

UNIVERSITY OF NOVA GORICA  
SCHOOL OF ENVIRONMENTAL SCIENCE

**HEAT TRANSFER IN STRUCTURED PACKINGS FOR  
FISCHER-TROPSCH SYNTHESIS**

Diploma thesis

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## **Statement**

This diploma thesis is a result of my own research work. Results which have been created/provided by other researchers either in collaboration or separately are properly cited in this thesis.

Jure Lešnik



## **Acknowledgment**

At the same time last year I got a chance to go study at TU Delft in 2010. In the beginning it was really a hard decision. I did not know if I should go or not. There were so many things to arrange and the hardest one was to find a title for the diploma thesis. In the beginning I even did not know on which field should I work because the study program was different. After a long search I found prof. Ruud van Ommen who offered me a topic for my research project.

Over the last 5 and half months I learned a lot about Fischer-Tropsch process, reactor design, and much more. The reason for that was especially the lack of knowledge and experiences on this field. During my study at University of Nova Gorica I never on focused challenges in that fields, so the start was quite difficult.

During this period at Proeffabriek I realized that work can be also fun. This was due to the whole Proeffabriek team. Most of the time I spent with working in laboratory or with computer but all coworkers contributed to a better atmosphere during coffee breaks or barbecues. Because of this I want to thank my colleagues in Proffabriek. My special thanks are going to both my supervisors prof. Ruud van Ommen and David Vervloet which helped me with the project. Especially David, who helped me with the experiments, among other things. I can state that I learned a lot from him. Last but not least I want to thank my family, who was supporting me through good and bad times during my study.

I think this decision, to go study abroad, was one of the best in my life. Not just because of learning experiences, but also life experiences which came with living in the Netherlands. I think this was the perfect conclusion of my student years, and I feel more prepared for the next chapter in my life.



## Abstract

The main purpose of this thesis is to contribute ideas and results to help solving heat transfer issues in multi-tubular reactors for F-T synthesis with help of a structured reaction environment.

Currently global energy demand is still increasing and the prognosis is that it will keep increasing in the coming decades. One of the biggest energy problems in the world today is the problem with quantity of remaining fossil fuels. The experts are predicting that the reserves of the world's fossil resources are sufficient for next 40 years. Because of this problem scientists are looking for alternative solutions. One of the possible solutions is the Fischer-Tropsch process. In F-T synthesis gas or syngas (carbon monoxide and hydrogen) is converted to hydrocarbons and water over a Co- or Fe-based catalyst.

For now, mainly natural gas and coal are used as a feedstock for syngas production. Nowadays, there are more sustainable ways for producing syngas by using biomass and municipal solid waste as a feedstock. Especially biomass is a very interesting source for the future F-T process. During the growth, biomass is absorbing almost all CO<sub>2</sub> that is produced in the F-T process. Another advantage of F-T diesel is lower emissions during combustion. This can be explained with purity of the F-T diesel (does not contain sulphur) which makes it more environmentally friendly.

Since the F-T reaction is highly exothermic it is important to rapidly remove the heat of reaction from catalyst particles in order to avoid overheating. One of the promising ways for improving heat transfer properties are structured packings (cross flow structures). In this research heat transfer properties of cross structured packings were investigated, to look for their feasibility in F-T synthesis.

The packings used in experiments were glass beads (which represents a random packed bed used which is used in industry nowadays), wire gauze packing, closed cross flow structures (CCFS) and open cross flow structures (OCFS). Additional modifications were made on CFS to avoid the problem with bypassing. The experiments were done on a heat transfer set-up from which I got temperature profiles data, which were later calculated into a heat transfer rate. Because of modifications used in experiments, additional experiments were done. This was a maldistribution experiment which is giving us distribution data inside packing for better understanding of flow dynamics.

The most promising packing used in experiment were CCFS and OCFS which show the best heat transfer properties (up to 44.2% larger heat transfer compared to randomly packed bed). These packings had the best heat transfer properties which were later analyzed also by modeling. Results of heat transfer on CCFS and OCFS packings with modifications were not much different from results on same packing without modification. This proved that modifications do not influence heat transfer properties significantly. Results of wire gauze packing had the lowest heat transfer properties, also lower than glass beads (random packed bed). Because of the low heat transfer performance, we stopped experiments on wire gauze packings.

Maldistribution experiments were made on OCFS and CCFS packing and also on the same packings with modifications. These results showed us that different packings are behaving differently with using modification. Results for CCFS packings showed that, if

modifications were in use, that contributed to a better distribution of liquid inside packing. In results for OCFS packings this was not a case. The results showed that modifications used on OCFS packings are affecting distribution badly and causing maldistribution of liquid inside packing.

Keywords: Fischer-Tropsch synthesis, heat transfer, multi-tubular reactor, structure reactor, syngas, structured packing



## **Povzetek**

Prvotni namen diplomske naloge je prispevek idej in eksperimentalnih rezultatov, ki bi pomagali pri izboljšanju toplotnega prenosa znotraj cevastih reaktorjev ("multi-tubular fixed bed reactors" ali MTFBR), ki se uporabljajo za Fischer-Tropsch sintezo. Optimizacijo oziroma rešitev, s katero bi izboljšali toplotni prenos znotraj reaktorja, bi lahko dosegli s strukturiranim reaktorjem (oz. strukturiranimi reaktorskimi polnili).

