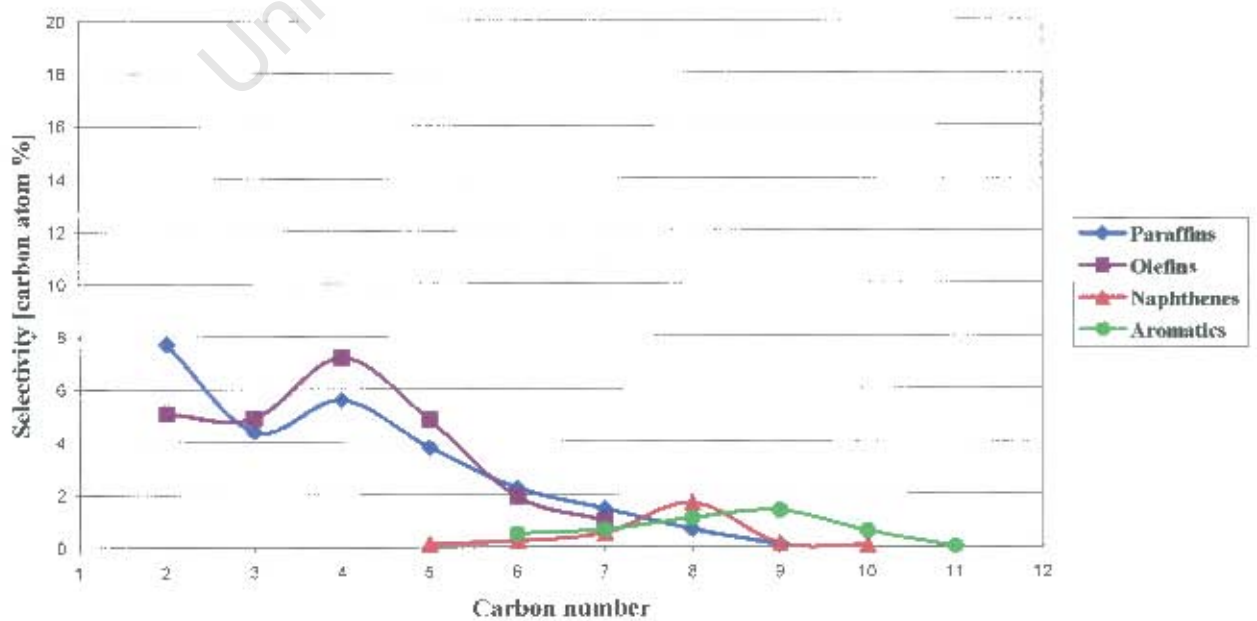


Figure 5.10.1: C_1 to C_4 paraffin selectivity as a function of time on line –
Bifunctional process, physical admixture of catalysts

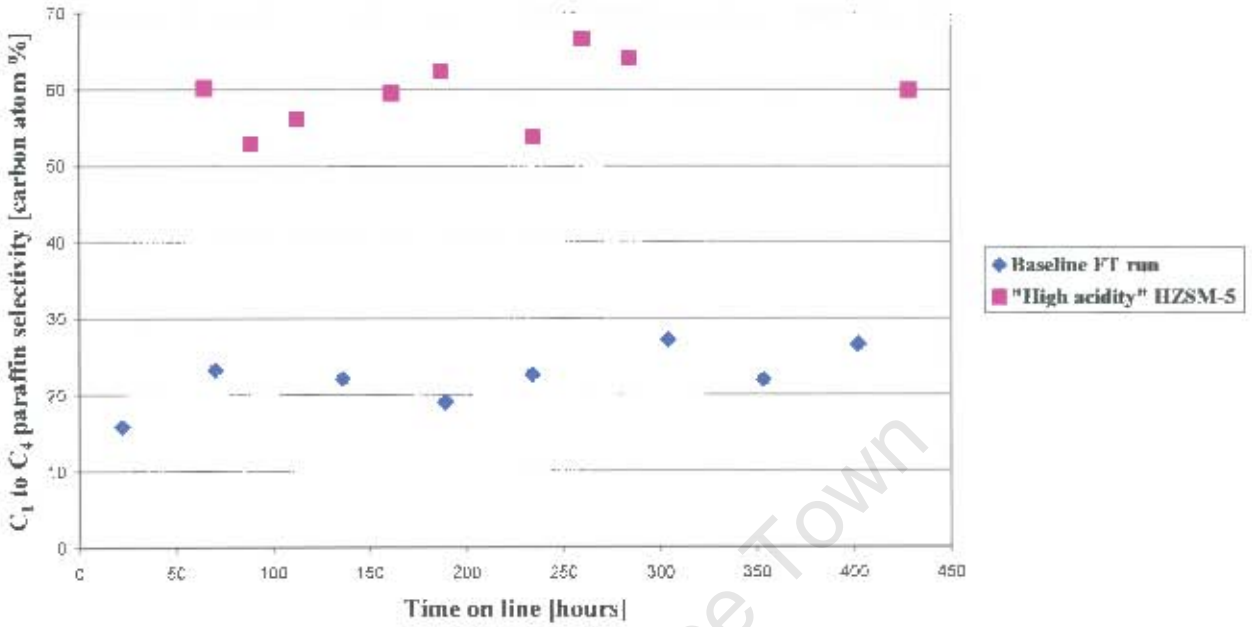


Figure 5.10.2: Gasoline (C_5 to C_{11}) selectivity as a function of time on line –
Bifunctional process, physical admixture of catalysts

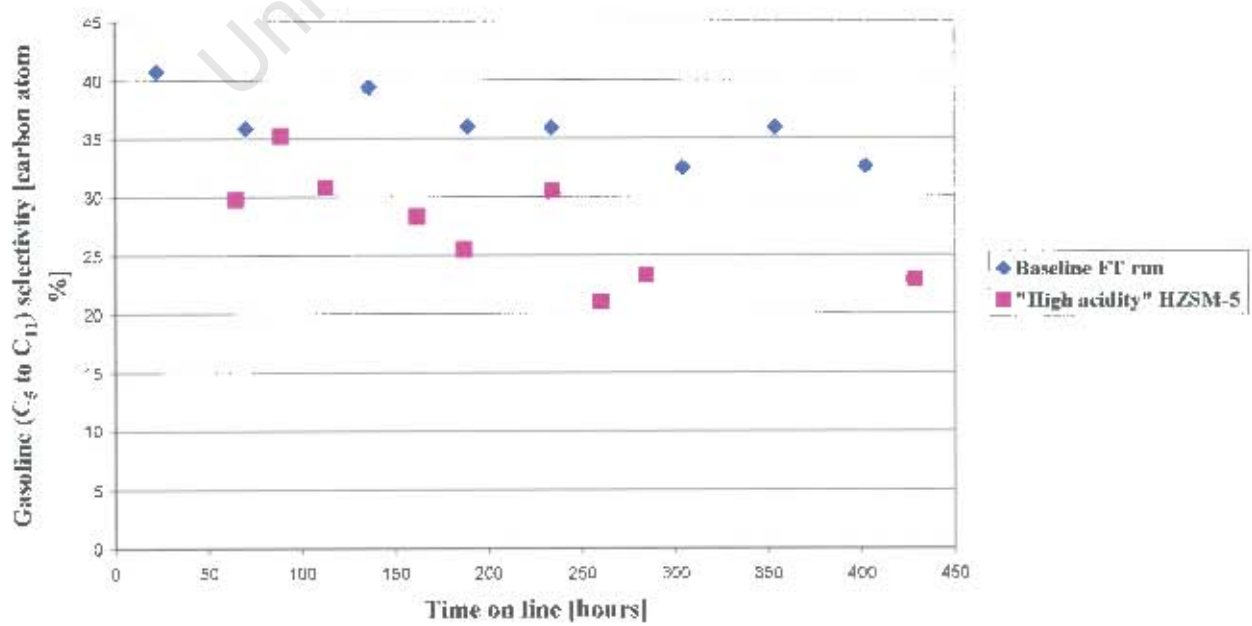


Figure 5.11.1: Methane selectivity as a function of time on line –
Bifunctional process, separate catalyst layers

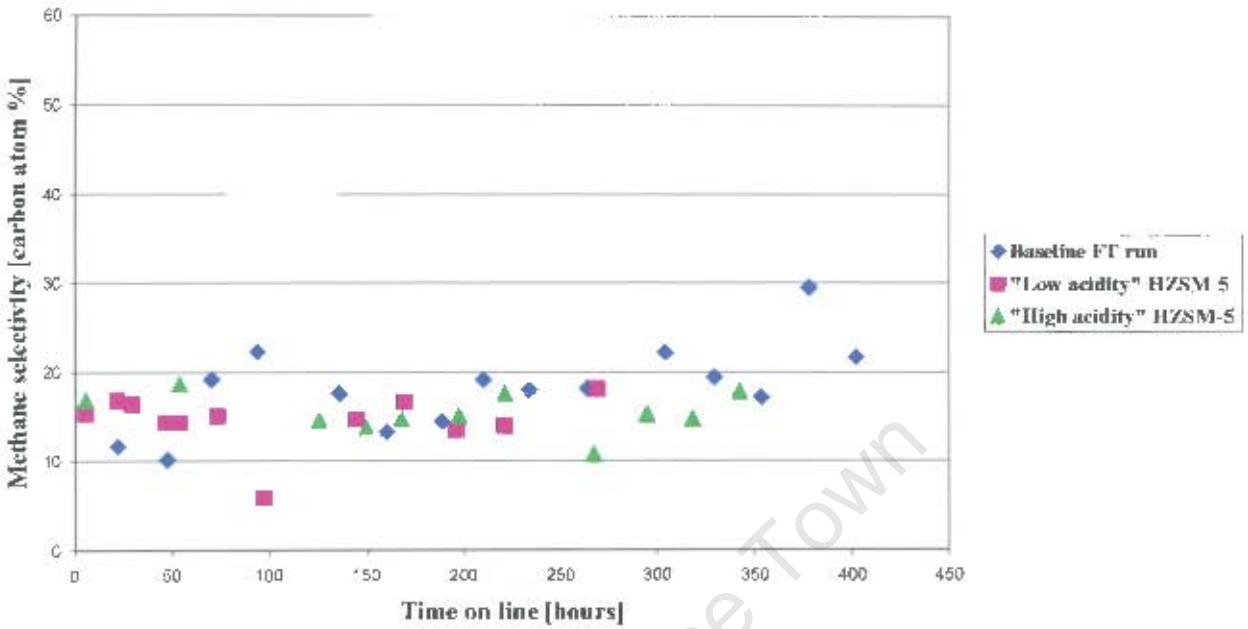


Figure 5.11.2: Hydrogen / carbon ratio of overall hydrocarbon product spectrum as a function of time on line –
Bifunctional process, separate catalyst layers

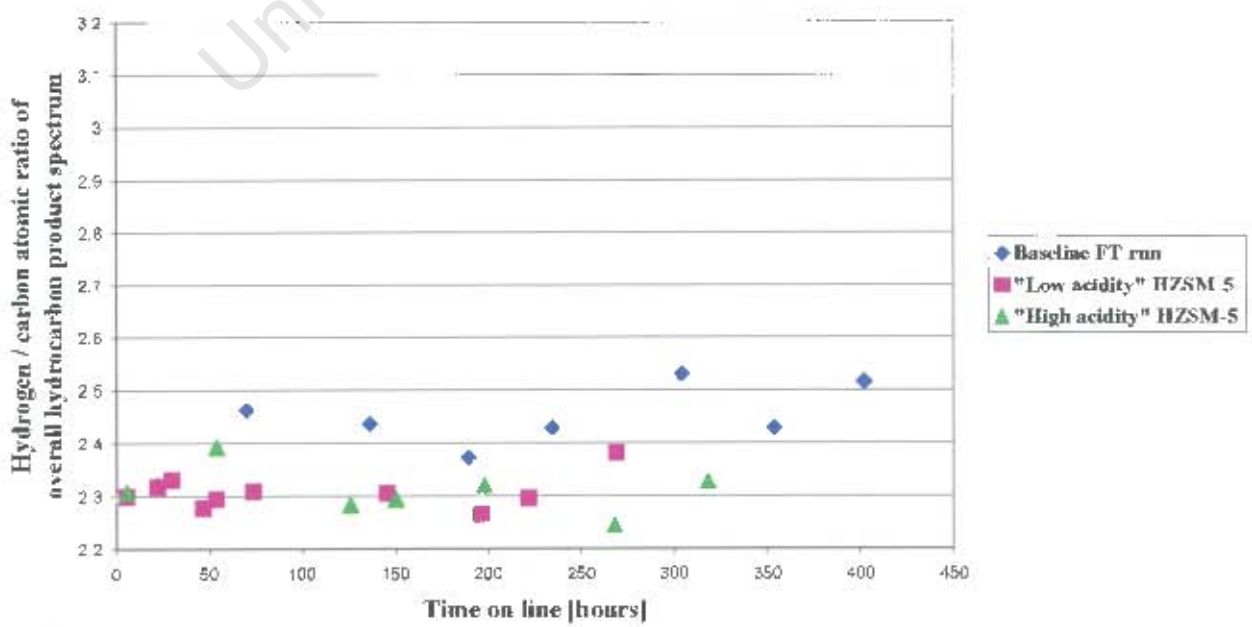


Figure 5.11.3: Hydrogen / carbon ratio of C_{2+} fraction of product spectrum as a function of time on line –
Bifunctional process, separate catalyst layers