## Ozadje in zgodovina

Trenutne globalne energijske potrebe naraščajo in napovedi predvidevajo, da se bo ta trend nadaljeval tudi v bližnji prihodnosti. Eden največjih energetskih problemov predstavlja preostanek fosilnih goriv. Najbolj uporabljeno fosilno gorivo je še vedno nafta. Po podatkih British Petroleum Statistics trenutne svetovne naftne rezerve zadoščajo za nadaljnjih 40 let.

Da bi se izognili problemu, znanstveniki že dolga leta iščejo ekonomično realno rešitev. Ena izmed možnih rešitev je Fischer-Tropscheva sinteza (F-T sinteza), ki je zelo perspektivna pot za pridobivanje transportnih goriv. Kot surovine v F-T sintezi se lahko uporabljajo zemeljski plin, premog ali biomasa.

F-T sintezo sta v zgodnjih 20. letih prejšnjega stoletja iznašla nemška znanstvenika F. Fischer in H. Tropsch. Zaradi pomanjkanja nafte so v II. svetovni vojni Nemci in Japonci uporabljali F-T sintezo za pridobivanje nadomestnih transportnih goriv. Leta 1938 je bilo v Nemčiji zgrajenih devet tovarn s skupno proizvodno kapaciteto 660.000 t na leto. Kasneje, še v času vojne, so bile tovarne skoraj povsem uničene. Uporabnost postopka je sprožila veliko zanimanje po vsem svetu. Še najbolj očitno je to izkoristilo južnoafriško podjetje Sasol, ki zaradi političnih razlogov ni smelo uvažati nafte. V 50. letih prejšnjega stoletja so začeli iz premoga proizvajati nafto s pomočjo F-T sinteze. Naftna kriza v 70. letih je Sasol tako opogumila, da so zgradili še dve novi tovarni, ki sta bili veliko večji od prve. Takratna skupna kapaciteta je znašala 6.000.000 t na leto. Dandanes je cena nafte že tako visoka, da se naftni giganti odločajo za ta alternativni postopek. Eden od njih je tudi Shell; ta trenutno gradi največjo tovarno (Pearl), ki uporablja F-T postopek.

F-T sinteza je postopek, ki uporablja "syngas" ali sintetični plin (mešanico CO in H<sub>2</sub>) kot surovino za pridobivanje tekočih ogljikovodikov. Mešanica tega plina reagira do tekočih ogljikovodikov preko kobaltovega ali železovega katalizatorja. Ker je reakcija zelo eksotermne narave, se med postopkom sprosti veliko toplote. Med formacijo 1 mola -CH<sub>2</sub>- se sprosti 165 kJ toplote. Zaradi tega je potrebno to toploto čim prej odvesti iz reaktorja, kajti v nasprotnem primeru lahko pregrejemo katalizator, ki kasneje ne bo več uporaben.

Večina tovarn, ki se trenutno poslužujejo F-T sinteze, uporablja premog in zemeljski plin za proizvodnjo sintetičnega plina. Vendar zdaj že poznamo veliko bolj okoljsko sprejemljive surovine, kot so biomasa ali komunalni odpadki, ki imajo precej prednosti pred drugimi postopki.

## Primerjava okoljskih vplivov med F-T dizlom in nafto fosilnega izvora

V eni izmed raziskav, ki jih je naredil J.J. Morano z sodelavci, so preučevali količino proizvedenih toplogrednih plinov pri proizvodnji nafte. Naredili so celotno študijo življenjskega cikla toplogrednih plinov za proizvodnjo nafte po konvencionalnem postopku (črpanje iz vrtin in rafinacija) in po postopku F-T sinteze. Za konvencionalni postopek so uporabili nafto iz 8 različnih vrtin, ki so bile razporejene po vsem svetu:

- nafta iz Wyominga,
- iz Kanade,
- iz Severnega morja,
- z Arabskega polotoka,
- z Aljaske,
- iz Alberte in
- dveh vrtin v Venezueli.

Za proizvodnjo po F-T postopku so uporabili 3 različne surovine, ki so bile lokalizirane v Severni Ameriki. Te surovine so bile:

- premog (iz Illinoisa in Wyominga),
- biomasa,
- zemeljski plin (iz plinovoda v Venezueli in na Aljaski).

Raziskava je pokazala, da imajo postopki, narejeni po F-T sintezi, načeloma višje emisije toplogrednih plinov kot konvencionalni. Razlogi za to sta lahko dve:

- V raziskavi so upoštevali tehnologije za F-T sintezo, ki so bile v uporabi v 90. letih prejšnjega stoletja in še niso bile tako dobro razvite kot danes.
- Drugi razlog je ta, da F-T sinteza zajema precej več procesov kot konvencionalni postopki.

Pri uporabi biomase kot surovine za proizvodnjo nafte po F-T postopku so ugotovili, da je skupek emisij znatno manjši kot pri proizvodnji iz drugih surovin oziroma pri proizvodnji po konvencionalnih postopkih. Razlog za to je, da biomasa v času rasti absorbira večino CO<sub>2</sub>, ki se sprosti med postopkom. Če odmislimo ekonomičnost in druge parametre, vidimo, da je biomasa idealna surovina za proizvodnjo nafte po F-T sintezi.

Podobno raziskavo so naredili tudi za avstralsko vlado, vendar so se osredotočili le na končno porabo transportnih goriv. V raziskavo je bil vključen tudi F-T dizel. Razlog: Avstralija ima relativno velike zaloge zemeljskega plina, zato preučujejo možnosti proizvodnje alternativnih transportnih goriv. Preučevali so tri različna dizelska goriva:

- nafto z nizko vsebnostjo žvepla,
- nafto z ultranizko vsebnostjo žvepla in
- F-T nafto.

Raziskave so bile narejene na emisijah pri končni uporabi. Merili so emisije CO<sub>2</sub>, PM10, NO<sub>x</sub> in ogljikovodike v emisijah, ki niso vsebovale metana. Rezultati so pokazali, da je F-T nafta v skoraj vseh pogledih povzročila manj emisij kot ostali dve nafti.

## Reaktorske tehnologije

Pri razvoju F-T sinteze so uporabljali veliko reaktorskih tehnologij. Trenutno za F-T sintezo ne poznamo optimalne reaktorske tehnologije. Vsak reaktor ima svoje prednosti in slabosti. Večina tovarn, ki izvajajo ta postopek, uporablja enega izmed naslednjih dveh reaktorjev:

- cevast reaktor ali
- blatno mehurčni kolonski reaktor (slurry bubble column reactor ali SBCR).

Tretja opcija je relativno nova in ima veliko prednosti pred prvima dvema. Imenuje se mikro cevast reaktor (micro-tubular reactor). Edina pomanjkljivost te reaktorske tehnologije je ta, da je precej draga.

## Eksperimentalni postopek in metode

V raziskavi sem delal preizkuse na reaktorju, ki simulira podobne pogoje, kot jih imamo v F-T sintezi. Naprava je predstavljala cevast reaktor; to je reaktor, ki se trenutno uporablja v petrokemijskem gigantu Shell. Ena izmed največjih pomanjkljivosti tega reaktorja je, da je odvečno toploto, ki nastaja med reakcijo, zelo težko odvajati iz samega reaktorja. Posledica tega je lahko deaktivacija katalizatorja. Zato je bil cilj diplomske naloge ugotoviti, ali lahko postopek optimiziramo in zagotovimo večji prenos toplote iz reaktorja.

Za eksperimente toplotnega prenosa sem uporabljal "set-up", ki je bil sestavljen iz kolone (oziroma reaktorja), raznih grelcev (za plin in tekočino) in naprav za merjenje prenosa toplote. Naprave za merjenje temperature so zajemale več kot 200 toplotnih senzorjev, ki so merili temperaturne profile znotraj reaktorja (v horizontalni in vertikalni smeri) in temperature hladilne vode, ki so bile potrebne za kalkulacijo toplotnega prenosa.

Pri izvajanju eksperimentov sem simuliral podobne pogoje kot v F-T procesu. Najprej sem moral segreti tekočino (izopar-M) in plin (N<sub>2</sub>) na 60°C (s pomočjo grelcev plina in tekočine) in ju voditi skozi reaktor, v katerem je prišlo do toplotnega prenosa. Toplotni prenos mi je zagotavljalo vodno hlajenje, ki je obdajalo reaktor. Znotraj reaktorske kolone so se nahajala polnila, ki so predstavljala katalizator.

Temperaturni prenos sem spremljal s pomočjo računalniškega progama LabVIEW, ki je nadzoroval spremembe temperaturnih profilov znotraj reaktorja in temperaturo hladilne vode. Računalniški program je beležil celotni eksperiment (10 minut). Kasneje sem te podatke obdelal s pomočjo Microsoft Excela in jih podal kot toplotni prenos. To sem določil s pomočjo sledeče enačbe:

$$Q = U_o \times A \times LMTD$$

Elementi enačbe so:

Q – skupek toplotnega prenosa [W]

U<sub>o</sub> – skupni toplotni prenosni koeficient [W/m<sup>2</sup>K]

A – površina [m<sup>2</sup>]

LMTD – logaritmična glavna temperaturna razlika [K]

Člen  $U_o$  sem vzel kot glavno lastnost za ovrednotenje toplotnega prenosa določenega polnila znotraj reaktorja.  $U_o$  je predstavljal sposobnost toplotnega prenosa posameznega polnila.

V industrijskih reaktorjih trenutno uporabljajo katalizatorje v obliki kroglic, ki naključno zapolnjujejo prostor reaktorja. Ta polnila označujemo z angleškim izrazom "randomly packed bed". Takšna oblika katalizatorjev ima prednosti in slabosti. Zaradi nepredvidljive dinamike tekočine in plina znotraj takšnih polnil se predvideva, da je lahko toplotni prenos v strukturiranih polnilih boljši. Zato je bil glavni cilj diplomske naloge ovrednotiti, ali se lahko s pomočjo strukturiranih polnil izboljša tudi toplotni prenos.