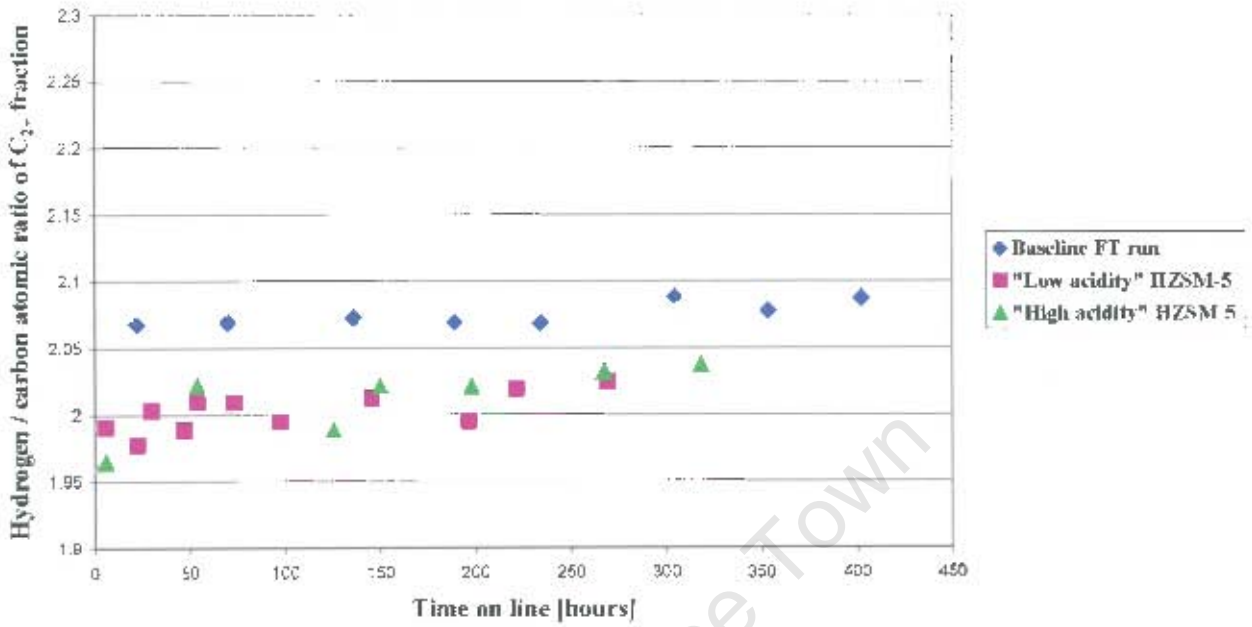


Figure 5.12.1: CO conversion as a function of time on line –
Bifunctional process, separate catalyst layers

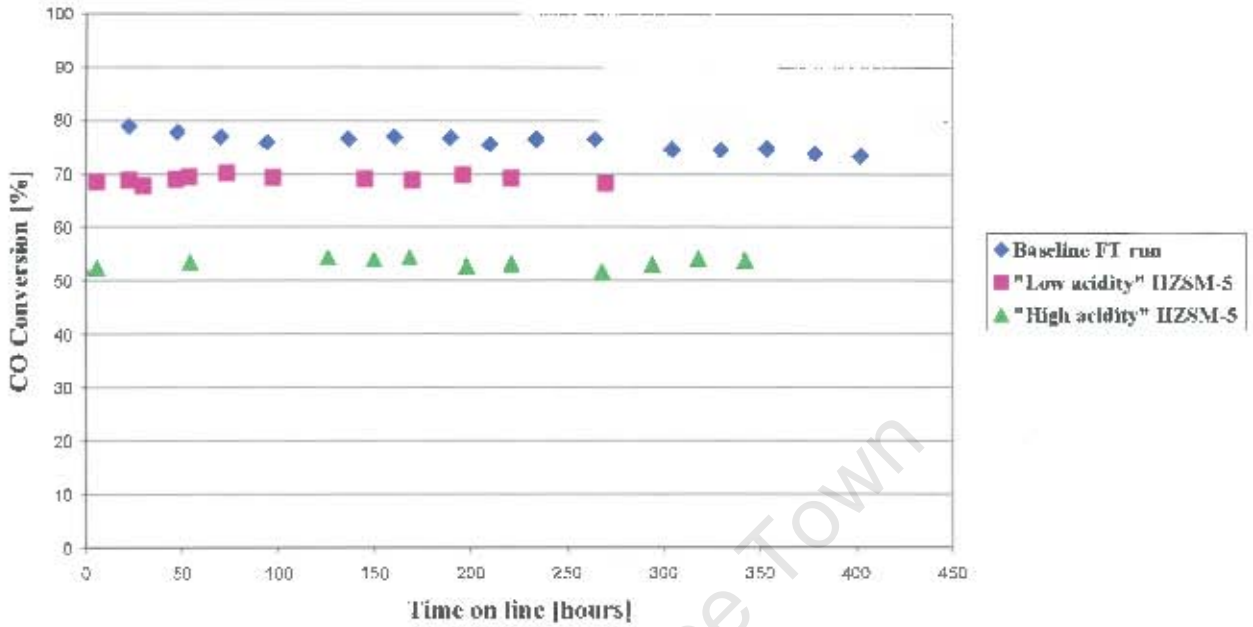


Figure 5.12.2: ($CO+CO_2$) conversion as a function of time on line –
Bifunctional process, separate catalyst layers

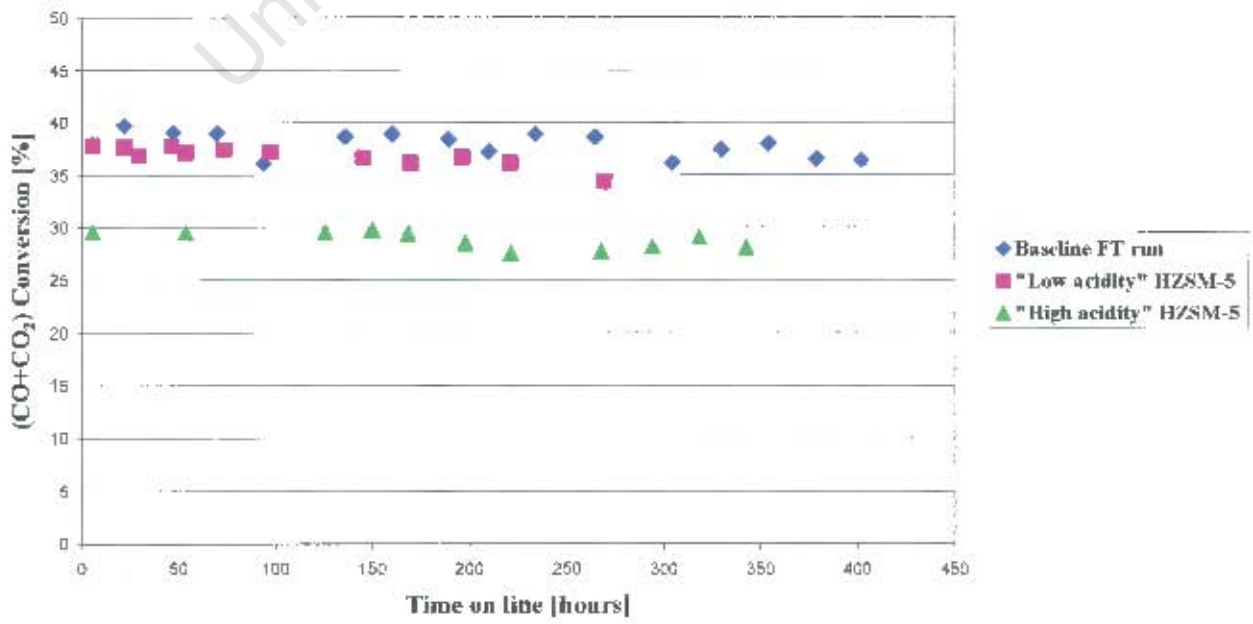


Figure 5.13.1: Propane selectivity as a function of time on line –
Bifunctional process, separate catalyst layers

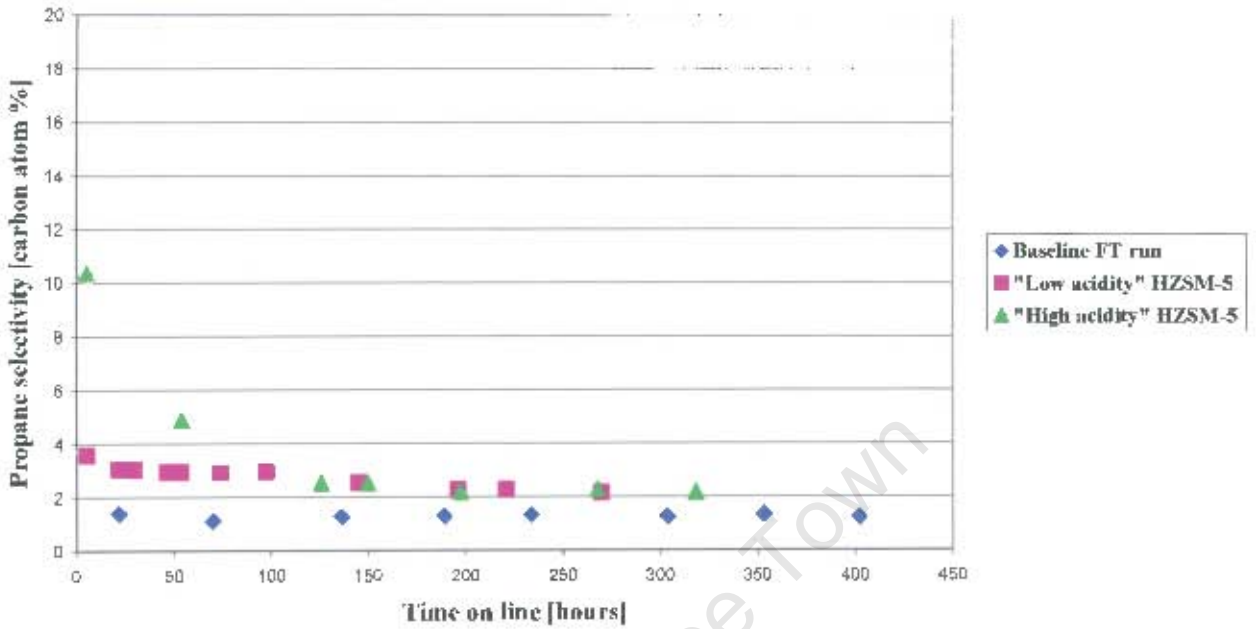


Figure 5.13.2: Propylene selectivity as a function of time on line –
Bifunctional process, separate catalyst layers

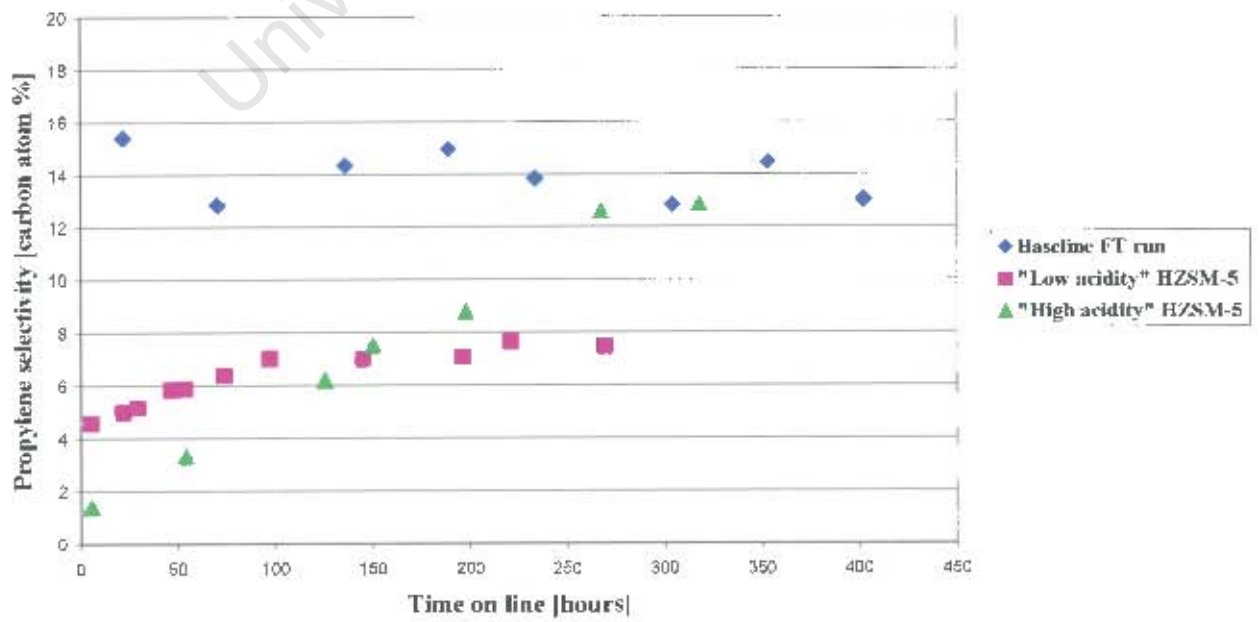


Figure 5.14.1: Linearity of C_6 paraffin fraction as a function of time on line –
Bifunctional process, separate catalyst layers