Kot strukturirana polnila so trenutno najbolj zanimiva t.i. "cross flow structures" ali CFS, ki sem jih uporabljal tudi v eksperimentih. Ta so bila:

- "Close cross flow structure" ali CCFS,
- "Open cross flow structure" ali OCFS in
- "Wire gauze" polnilo, ki je tudi neke vrste CFS, vendar opremljeno z dodatnimi modifikacijami za preprečevanje fenomena "bypassing".

Znotraj strukturiranih polnil lahko pride do fenomena "bypassing", kar pomeni, da lahko tekočina in plin zaobideta polnilo in prehajata vzdolž reaktorja skozi majhno špranjo med reaktorjem in polnilom, ki se ne prilagaja tesno steni reaktorja. Če se ta fenomen dogaja v industrijskih reaktorjih, nam lahko to povzroči obilo preglavic. Če plin prehaja vzdolž reaktorja, ne da bi bil v stiku s katalizatorjem, ne dobimo želenih produktov.

Da bi se izognili fenomenu "bypassing", smo za strukturirana polnila pripravili posebne modifikacije. "Wire gauze" polnilo je že v osnovi imelo krilca, ki so obdajala polnilo. Namen teh krilc je zbirati plin in tekočino, ki se nahaja na steni reaktorja, in jo voditi nazaj v notranjost polnila. Ostala strukturirana polnila (CCFS in OCFS) v osnovi niso imela teh modifikacij. Da sem se izognil fenomenu "bypassing", sem uporabil aluminijasta tesnila. To so bili aluminijasti obročki, ki so imeli notranji premer 4,2 mm in zunanje 5 mm.

Da sem lahko primerjal toplotni prenos v industrijskih reaktorjih s toplotnim prenosom strukturiranih polnil, sem najprej moral narediti eksperiment na "randomly packed bed" polnilih. Za take vrste polnilo sem uporabil steklene kroglice premera 2 mm. To je bil moj prvi eksperiment in osnova za ovrednotenje vseh nadaljnjih rezultatov.

Kasneje sem opravil iste eksperimente tudi za strukturirana polnila in jih primerjal z "randomly packed bed" polnili. Zadnji eksperimenti za toplotni prenos pa so bili eksperimenti na CCFS in OCFS polnilih z modifikacijami (z Al tesnili).

Ker me je zanimal razlog takšnih sprememb pri toplotnem prenosu znotraj (CCFS in OCFS) polnil z modifikacijami in brez njih, sem študijo nadaljeval. Ker me je zanimalo, kako se tekočina vede v polnilih, z uporabo in brez uporabe modifikacij, sem nadaljeval z eksperimentom distribucije ali porazdelitve. Ta eksperiment je bil dokaj enostaven. Skozi reaktorsko kolono, v kateri so se nahajala polnila, sem spuščal plin in tekočino 3 minute. Na koncu reaktorske kolone se je nahajalo zbiralno polnilo, ki je zbiralo vso tekočino, ki je tekla skozi kolono. To zbiralno polnilo je bilo razdeljeno v 13 delov; iz vsakega je po cevki tekla tekočina v posamezno posodo. Na koncu eksperimenta

sem vsako posodo stehal, razliko odštel in tako sem dobil odstotek mase za vsako regijo znotraj polnila.

Po koncu eksperimentalnega in analiznega dela s pomočjo Microsoft Excela sem rezultate analiziral še v dveh modelih s pomočjo programa Matlab. Modela sta predhodno naredila študenta, ki sta se ukvarjala s podobno tematiko. Razlog te naloge je bil preveriti, ali lahko modela simulirata podobne pogoje, kot se dogajajo v eksperimentih. Analiza je pokazala, da sta modela dokaj natančna in dajeta skoraj iste rezultate kot analiza z Microsoftovim Excelom.

### Rezultati in zaključki

Po prvem eksperimentu na "randomly packed bed" polnilih sem opazil, da imajo polnila, ki so v uporabi v industriji, relativno dober toplotni prenos.

Eksperiment številka dve je bil narejen na "Wire gauze" polnilih. Pred eksperimentom smo predvidevali, da bi to polnilo moralo imeti zelo dobre lastnosti glede toplotnega prenosa. Rezultati so pokazali, da je toplotni prenos precej manjši od "randomly packed bed" polnila (za skoraj 63%). Razlaga za to je lahko:

- "Wire gauze" polnilo ima tri krilca, ki obdajajo polnilo in usmerjajo ves plin in tekočino od reaktorske stene nazaj v polnilo. Problem pa je ta, da se ves toplotni prenos dogaja na steni reaktorja.
- Drugi razlog je lahko bil tudi ta, da ima "Wire gauze" polnilo veliko večje kanalčke, kar ima za posledico, da plin in tekočina tečeta skozi polnilo.

Eksperiment tri je bil narejen na CCFS polnilih. Ta polnila so dosegla ene izmed najboljših rezultatov toplotnega prenosa, ki so bili znatno boljši od rezultatov s "randomly packed bed" polnil. Toplotni prenos se je izboljšal tudi do 37,2%.

Eksperiment štiri je bil narejen na OCFS polnilih. Ta polnila so dosegla ene izmed najboljših rezultatov toplotnega prenosa, tako kot CCFS polnila, ki so bili znatno boljši od rezultatov s "randomly packed bed" polnil. Toplotni prenos se je izboljšal tudi do 39,1%.