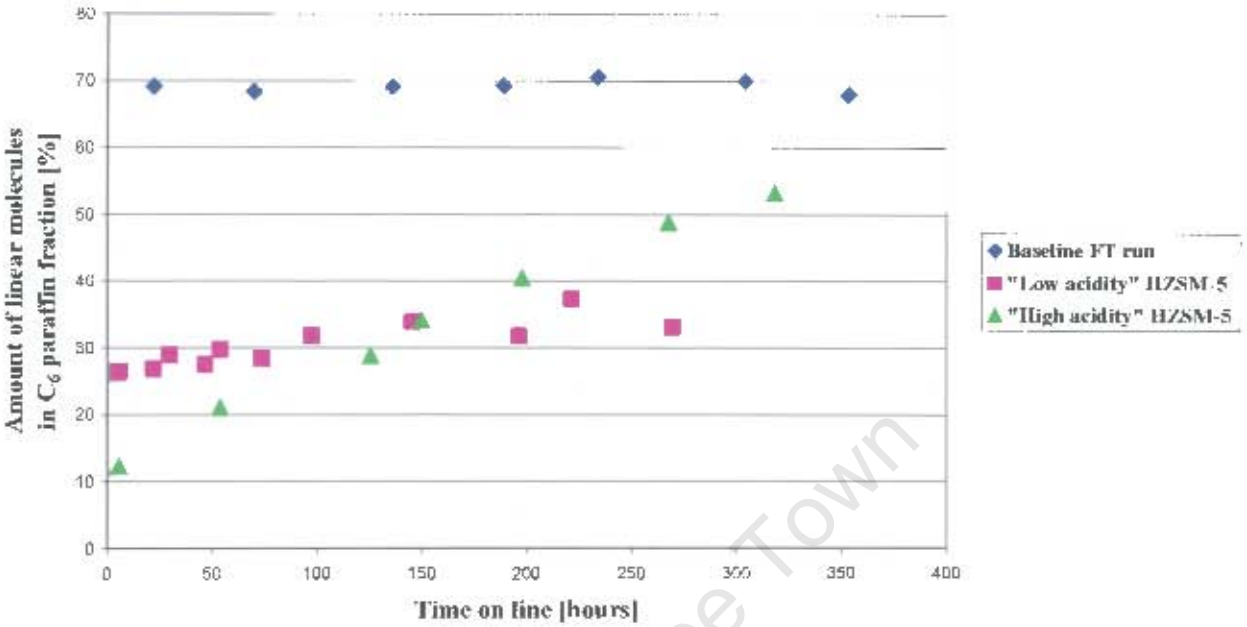
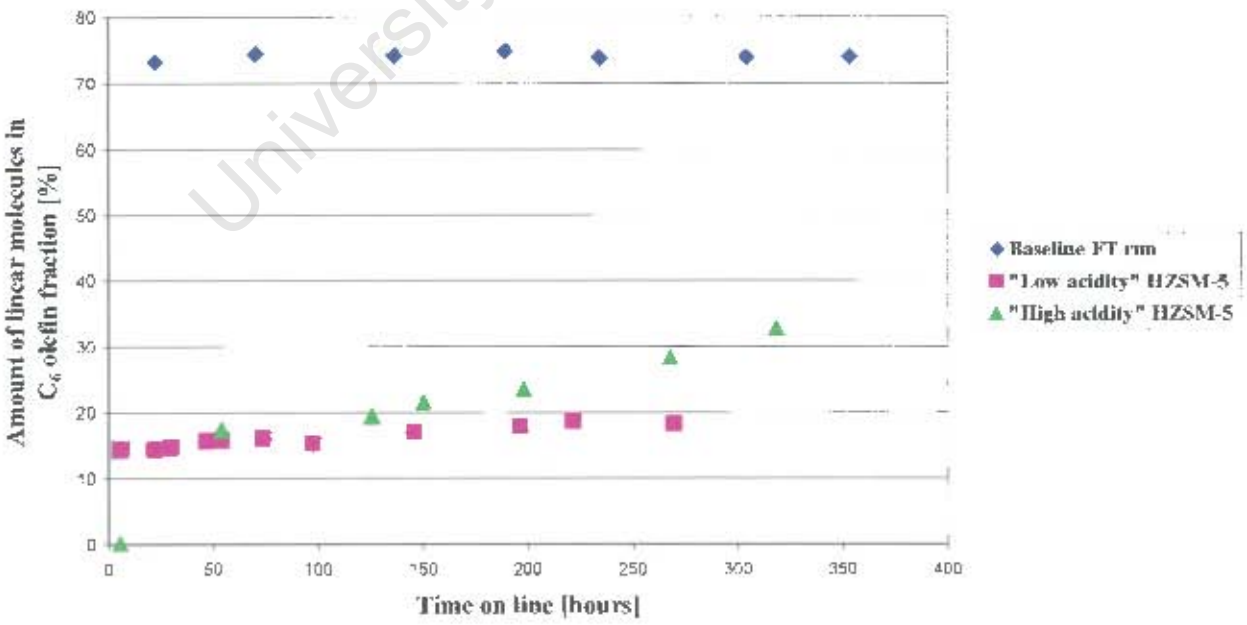


Figure 5.14.2[iv]: Linearity of C_6 olefin fraction as a function of time on line –
Bifunctional process, separate catalyst layers



[iv] The data point that reports a 0 % linearity for olefins in the C_6 fraction is somewhat artificial. If the overall selectivity of the linear C_6 olefins is very low, the peaks on the chromatogram are so small that they are not integrated.

Figure 5.15: Aromatic content of C_8 carbon number fraction as a function of time on line –
Bifunctional process, separate catalyst layers

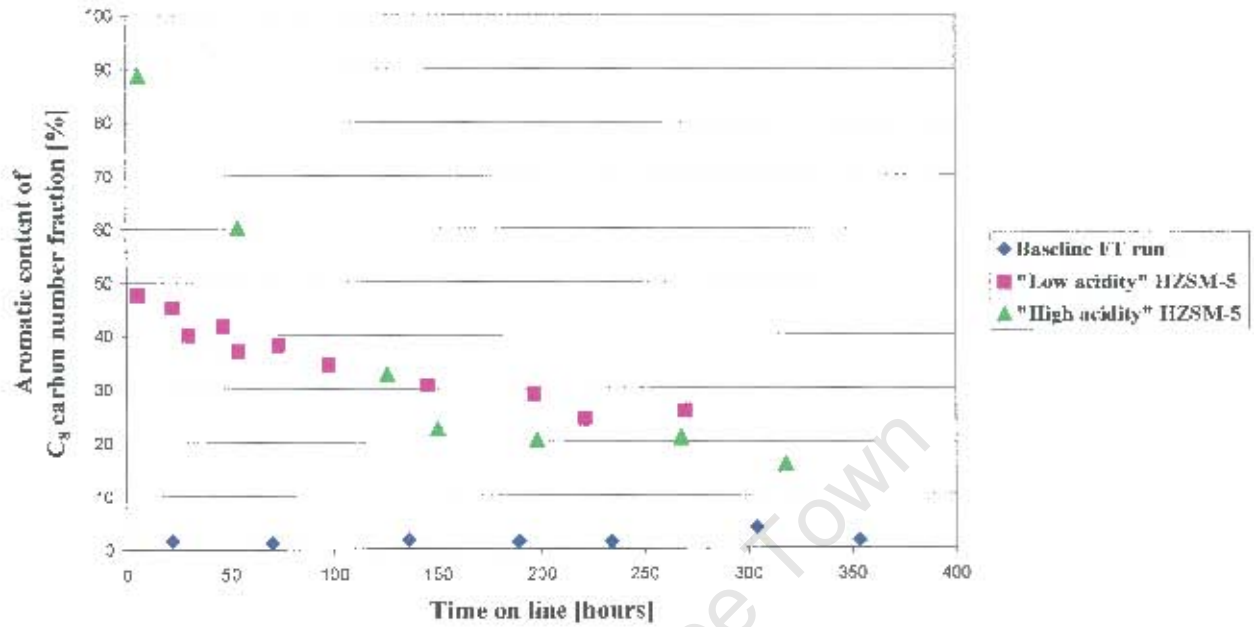


Figure 5.16.1: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZSM-5, separate catalyst layers, 5 hours no line

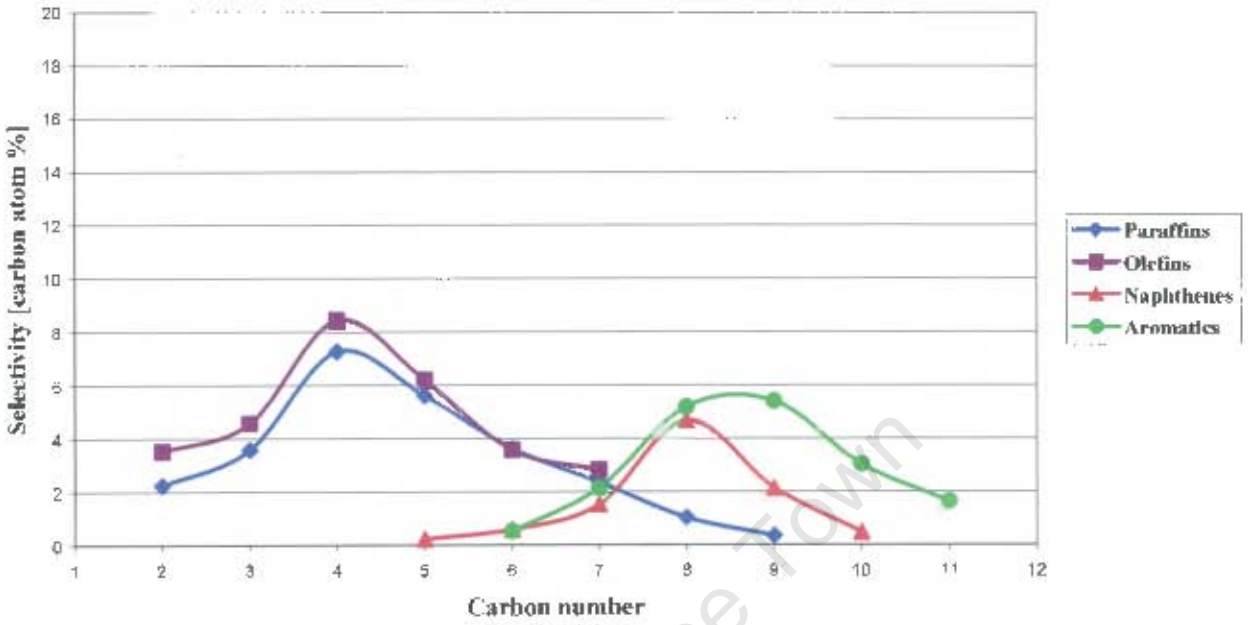


Figure 5.16.2: Hydrocarbon product distribution –
Bifunctional process, "low acidity" HZSM-5, separate catalyst layers, 269 hours no line

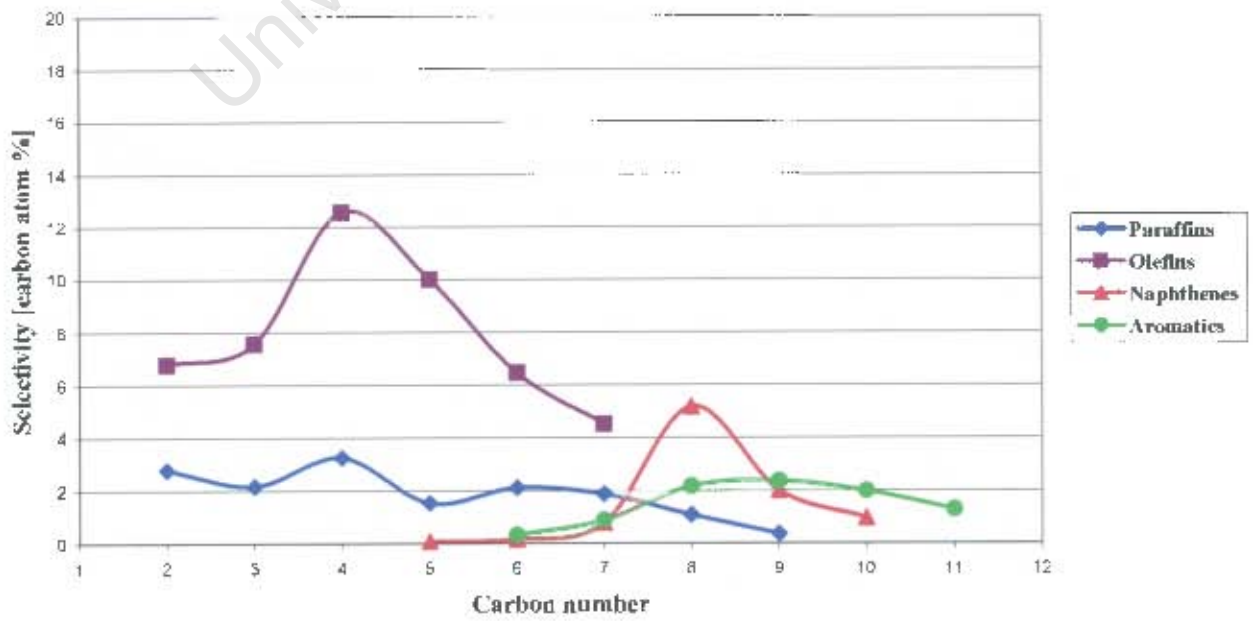


Figure 5.17.1: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZSM-5, separate catalyst layers, 6 hours no line

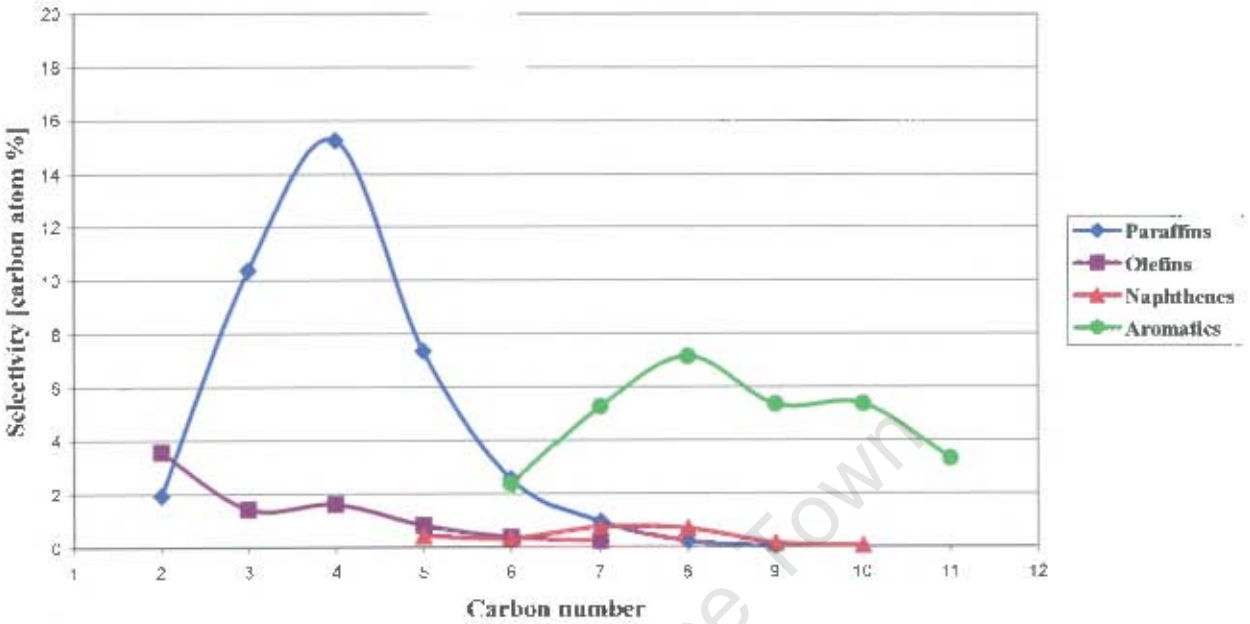


Figure 5.17.2: Hydrocarbon product distribution –
Bifunctional process, "high acidity" HZSM-5, separate catalyst layers, 268 hours no line

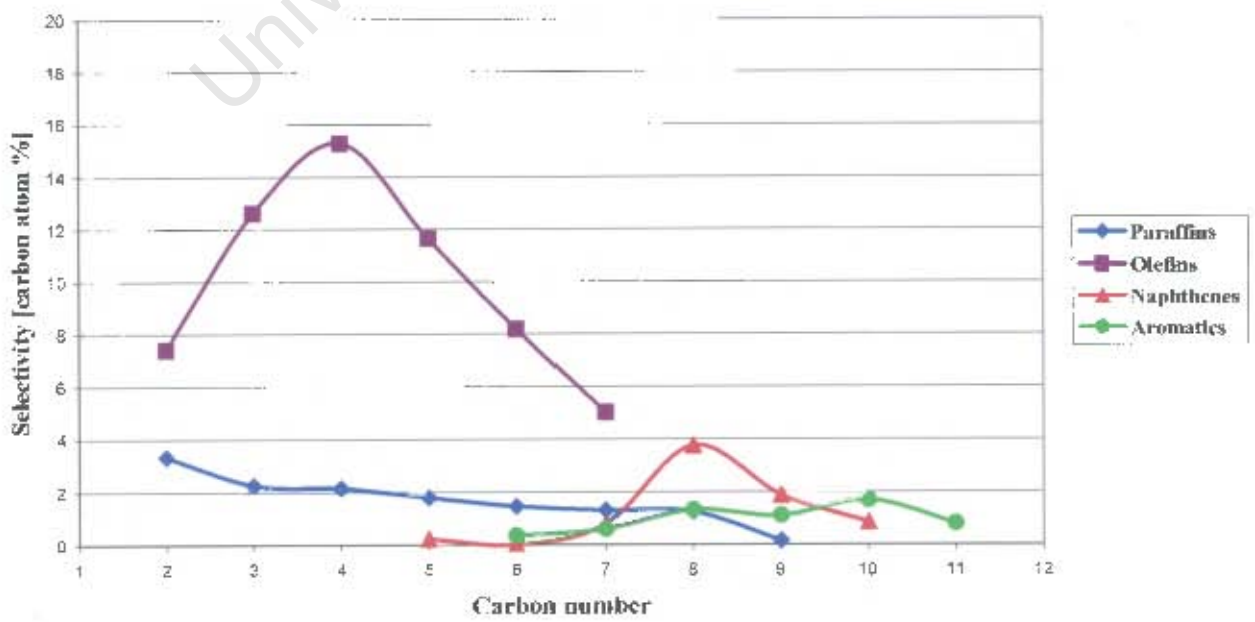


Figure 5.18.1: Overall carbon number distribution –
Bifunctional process, separate catalyst layers,
Beginning of run (active HZSM-5)

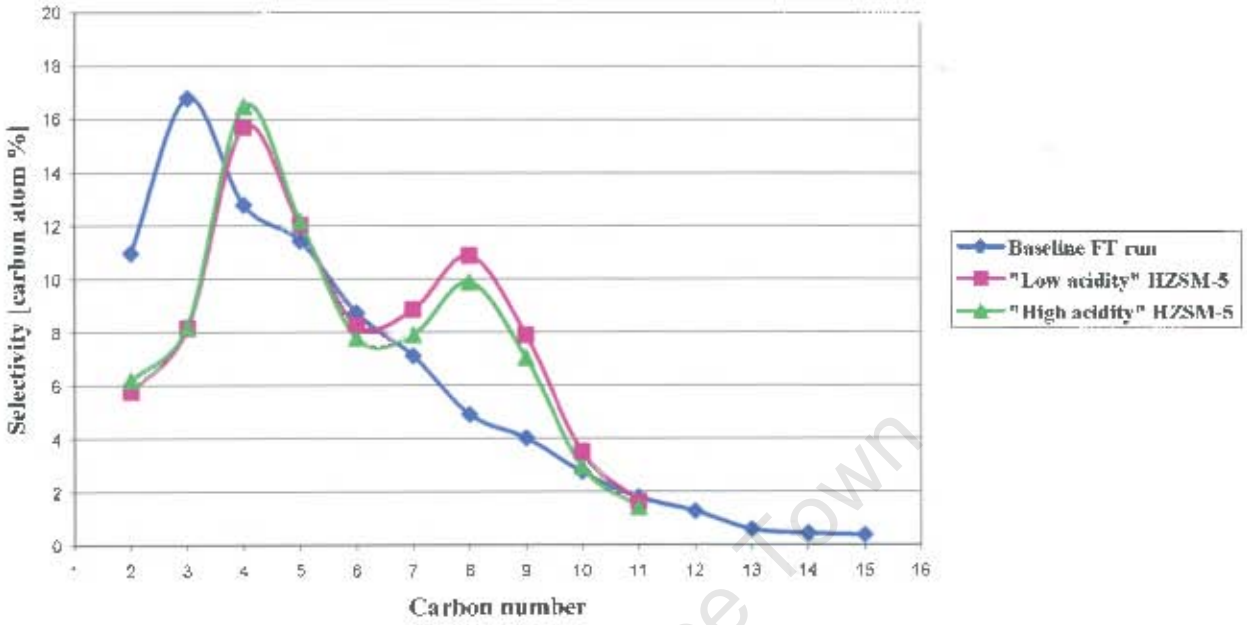


Figure 5.18.2: Overall carbon number distribution –
Bifunctional process, separate catalyst layers,
End of run (deactivated HZSM-5)

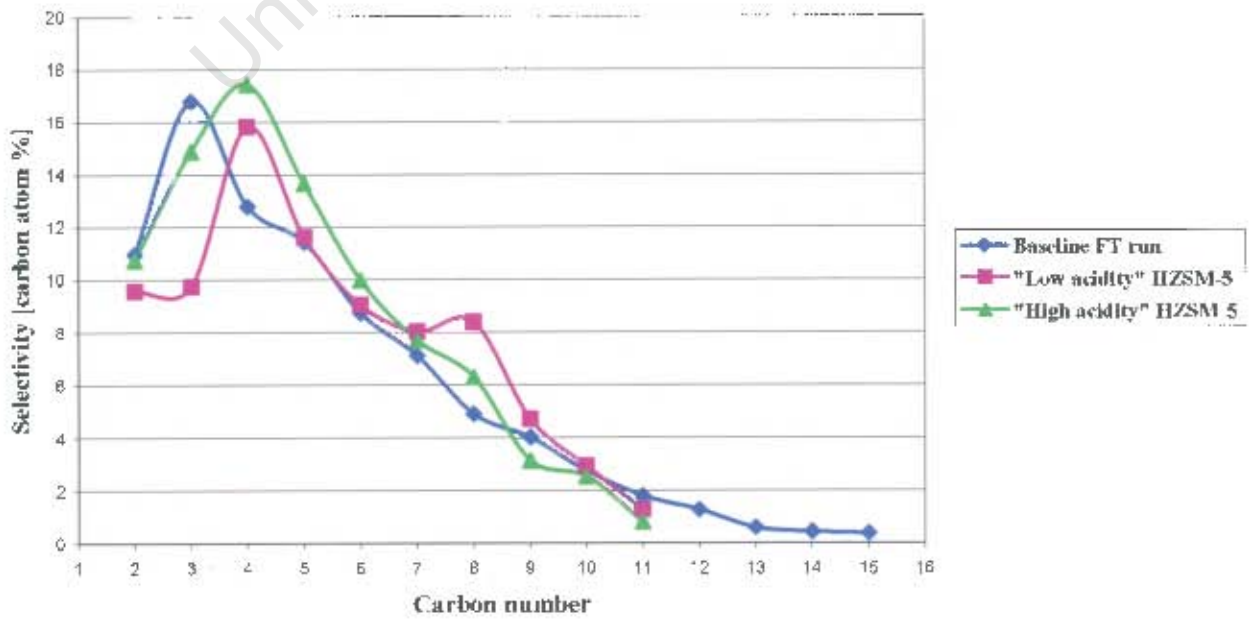


Figure 5.19: Gasoline (C_5 to C_{11}) selectivity as a function of time on line –
Bifunctional process, separate catalyst layers

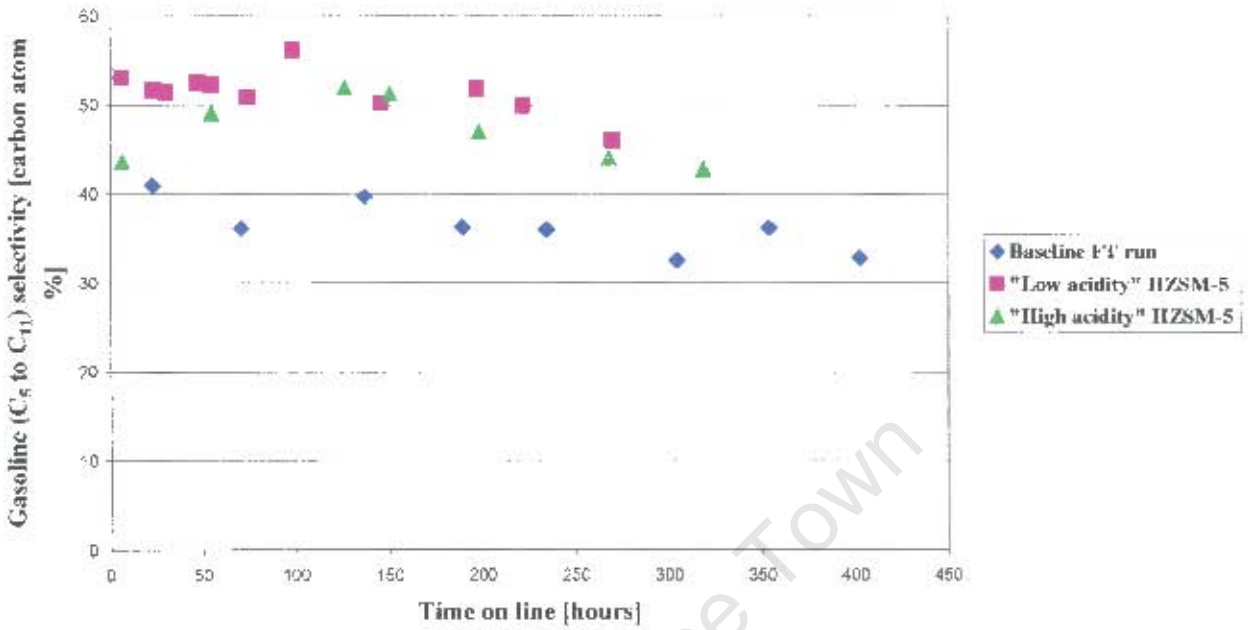


Figure 5.20.1: Benzene content of C_5 to C_{11} fraction as a function of time on line –
Bifunctional process, separate catalyst layers

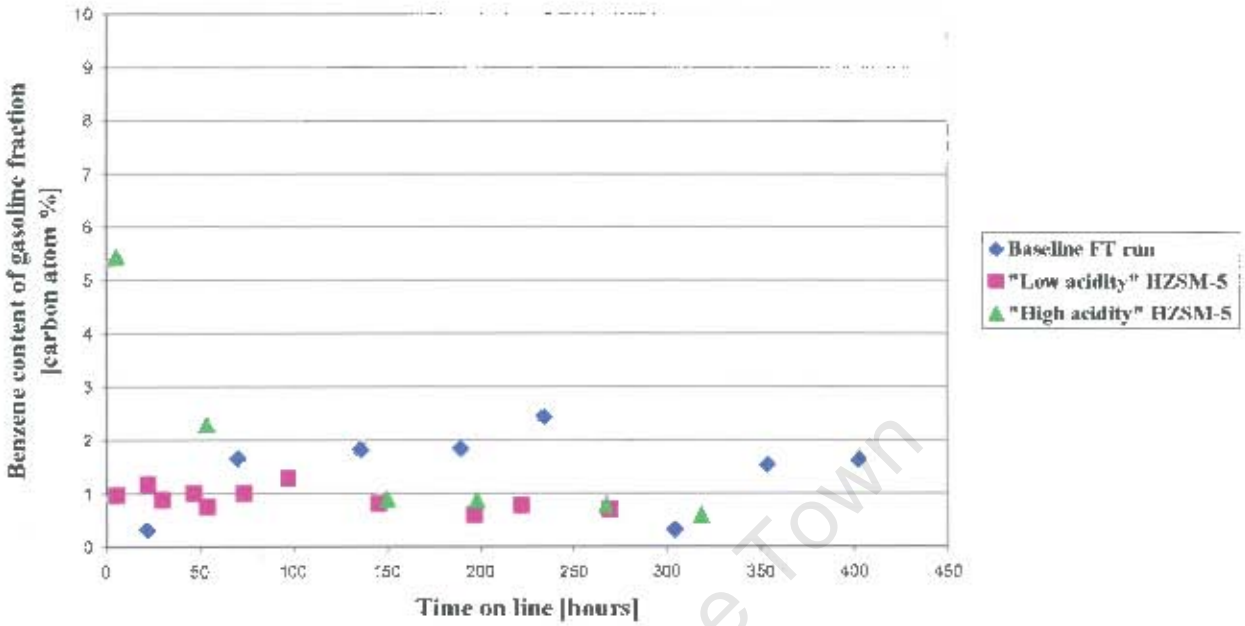


Figure 5.20.2: BTXE aromatic content of C_5 to C_{11} fraction as a function of time on line –
Bifunctional process, separate catalyst layers