Eksperiment pet je bil izvedena na CCFS polnilih, vendar so ta polnila vsebovala modifikacije (Al tesnila). Rezultati so bili podobni kot pri eksperimentih brez tesnil. Pri CCFS polnilu z modifikacijami se je toplotni prenos malo zmanjšal (za 5,1%).

Eksperiment šest je bil izvedena na OCFS polnilih, vendar so ta polnila vsebovala modifikacije (Al tesnila). Rezultati so bili podobni kot pri eksperimentih brez tesnil.. Pri OCFS polnilu se je toplotni prenos minimalno povečal (za 5,1%).

Pred eksperimentomi s tesnili smo predvidevali, da bodo modifikacije povzročile boljše razporeditev tekočine znotraj polnil, vendar so rezultati pokazali, da ni povsem tako.

Pri eksperimentu s CCFS polnilom so rezultati pokazali, da se porazdelitev tekočine z uporabo modifikacij izboljša. Pred uporabo modifikacij je bil večji del tekočine v območju reaktorske stene, kar je imelo za posledico boljši toplotni prenos.

Pri eksperimentu s OCFS polnilom so rezultati pokazali, da modifikacije povzročajo ravno obratno kot pri eksperimentu z CCFS polnilom. Pred uporabo modifikacij je bila

porazdelitev tekočine znotraj kolone boljša kot pa kasneje z uporabo modifikacij. Z uporabo modifikacij je bil večji del tekočine zunaj polnila na steni kolone. Rezultat tega je bil večji toplotni prenos.

Rezultati analize so pokazali, da sta modela v Matlabu dokaj natančna in dajeta skoraj iste rezultate kot analiza z Microsoftovim Excelom.

V raziskavi sem prišel do nekaj ključnih zaključkov. Toplotni prenos v "Multi-tubular fixed bed" reaktorju, ki se trenutno uporablja v industriji, se lahko izboljša. K temu lahko največ pripomore zamenjava trenutnih polnil s strukturiranimi, ki imajo boljše lastnosti (kar se tiče toplotnega prenosa). Najbolj obetavni strukturirani polnili sta CCFS in OCFS polnili. S pomočjo modifikacij, kot so AI tesnila, se lahko izognemo problemom, kot je "bypassing", hkrati pa nam lahko zagotovijo bolj celovito uporabo katalizatorja.

Ključne besede: Fischer-Trposch sinteza, toplotni prenos, sintetični plin, strukturiran reaktor, strukturirana polnila.

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## List of symbols and abbreviations

### Roman symbols

bbbl	Oil barrel (158.98 liters)
CCFS	Close cross flow structure
CFS	Cross flow structure
CO <sub>2</sub> -eq	CO <sub>2</sub> equivalent
D, d	Diameter [m]
F-T	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis
GHG	Green house gases
h	Wall heat transfer coefficient [W/m <sup>2</sup> K]
HC	Hydrocarbons
LCA	Life cycle analysis
LCI	Life cycle inventory
LMTD	Log mean temperature difference [K]
MSW	Municipal solid waste
MTFBR	Multi-tubular fixed bed reactor
OCFS	Open cross flow structure
PH2DPFM	Pseudo homogeneous 2D plug flow model or PH2DPFM
Q	Energy flow rate [W]
SUV	Sport utility vehicle
U	Heat transfer coefficient [W/m <sup>2</sup> K]
(U)LSD	(ultra)low Sulphur diesel
V	Velocity

### Greek symbols

$\alpha_w$	Wall heat transfer coefficient [W/m <sup>2</sup> K]
$\varepsilon$	Porosity [l]
$\lambda$	Conduction coefficient [W/mK]
$\rho$	Density [kg/m <sup>3</sup> ]
$\Theta$	Dimensionless temperature

### Subscripts

est	Estimated
g	Gas
h	Hydraulic
l	Liquid
o or ov	Overall
w	Wall
Pe	Peclet number
St	Stanton number



## 1. INTRODUCTION

The main purpose of this thesis is to contribute ideas and results to help solving heat transfer issues in multi-tubular reactors for Fischer-Tropsch synthesis (F-T synthesis) with the help of a structured reaction environment. For better understanding of the heat transfer properties the liquid distribution inside the structured reaction environment was also investigated. Other things that should be considered in F-T synthesis, but are not discussed in this thesis, are amongst others mass transfer, catalyst improvement, and pressure drop considerations.

### 1.1. Problem statement

Global energy demand is still increasing and the prognosis is that it will keep increasing in the coming decades. One of the biggest energy problems in the world today is the quantity of remaining fossil fuels. As we can see from Figure 1 [1] oil is the most used fossil fuel in the world today. According to the British Petroleum statistics the reserves of the world's fossil resources are sufficient for the next 40 years.