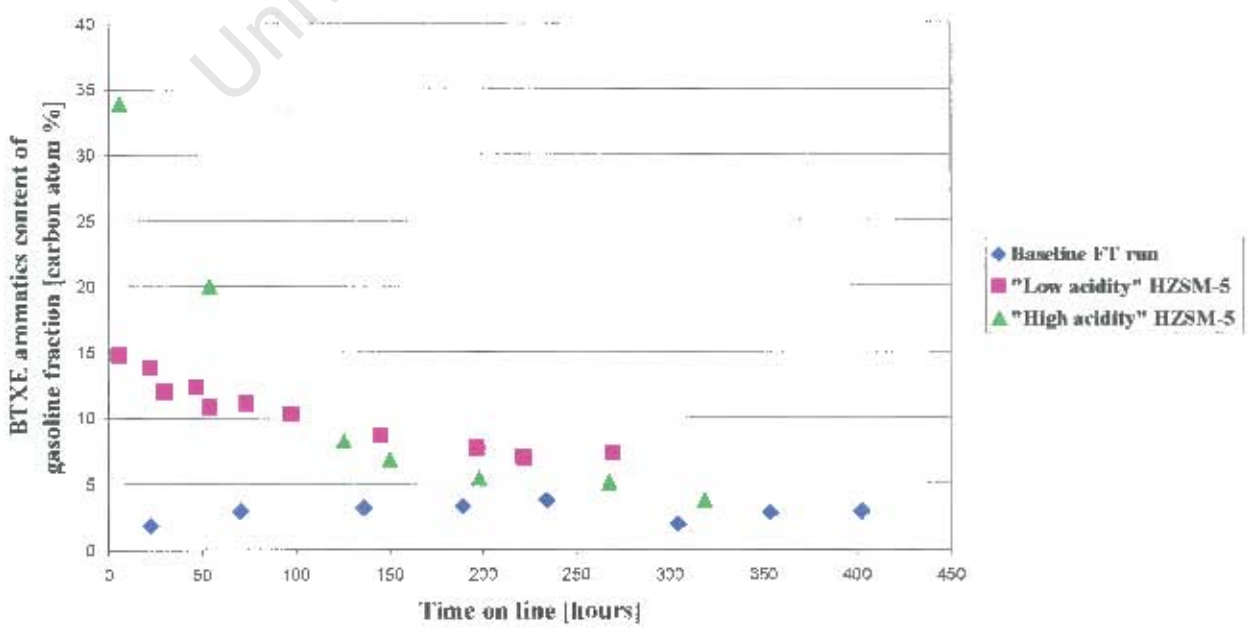


Figure 5.20.3: Total aromatic content of C_5 to C_{11} fraction as a function of time on line –
Bifunctional process, separate catalyst layers

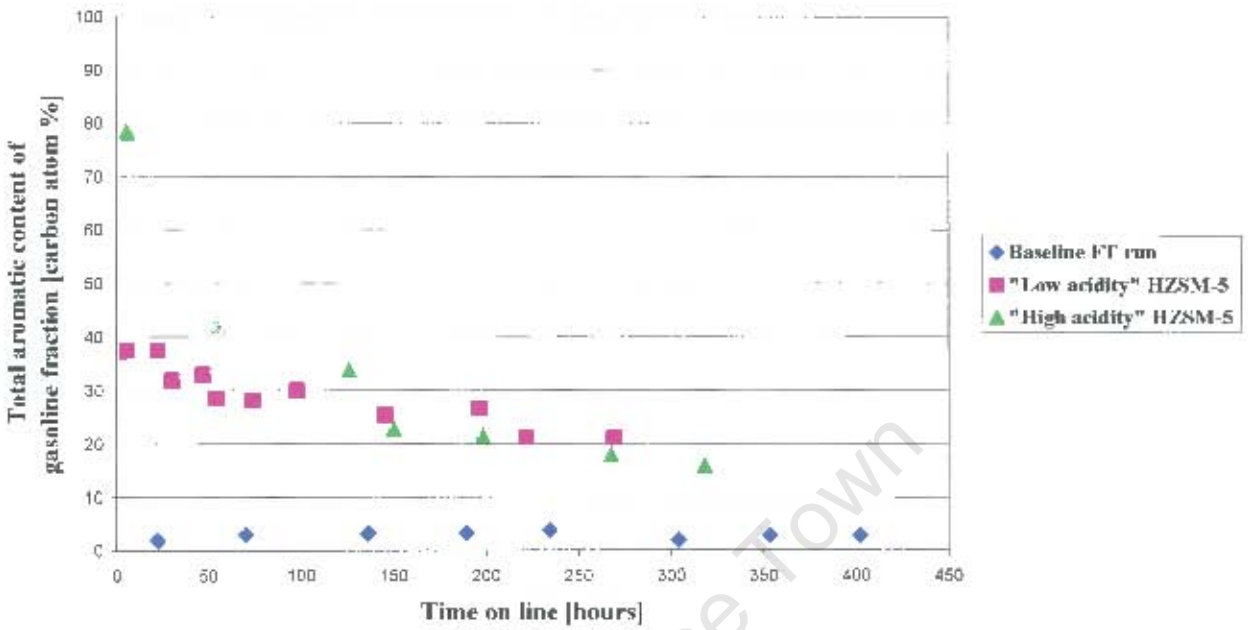
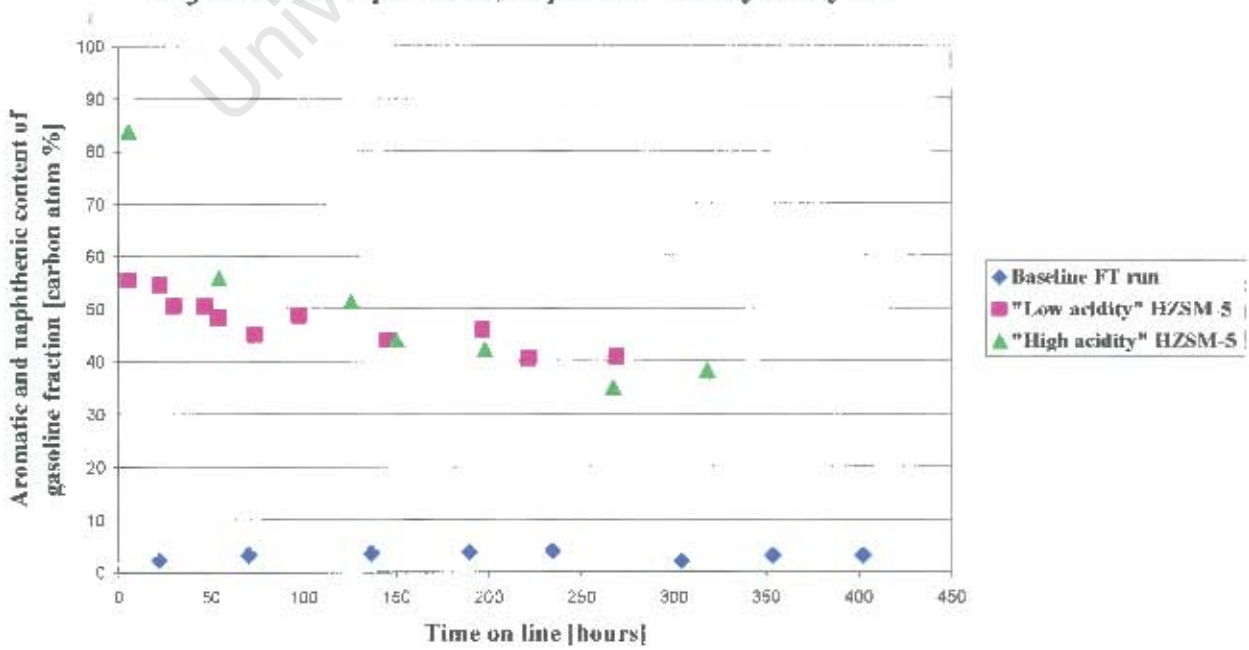


Figure 5.20.4: Total aromatic and naphthenic content of C_5 to C_{11} fraction as a function of time on line –
Bifunctional process, separate catalyst layers



CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This final chapter summarises the most important conclusions of the investigation into the addition of an acidic co-catalyst to the Fischer-Tropsch process. Some recommendations for future research will also be presented.

6.1 LITERATURE SURVEY

6.1.1 Proof of the concept

Numerous papers and patents have been published on the combination of the FT process with an acidic co-catalyst. For the most part, the expected improvements in the gasoline selectivity and quality have been realised. In some of the studies, gasoline-range product that forms nearly 70% of the total hydrocarbon product spectrum has been obtained (*Udaya*, 1990). This is a vast increase over the theoretical maximum gasoline selectivity of 48% that can be attained with the traditional FT process (*Dry*, 1981). The high aromatic content of the liquid fraction also implied a much higher octane value, and research octane numbers for the liquid product in excess of 90 have been reported in some publications (*Udaya*, 1990). This proves in principle that the bifunctional process has enormous benefits over the normal FT process as far as gasoline production is concerned.

6.1.2 Choice of catalysts

A variety of Fischer-Tropsch catalysts has been tested as the syngas conversion function of the bifunctional process (*Udaya*, 1990). However, in order to obtain the desired hydrocarbon reactions over acid catalysts, reaction temperatures above 300°C are generally needed (*Guan* et al., 1996; *Müller* et al., 1982). Therefore, if the two catalytic functions of the bifunctional process are to be contained in the same reactor, the Fischer-Tropsch catalyst would be required to have an acceptable selectivity (low methane selectivity and high selectivity towards olefinic and heavier hydrocarbons) at this high operating temperature. Cobalt and ruthenium as Fischer-Tropsch catalysts have very high methane selectivities at such high temperatures, while the increase in methane formation with increasing temperature is less excessive for iron based FT catalysts (*Schulz*, 1999). Furthermore, iron catalysts need alkali promotion to attain the desired activity and selectivity (*Schulz*, 1999). It is therefore concluded that an alkali promoted iron catalyst currently seems to be the only feasible choice of FT catalyst for a bifunctional process where the two catalytic functions are contained in the same reactor.

Even though different types of acid catalysts have been employed for the purpose of the bifunctional process, ZSM-5 has been the most popular choice by far. The reasons are its shape selective properties that essentially limit the liquid fraction of the product spectrum to the gasoline boiling range, the high acidity which gives it a high activity for acid catalysed reactions, its resistance to coke formation and its

hydrothermal stability (*Jothimurugesan* et al., 1998; *Udaya* et al., 1990). In view of the above, it appears as though the combination of an alkali promoted iron catalyst and an HZSM-5 zeolite is the most feasible bifunctional catalyst system for gasoline production.

6.1.3 Technical challenges

There are two important technical challenges associated with combining an alkali promoted iron catalyst and an acidic zeolite in one reactor. The alkali promoters of an iron FT catalyst are mobile under reduction and synthesis conditions and migration of the alkali to the zeolite, with subsequent poisoning of the acid sites, have been cited as one of the technical problems of the iron / HZSM-5 bifunctional system (*Butter* et al., 1981). A further aspect that requires attention is the regeneration of the bifunctional system, most importantly to restore the activity of the coked zeolite. One way to reactivate the acid catalyst is to burn off the carbonaceous deposits. However, the iron FT catalyst must be in the reduced state to perform adequately; consequently, the oxidative treatment must be followed by a reduction step (*Schulz* et al., 1991). Since such a two-step regeneration procedure is not desirable for a commercial process, the technical challenge is thus to either prolong the lifetime of the acid catalyst or to devise a commercially viable regeneration procedure.

6.2 Experimental study

6.2.1 The experimental set-up

The fixed bed microreactor and the precipitated iron catalyst used for the preliminary investigation was clearly not an adequate experimental set-up to study the addition of HZSM-5 to the HTFT process. Carbon deposition on the iron catalyst led to plugging of the packed bed. The experiments normally had to be shut down after a few days of synthesis due to an increase in the pressure drop over the reactor. For temperature control purposes, the temperature was measured above the entrance to the bed (and not inside the bed itself). Due to the highly exothermic nature of the Fischer-Tropsch reaction, the temperature inside the bed might well have exceeded the set-point, which would have increased the rate of carbon deposition. The physical mixture of HZSM-5 powder with the iron catalyst aggravated the operating problems of the fixed bed reactor. Apparently, the fine zeolite powder decreased the void space of the reactor bed, so that the deposition of carbon on the iron catalyst plugged the bed more quickly. The deposited carbon not only affected the operation of the process, but also had a serious influence on the synthesis performance of the FT catalyst. Due to the migration of alkali from the iron catalyst to the carbon, the performance of the FT catalyst became consistent with that of a low alkali catalyst, producing a light, paraffinic product spectrum that would not be acceptable for a commercial process. Furthermore, the erratic variations in the CO conversion observed during the course of most of the bifunctional process runs in the fixed bed reactor were ascribed to a maldistribution of gas due to the formation of channels in the packed bed.

Even though there are various ways in which the operation of the fixed bed reactor may be improved, the final experimental study was rather performed in a Berty

mircoreactor. The high internal gas recycle rate of this type of reactor ensures that the reaction heat is dissipated effectively, so that significant temperature gradients in the catalyst layer are avoided. Furthermore, a fused iron catalyst (the same type of catalyst used for Sasol's commercial HTFT process) was employed during the Berty study. For the Berty experimental set-up, a baseline FT run was performed for which the conversion, the methane selectivity and the olefin content of the product spectrum were fairly constant over two weeks of synthesis. The stability of the iron catalyst with respect to activity and selectivity therefore showed that this experimental set-up was quite appropriate to study the traditional HTFT process, as well as the addition of an acidic co-catalyst to the process. In view of these findings, it was concluded that the characteristics of the Berty microreactor and the stability of the fused iron catalyst made this experimental set-up a more preferred choice than the fixed bed microreactor with the precipitated iron catalyst for the purpose of studying the bifunctional process at HTFT operating conditions.

6.2.2 The effect of contact between the catalytic functions

During both the fixed bed and the Berty experimental programs, it was found that an intimate contact between the two catalytic functions of the bifunctional process resulted in extensive alkali migration from the iron catalyst to the zeolite. However, because of the low alkali content the iron catalyst, this migration did not have such a significant poisoning effect on the zeolite as was anticipated in the literature, but rather depleted the iron catalyst of alkali. The result was a severe shift in the selectivity of the FT catalyst towards light paraffins that cannot readily be converted to higher value products by the zeolite. The selectivity of the light paraffins was so high that the commercial viability of a bifunctional process in this mode is doubtful. The prospect of having both catalytic functions on one particle therefore also seems unfeasible with the alkali promoted iron / HZSM-5 bifunctional system.

In a fluidised bed reactor, alkali transfer between separate iron and zeolite particles is also expected to occur during collisions between the particles. The extent of this migration would be dependent on the overall time of contact between the particles. It has been found that the one extreme (continuous contact) is not a commercially viable process. The Berty experiments performed in the "dual layer" configuration (catalysts separated by a wire mesh) was quite successful, but this represents the best case scenario of the bifunctional process performed in a fluidised bed reactor. It is therefore recommended that the issue of alkali migration be studied in a fluidised bed system, since this is one of the critical technical challenges for the commercialisation of the bifunctional process.

6.2.3 Acid catalyst lifetime

Little deactivation of the acid catalyst function was observed during the fixed bed microreactor experiments. This was ascribed to the light, paraffinic product spectrum produced by the iron FT catalyst during these experiments. For the case of the Berty microreactor experiments, the selectivity of the iron catalyst was more in line with what would be expected from a commercial process. The higher production rate of olefins and long chain paraffins (the components that can easily be converted over an

acidic zeolite) was the proposed reason for the substantial deactivation observed for the HZSM-5. The rate of deactivation was dependent on the aluminium content of the zeolite, since the "high acidity" HZSM-5 deactivated much more rapidly than the "low acidity" HZSM-5. In fact, despite the much higher initial activity of the "high acidity" zeolite, its activity seemed to drop below that of the "low acidity" HZSM-5 after 150 hours of synthesis. Because of the rapid deactivation of the "high acidity" HZSM-5, the product spectrum changed extensively over the first few days of synthesis. Such variations in the product spectrum would be undesirable for a commercial process. The more stable activity and longer useful lifetime of the "low acidity" HZSM-5 makes this zeolite a more preferred acidic co-catalyst for the purpose of the bifunctional process.

6.2.4 Gasoline production with the bifunctional process

The experimental results have shown that the addition of an acidic co-catalyst to the HTFT process generally increases the gasoline selectivity. Long chain hydrocarbons that are heavier than the gasoline range are cracked down to lighter products, whereas light olefins are converted to gasoline range components by means of the oligomerisation, cyclisation and aromatisation reactions. For a highly active zeolite, this increase in the gasoline selectivity is not significant. The reason is the extensive aromatisation achieved over such a zeolite, which is accompanied by the formation of a large amount of light paraffins that fall outside the gasoline range. However, as the zeolite deactivates or if a zeolite with a lower initial activity is employed, the product spectrum shifts away from aromatics towards naphthenes and medium chain length branched aliphatics. Since less light paraffins are formed over an acid catalyst with a lower activity, the increase in the gasoline selectivity is quite substantial. It is thus concluded that, in order to optimise the gasoline selectivity of the bifunctional process, HZSM-5 with a low aluminium content should be used. In fact, for the case of the "low acidity" HZSM-5 in the current set of experiments on the bifunctional process, the gasoline selectivity was as high as 52% (carbon atom basis), while the maximum achieved with the baseline FT run was merely 41%.

It was also found that the liquid product from the bifunctional process was rich in aromatics, naphthenes and branched aliphatic compounds. This product will therefore have a much higher octane number than the predominantly linear aliphatic compounds produced by the traditional HTFT process. Benzene, which is by far the most dangerous aromatic compound from an environmental point of view, was produced in small amounts and generally constituted around 1% (carbon atom basis) of the gasoline fraction. In view of the above, it is therefore clear that the addition of an acidic co-catalyst to the HTFT process successfully improved both the quality and the selectivity of the gasoline fraction.

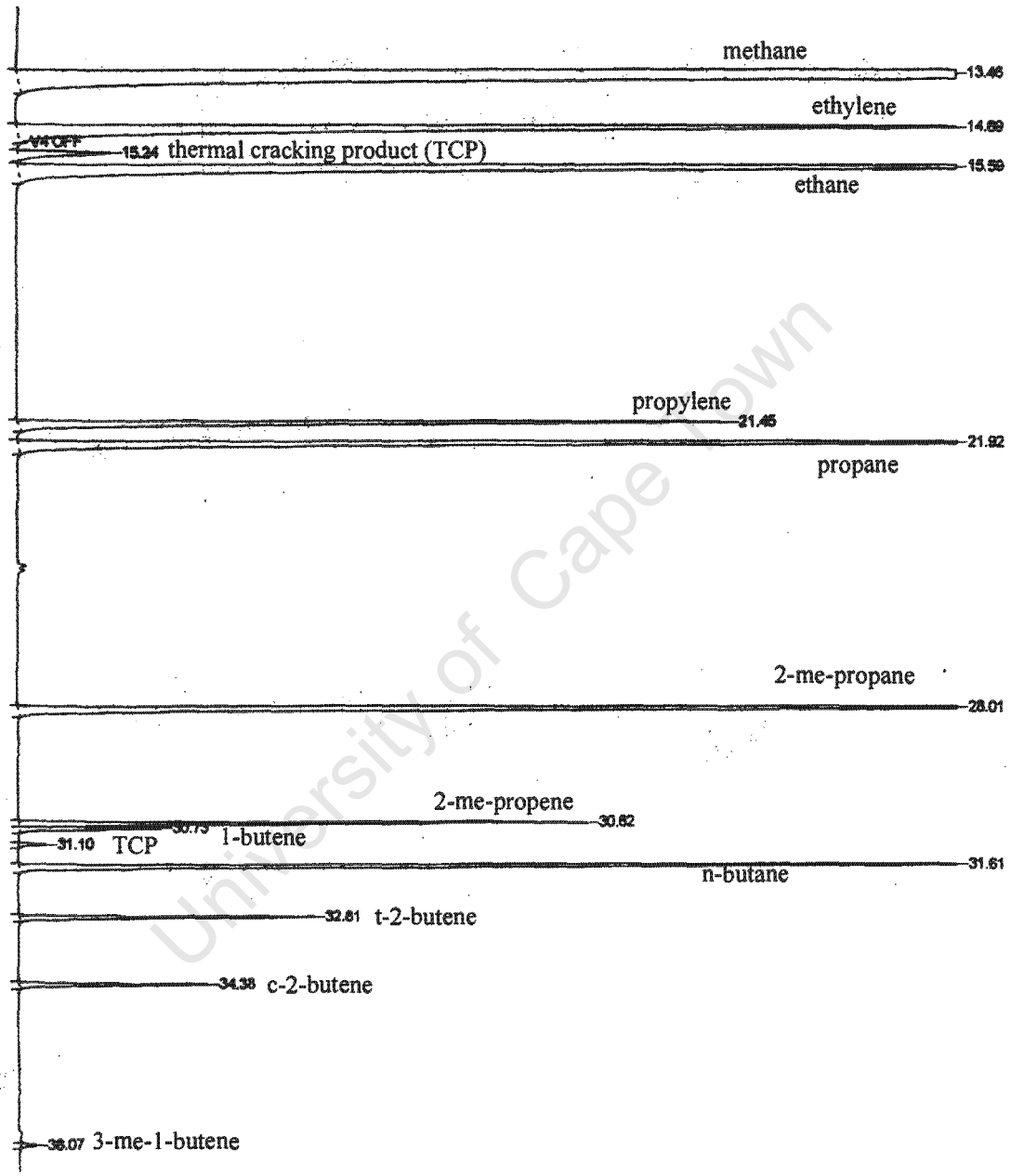
It should also be noted that the yield of high octane gasoline from the bifunctional process can be increased further by additional product work-up. Isobutane is formed in reasonable amounts by the bifunctional process. The alkylation of this isobutane with light olefins (also present in the product spectrum) to highly branched paraffins (e.g. isooctane) will convert light molecules to gasoline range components with a high octane number.

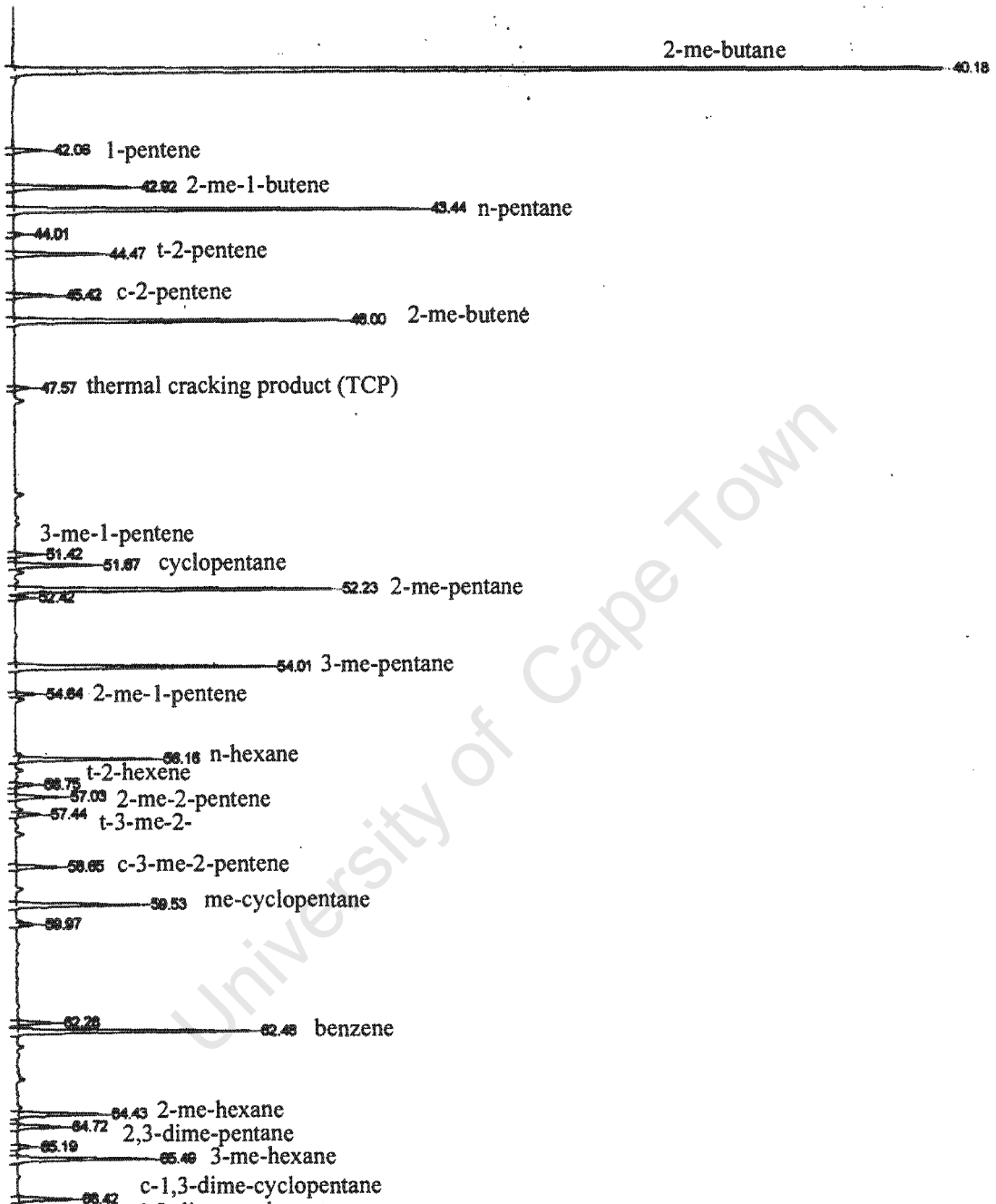
6.2.5 The aluminium content of the HZSM-5

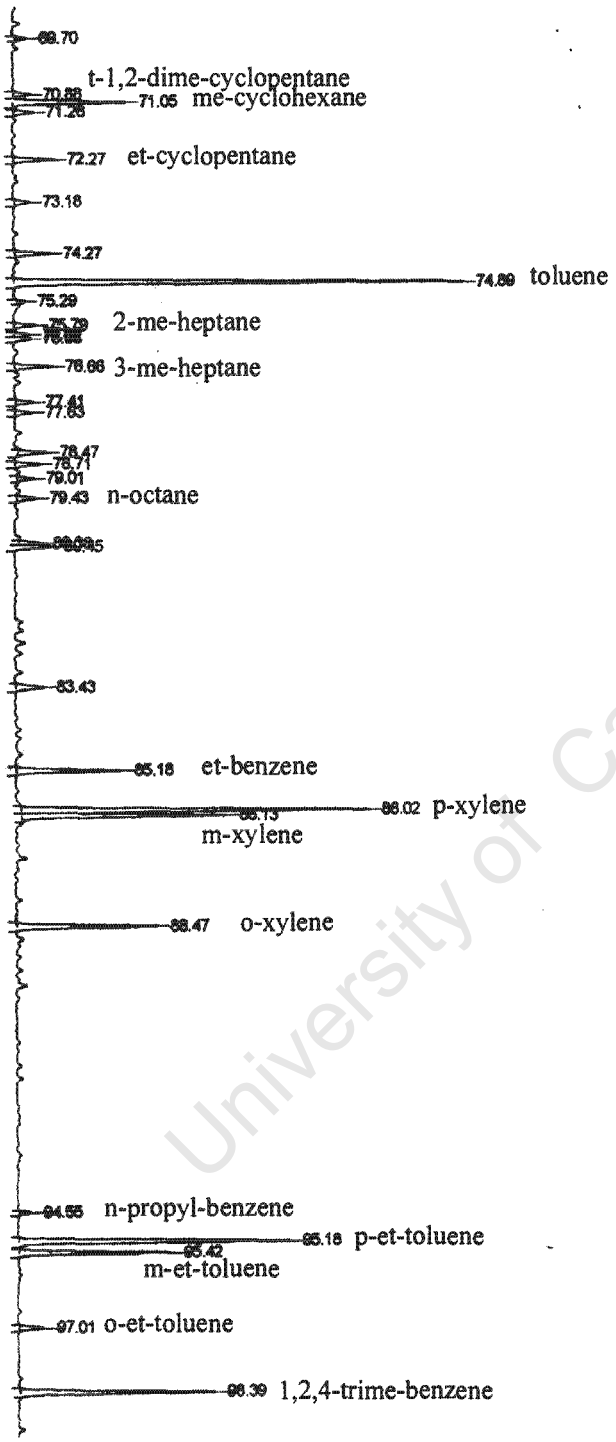
During the final experimental program, only two types of zeolite were tested, namely the "high acidity" and the "low acidity" HZSM-5. From the results of the experiments, it was concluded that the latter seems to be a more preferred choice of co-catalyst for the HTFT process. The "low acidity" zeolite had a higher selectivity towards the gasoline fraction (desired product). It also had a longer lifetime than the "high acidity" zeolite and therefore produced a product with a more stable composition over the course of the run. In fact, after about 150 hours on line, the product formed over the "low acidity" HZSM-5 seemed to be superior to that formed over the "high acidity" zeolite (more rich in aromatics and branched compounds).