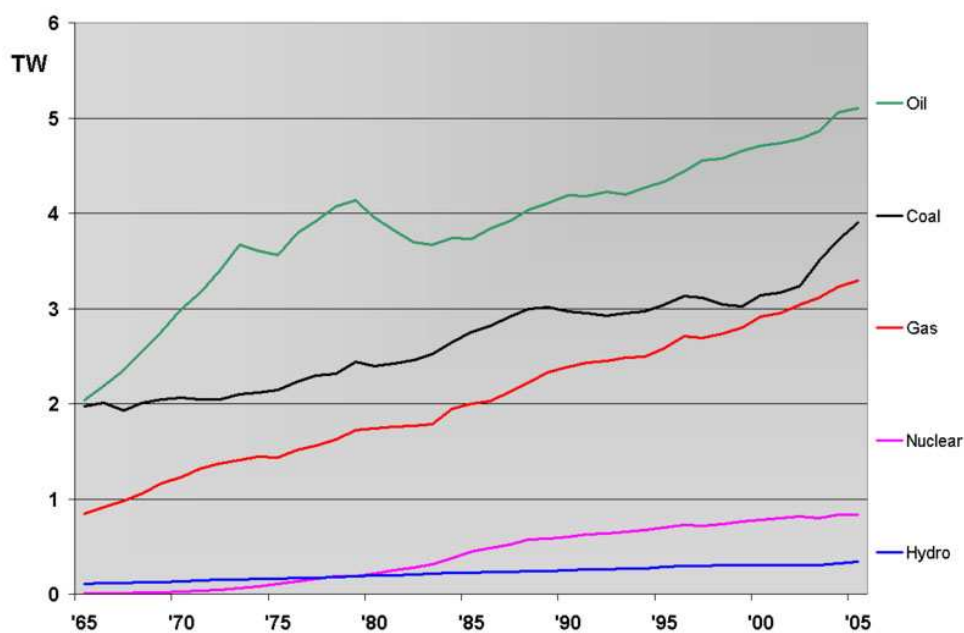


Figure 1: Global energy demand [1]

For a long time scientists are looking for an economically reasonable solution to overcome this problem. One of the solutions is the Fischer-Tropsch synthesis (F-T synthesis) which is a promising way of producing transportation fuels, for example, from natural gas, biomass, or coal.

### 1.2. The approach and thesis objectives

Fischer-Tropsch synthesis (FTS) is a highly exothermic reaction and because of that this diploma thesis is focused on investigations of different approaches that could

increase the phenomena of heat transfer. This work is focused on different packings inside the multi-tubular fixed bed reactor type, which can be used as a catalyst support structure. Currently industrial processes are using randomly packed beds that have quite poor heat transfer. That is the reason that I wanted to investigate different structured packing which could increase heat transfer and consequently solve associated problems to optimize fixed bed reactor performance.

In this project I experimented on different kind of structured packing in the fixed bed reactors. I measured heat transfer as a function (or change) of gas flow and liquid flow. Finally, I compared different structured packings.

To investigate the heat transfer of structured packing I used a test-rig. This set-up is equipped with almost 200 temperature sensors, in order to obtain accurate temperature profiles in both radial and axial directions. Advanced modeling software was available to convert the obtained temperature into heat transfer properties.

In order to investigate the heat transfer problem, we have set the following objectives:

- The main objective of this work was to investigate and quantify heat transfer in different structured packings inside of the main reactor. I used different kind of structured packings (CCFS, OCFS, gauze wire OCFS with skirts and some other modifications) and I compared them with the results of a randomly packed bed.
- The other objective was to collect and compare environmental data (small LCA study) such as which ways are the best to produce primary material for F-T synthesis (methane gas or  $H_2$  and CO), and which impacts have those processes on the environment (mainly green house gas emissions). After all data was collected and investigated I made some conclusions which impacts those processes have on the environment.



## **2. THEORETICAL PART**

In this chapter all the theoretical part is explained. It contains all major explanations about the history of Fischer-Tropsch process, reactor design, heat transfer, flow dynamics, packings used in the experimental set-up.

### **2.1. Fischer-Tropsch synthesis**

#### **2.1.1. History**

The Fischer-Tropsch (F-T) synthesis was discovered in the 1920s by the German chemists F. Fischer and H. Tropsch who were working at the Kaiser Wilhelm Institute in Germany [2]. The process was invented in petroleum poor but coal rich Germany in the 1920s, to produce liquid fuels.

It was used by Nazi Germany and Japan during World War II to produce substituent fuels (ersatz fuels). The industrial application of FT process started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660,000 tonnes per year [3]. However, the bombing of Germany oil facilities during World War II paralyzed much of Germany's synthetic fuel production.

It was briefly used by Germany before and during World War II to produce fuels, and has generated varying levels of interest worldwide since that time. Even though these plants ceased to operate after World War II, interest in the F-T process remained because at that stage there was the persistent precipitation that the reserves of crude oil were very limited.

Based on syngas production from methane, an F-T plant with a capacity of 360,000 t per year was built and operated in Brownsville, Texas, during the 1950s but a sharp increase in the price of methane caused the plant to be shut down. During the same time period, based on the world-wide prediction of increasing crude oil prices an F-T plant based on coal came on line in Sasolburg, South Africa. Even before construction of this plant was completed, soon the discovery of big oil fields, e.g. in Saudi Arabia, Alaska, the North Sea and other areas changed the scenario. As a consequence, any coal-based F-T synthesis was not economic (the South Africa case being an exception for political reasons). The oil crises of the mid 1970s prompted Sasol to construct two much larger coal-based F-T complexes and this time things worked out better as these two plants come on-line in 1980 and 1982 when the price of crude oil exceeded US\$ 30 per barrel. At this time the combined capacity of the three Sasol plants was about 6,000,000 t per year.