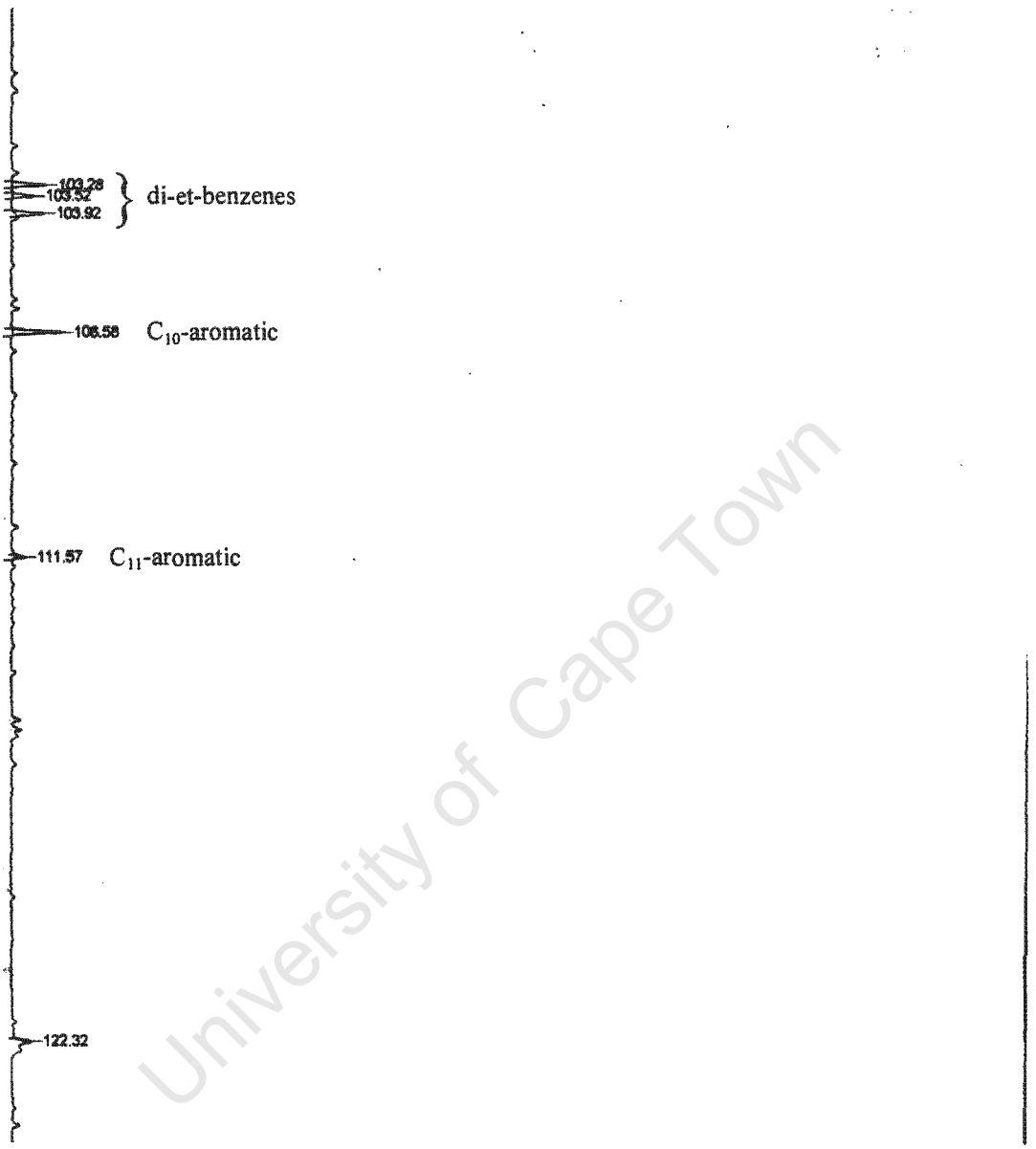
Since the aluminium content of the HZSM-5 has such an important influence on the lifetime of the acid catalyst and the product spectrum of the bifunctional process, it is recommended that further experiments be performed in order to optimise the silica / alumina ratio. Since some other properties of the zeolite (e.g. crystallite size) may also affect its performance in the bifunctional process, these can be studied as well. It is also proposed that the influence of the synthesis temperature on the acid catalyst lifetime be investigated, since a slight increase in the temperature (to about 350°C) may improve the lifetime of the HZSM-5 considerably (*Schulz*, 1991).

APPENDIX I: TYPICAL CHROMATOGRAM OF PRODUCT FROM THE BIFUNCTIONAL PROCESS - "HIGH ACIDITY" HZSM-5

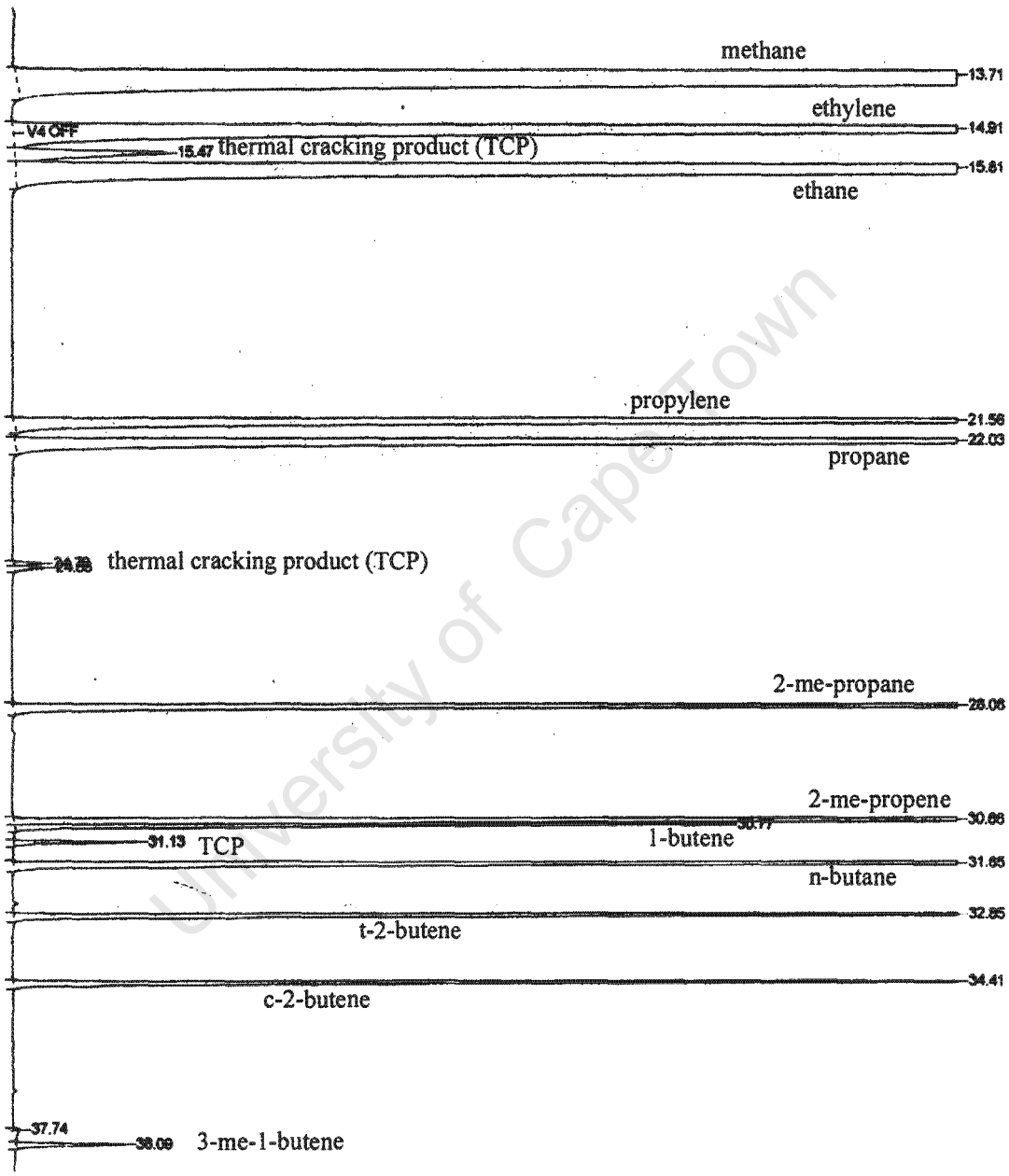


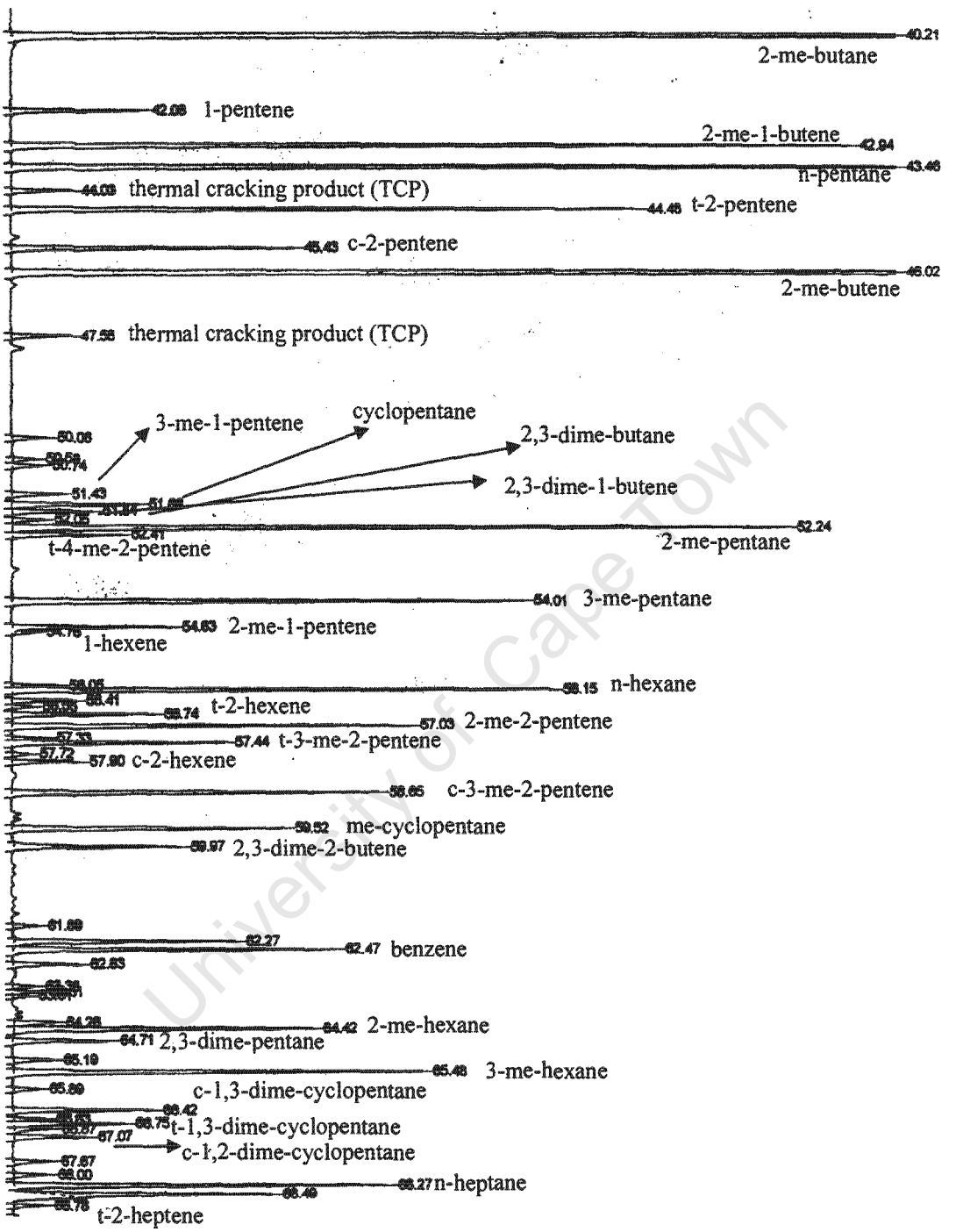


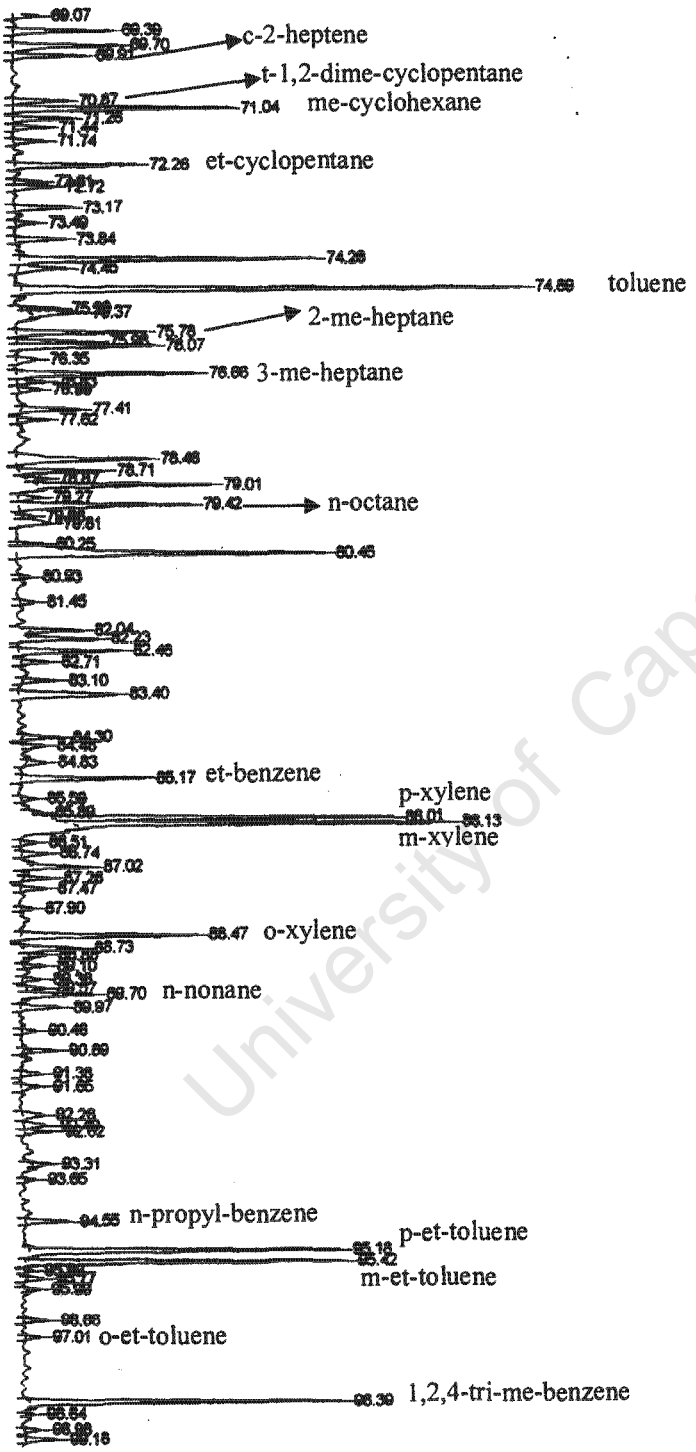


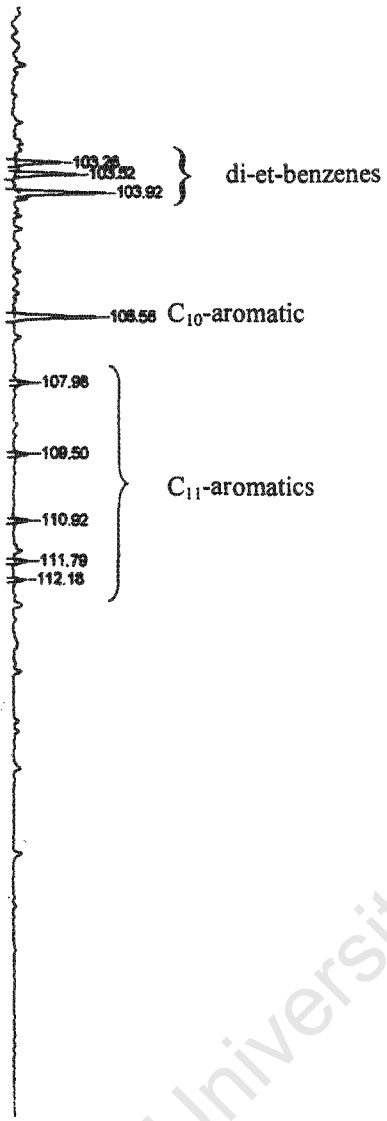


APPENDIX II: TYPICAL CHROMATOGRAM OF PRODUCT FROM THE BIFUNCTIONAL PROCESS - "LOW ACIDITY" HZSM-5









APPENDIX III: SAMPLE CALCULATION FOR TABLE 4.11

In Table 4.11, the ratio of the number of sodium atoms contained by the iron catalyst to the number of acid sites of each of the different HZSM-5 zeolites is presented. In this appendix, a sample calculation is presented for the case of the "low acidity" HZSM-5.

If $SiO_2 / Al_2O_3 = 280$

Then $Si / Al = (280 / 2) = 140$

Unit cell formula for HZSM-5: $H_n Al_n Si_{96-n} O_{192} . 16H_2O$

Thus $[(96 - n) / n] = 140$

$n = 0.6809$

Mr (HZSM-5) = 6048.0 g / mol

Per gram of HZSM-5: HZSM-5 = 1000 (1 / 6048.0) = 0.1653 mmol

Al = n x 0.1653 = 0.1126 mmol

Acid sites = Al = 0.1126 mmol

Per gram of iron catalyst: Fe = 61.9% of catalyst weight = 0.619 g

Na_2O = 0.24 g / 100 g Fe

Na_2O = (0.619 / 100) x 0.24 g = 0.001488 g

Na_2O = 1000 (0.001488 g) / (62 g / mol)
= 0.02396 mmol

Na = 2 x 0.02396 = 0.0479 mmol

Number of Na atoms per number of acid sites = 0.0479 mmol / 0.1126 mmol
= 0.426
= 42.6%

REFERENCES

Anderson, R.B., "Kinetics and reaction mechanism of the Fischer-Tropsch Synthesis" in "Catalysis" (P.H. Emmet, ed.), Vol. IV, Reinhold Publishing Corporation, pp. 257-372 (1956)

Baerns, M., Guan, N., Körting, E., Lindner, U, Lohrengel, M., Papp, H., Catalyst development for selective conversion of syngas to mainly aromatic hydrocarbons, *International Journal of Energy Research*, **18**, pp. 197 – 204 (1994)

Barthomeuf, D., Zeolite acidity dependence on structure and chemical environment. Correlations with catalysis, *Materials Chemistry and Physics*, **17**, pp. 49 – 71 (1987)

Bäurle, G., Guse, K., Lohrengel, M., Papp, H., Conversion of syngas to aromatic hydrocarbons on cobalt-manganese-zeolite catalysts, *Studies in Surface Science and Catalysis*, **75**, pp. 2789 – 2792 (1993)

Bromfield, T.C., Principal scientist – Sasol Technology (R&D Division), Personal communications (2001)

Bruce, L.A., Hope, G.J., Mathews, J.F., Conversion of synthesis gas to aromatic-containing hydrocarbons under mild conditions, *Applied Catalysis*, **9**, pp. 351 – 359 (1984)

Butter, S.A., Chester, A.W., Schwartz, A.B., United States Patent 4 298 695 to Mobil Oil Corporation (1981)

Caeser, P.D., Brennan, J.A., Garwood, W.E., Ciric, J., Advances in Fischer-Tropsch Chemistry, *Journal of Catalysis*, **56**, pp. 274-278 (1979)

Chang, C.D., Lang, W.H., Silvestri, A.J., United States Patent 4 086 262 to Mobil Oil Corporation (1978)

Chang, C.D., Lang, W.H., Silvestri, A.J., Synthesis gas conversion to aromatic hydrocarbons, *Journal of Catalysis*, **56**, pp. 268-273 (1979)

Chen, H., Adesina, A.A., Improved alkene selectivity in carbon monoxide hydrogenation over silica supported cobalt-molybdenum catalyst, *Applied Catalysis A: General*, **112**, pp. 87 – 103 (1994)

Dry, M.E., "The Fischer-Tropsch Synthesis" in "Catalysis – Science and Technology" (J.R. Anderson and M Boudart, eds.), Vol. I, Springer-Verlag, pp. 159-255 (1981)

Dry, M.E., "The Sasol Fischer-Tropsch Processes" in "Applied Industrial Catalysis" (B.E. Leach, ed.), Vol. 2, Academic, pp. 167-213 (1983)

Dry, M.E., Practical and theoretical aspects of the catalytic Fischer-Tropsch process, *Applied Catalysis A: General*, **138**, pp. 319-344 (1996)

Egiebor, N.O., Cooper, W.C., Wojciechowski, B.W., Synthesis of motor fuels from HY-zeolite suported Fischer-Tropsch iron catalysts, *Applied Catalysis*, **55**, pp. 47 - 64 (1989)

Espinoza, R.L., Steynberg, A.P., Jager, B., Vosloo, A.C., Low temperature Fischer-Tropsch synthesis from a Sasol perspective, *Applied Catalysis A: General*, **186**, pp. 13-26 (1999)

Gormley, R.J., Rao, V.U.S., Anderson, R.R., Schehl, R.R., Chi, R.D.H., Secondary reactions on metal-zeolite catalysts used in synthesis gas conversion, *Journal of Catalysis*, **113**, pp. 193 – 205 (1988)

Guan, N., Liu, Y., Zhang, M., Development of catalysts for the production of aromatics from syngas, *Catalysis Today*, **30**, pp. 207 – 213, (1996)

Horsley, J.A., Corma, A., Derouane, E.G., Guisnet, M., "New zeolite applications in the petroleum and petrochemical industries", Catalytica Studies Division, 223 pages (1993)

Jothimurugesan, K., Gangwal, S.K., Titania-supported bimetallic catalysts combined with HZSM-5 for Fischer-Tropsch synthesis, *Ind. Eng. Chem. Res.*, **37**, pp. 1181 – 1188 (1998)

Moulijn, J.A., Sheldon, R.A., Van Bekkum, H., Van Leeuwen, P.W.N.M., Catalytic processes in industry, *Studies in Surface Science and Catalysis*, **79**, pp. 27 – 34 (1993)

Müller, K., Deckwer, H.D., Ralek, M., Fischer-Tropsch synthesis on polyfunctional manganese/iron – pentasil zeolite catalysts, *Studies in Surface Science and Catalysis*, **12**, pp. 267 – 274 (1982)

Niederberger, H.L., Zeitliche Änderung der Aktivität und der Selektivität bei der Umsetzung CO-reicher Synthesegase an einem Eisen / H-ZSM-5-Kombinationskatalysator (Time change of activity and selectivity during the conversion of syngas, that is rich in CO, over an iron-HZSM-5 composite catalyst): Dr.-Ing. Disseration, University of Karlsruhe, 144 pages (1988)

Nieuwenhuys, B.E., Ponec, V., Van Koten, G., Van Leeuwen, P.W.N.M., Van Santen, R.A., Bonding and elementary steps in catalysis, *Studies in Surface Science and Catalysis*, **79**, pp. 138 – 140 (1993)

Rao, V.U.S., Gormley, R.J., Make olefins from syngas, *Hydrocarbon Processing*, **59** (11), pp. 139 – 142 (1980)

Rao, V.U.S., Gormley, R.J., Shamsi, A., Petrick, T.R., Stencel, J.M., Schehl, R.R., Chi, R.D.H., Obermyer, R.T., Promotion and characterisation of zeolitic catalysts used in the synthesis of hydrocarbons from syngas, *Journal of Molecular Catalysis*, **29**, pp. 271 – 283 (1985)

Schulz, H., Beck, K., Erich, E., Kinetics of Fischer-Tropsch selectivity, *Fuel Process. Technol.*, **18**(3), pp. 293 – 304 (1988a)

* Kibby, C.L., Kobylinski, T.P., Preprints, Division of Petroleum Chemistry, ACS (1978)

Schulz, H., Van Steen, E., Claeys, M., Studies in Surface Science and Catalysis, 81, pp. 45-50 (1994)

Schulz, H., Beck, K., Erich, E., Mechanism of the Fischer-Tropsch process, *Studies in Surface Science and Catalysis*, **36**, pp. 457 – 471 (1988b)

Schulz, H., Erich, E., Gorre, H., Van Steen, E., Regularities of selectivity as a key for discriminating FT-surface reactions and formation of the dynamic system, *Catalysis Letters*, **7**, pp. 157 – 168 (1990)

Schulz, H., Niederberger, H.L., Kneip, M., Weil, F., Synthesis gas conversion on Fischer-Tropsch iron/HZSM5 composite catalysts, *Studies in Surface Science and Catalysis*, **61**, pp. 313 – 323 (1991)

Schulz, H., Short history and present trends of Fischer-Tropsch synthesis, *Applied Catalysis A: General*, **186**, pp. 3-12 (1999)

Shamsi, A., Udaya, V., Rao, S., Gormley, R.J., Obermyer, R.T., Schehl, R., Stencel, J.M., Zeolite-supported cobalt catalysts for the conversion of synthesis gas to hydrocarbon products, *Ind. Eng. Chem. Prod. Res. Dev.*, **23**, pp. 513 – 519 (1984)

Shamsi, A., Rao, V.U.S., Gormley, R.J., Obermyer, R.T., Schehl, R.R., Stencel, J.M., Influence of preparative procedure on the activity and selectivity of FeZSM-5 catalysts in syngas conversion, *Applied Catalysis*, **27**, pp 55 – 68 (1986)

Steynberg, A.P., Espinoza, R.L., Jager, B., Vosloo, A.C., High temperature Fischer-Tropsch synthesis in commercial practice, *Applied Catalysis A: General*, **186**, pp. 41-54 (1999)

Udaya, V., Rao, S., Gormley, R.J., Bifunctional catalysis in syngas conversions, *Catalysis Today*, **6**(3), pp. 207-234 (1990)

Van der Laan, G.P., Beenackers, A.A.C.M., Kinetics and selectivity of the Fischer-Tropsch Synthesis: a literature review, *Catalysis Reviews: Science and Engineering*, **41**(3&4), pp. 255 – 318 (1999)

Varma, R.L., Jothimurugesan, K., Bakhshi, N.N., Mathews, J.F., Ng, S.H., Direct conversion of synthesis gas to aromatic hydrocarbons: variation of product distribution with time-on-stream, *The Canadian Journal of Chemical Engineering*, **64**, pp. 141 – 148 (1986)

Varma, R.L., Bakhshi, N.N., Mathews, J.F., Ng, S.H., Performance of dual-reactor system for conversion of syngas to aromatic-containing hydrocarbons, *Ind. Eng. Chem. Res.*, **26**, pp. 183 – 188 (1987)

Xu, L., Bao, S., O'Brien, R., Raje, A., Davis, B.H., Don't rule out iron catalysts for Fischer-Tropsch synthesis, *Chemtech*, **28**(1), pp. 47-53 (1998)