Today, the F-T process is used commercially to produce transportation fuels and chemicals at several sites in South Africa, both from coal and natural gas, and at a single site in Malaysia from natural gas [4]. However, there is considerable interest in this technology for the conversion of stranded natural gas reserves into an easily transportable, liquid product.

Now, two new factories are presenting the future in GTL (gas to liquid) technology. These are Oryx (Sasol and Qatar Petroleum) and Pearl (Shell and Qatar Petroleum) both placed in Qatar. Factories are using natural gas from Qatar's north field as a

feedstock to produce synthetic fuel. The capacity of Oryx is 30.000 barrels per day and capacity of pearl is 140.000 barrels per day [5, 6].

### 2.1.2. Process description

The Fischer–Tropsch process (or Fischer–Tropsch Synthesis) is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The process, a key component of gas to liquids technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil or as synthetic fuel. The F-T process has received intermittent attention for a variety of reasons, e.g. as a source of low-sulfur diesel fuel or to address the supply or cost of petroleum-derived hydrocarbons.

In F-T synthesis gas or syngas (carbon monoxide and hydrogen) is converted to hydrocarbons and water over a cobalt (Co) or iron (Fe) based catalyst. Although the chemistry of F-T synthesis is rather complex, the fundamental aspects can be represented by the generalized stoichiometric relationship in Table 1.

*Table 1: Major overall reactions in FTS [7]*

<b>Main reactions (desired):</b>	
Alkanes	$n\text{CO} + (2n+1) \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
Alkenes	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
Water-gas-shift	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
<b>Side reactions (undesired):</b>	
Alcohols	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{H}(-\text{CH}_2)_n\text{OH} + (n-1)\text{H}_2\text{O}$
Boudouard reaction	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$

The highly exothermic nature is a characteristic of the F-T reaction. The formation of 1 mole of  $-\text{CH}_2-$  is accompanied by a heat release of 165 kJ/mol. Since the F-T reaction is highly exothermic, it is important to rapidly remove the heat of reaction from catalyst particles in order to avoid overheating of the catalyst which would otherwise result in an increased rate of deactivation due to sintering and fouling and also the undesirable high production of methane.

Currently there are two operating modes. The high-temperature (300-350 °C) process with an iron-based catalyst is used for the production of gasoline and linear low molecular mass olefins. The lower temperature (200-240 °C) process with either iron or cobalt catalyst is used for the production of high molecular mass linear waxes [8].

## 2.2. Syngas

Syngas (or synthetic gas) is the name given for the gas mixture that contains carbon monoxide (CO) and hydrogen (H<sub>2</sub>). Examples of production methods include steam reforming of natural gas, gasification of coal or biomass (see Figure 2), and in some types of waste-to-energy gasification facilities [9]. Syngas is used as a raw material in producing synthetic petroleum for use as a fuel via F-T synthesis.

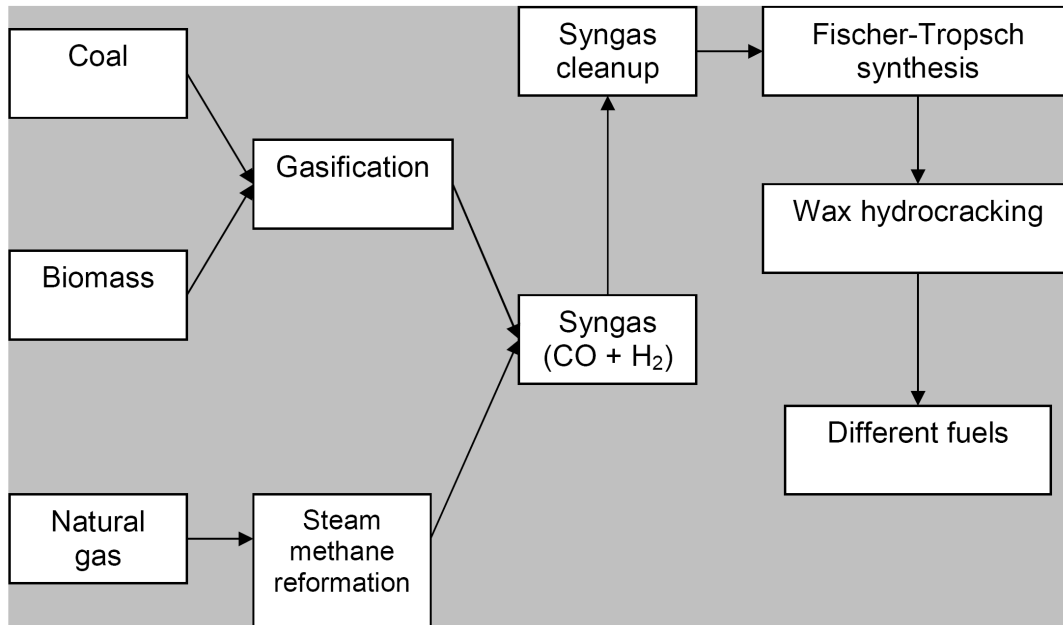


Figure 2: From feedstock to F-T fuels [2, 10]

Syngas primarily consists of  $H_2$ ,  $CO$ , and very often some  $CO_2$  is also present. It has less than half energy density of natural gas. Syngas is combustible and often used as raw material for the production of other chemicals.

In a F-T complex the production of purified syngas typically accounts for 60-70 % of the capital and running cost of the total plant [3]. For economical reasons, methane is preferred to coal for syngas production. Not only is the capital cost of the methane conversion plant about 30 % lower but the process is more efficient. In methane reforming about 20 % of the carbon is converted to  $CO_2$ , whereas with coal gasification the figure is about 50 % due to coal's much lower hydrogen content. But on the other hand the quantity of coal in the world is much bigger.

### 2.3. Catalysts used in F-T synthesis

Only the metals Fe, Ni, Co and Ru have the required F-T activity for commercial application. On a relative basis taking the price of scrap iron as 1.0 the approximate cost of Ni is 250, of Co is 1000 and of Ru is 50 000 [3]. Under practical operating conditions Ni produces too much  $CH_4$ . Besides the very high price for Ru the available amount is insufficient for large scale application. This leaves only Fe and Co as viable catalysts.

### 2.4. Commercially used reactors in F-T synthesis

#### 2.4.1. Slurry-phase reactors

Slurry-phase reactors (or slurry bubble column reactors-SBCR) are one of the two commercially used reactor types for the production of middle distillates. SASOL introduced this technology in 1993 in a unit with a capacity of 2500 bbl pre day [11]. Syngas is bubbled through slurry of heavy liquid products and catalyst particles. Un-

reacted synthesis gas and light products leave the reactor in the gas phase, while the liquid products are removed as a part of the slurry. Heat is removed by cooling coils mounted inside the reactor. A clear advantage of a slurry-phase reactor is the well-mixed liquid phase resulting in nearly isothermal operation. An associated disadvantage is the back-mixing of the gas phase bubbling through the slurry. Maretto and Krishna show that back-mixing in slurry bubble-column reactors leads to significant decreases in conversion per pass and reactor productivity. They suggest introducing stages in the dense phase (liquid and small bubbles) to increase the plug-flow behavior of the reactor. Particle sizes can be chosen small enough to avoid diffusion limitations. A serious issue in slurry-phase operation is catalyst attrition and separation from the waxy liquid product. Separation gets more difficult with smaller particle sizes. SASOL states that it was critical to control attrition and separation for commercial realization of their slurry process. Catalyst stability is an important topic. The iron catalyst suffers from a decrease in selectivity toward heavy products in the course of its lifetime. Continuous refreshing of the catalyst is therefore essential to obtain stable product yields in time. New designs are based on more active and stable cobalt catalysts. Together with other improvements, these new reactors can reach productivities of 15 000 bbl per day. In addition to SASOL, other oil companies such as EXXON Mobil are also considering using slurry bubble columns on a commercial scale.

#### 2.4.2. Multi-tubular fixed-bed reactors (MTFBR)

Another commercially used reactor type is the multi-tubular fixed-bed reactor. Many of the early designs were based on fixed-bed reactors [11, 12, 13]. The removal of heat is one of the major issues in these technologies, resulting in low productivities per unit reactor volume but on the other hand this process has many advantages to SBCR reactors (e.g. control of process, separation of catalysts and liquid products, etc). Also, the selectivity is strongly dependent on the reaction temperature. One of the biggest challenges in applying fixed-bed technology is solving the heat-removal problem. Radial heat removal is essential. Shell chose a multi-tubular reactor with a small tube diameter surrounded by boiling water to create enough heat-removal capacity. The reactor is operated under trickle-bed conditions by recycling liquid products, which increases the heat-transfer capacity. But even this configuration cannot prevent axial and radial temperature profiles near the inlet of the reactor. Fixed-bed technology also imposes limits on the minimum catalyst particle size that can be applied. Too small particles cause a high pressure drop over the reactor. But too large particles result in loss of selectivity and activity because of diffusion limitations. Finding a compromise between short diffusion lengths and acceptable pressure drop is essential for the feasibility of a fixed-bed FTS reactor. Shell did not publish how they solved the problem, but quadrulobes, eggshell catalysts or wide porous materials are obvious options. Moreover, the distribution of gas and liquid over the large number of parallel tubes is not straightforward. An even packing in a tube and equal flow resistance over the various tubes are necessary to ensure an even distribution between the various tubes. Catalyst stability is very important in F-T synthesis. SASOL suffered from considerable downtime using the ARGE fixed-bed reactor, the predecessor of their present slurry bubble column. Cobalt catalysts, as used by Shell, have considerable longer lifetime solving this problem. The reactors built by Shell originally had a capacity of 3000 bbl per day, which is five or six times more than the ARGE types as were used by SASOL. Further development and debottlenecking led to an increase in productivity of 30 % and in liquid selectivity of 20 % for the existing reactors. New plants will even have a higher productivity and selectivity.

### 2.4.3. Micro-reactors (or micro-tubular reactors)

Micro-reactors are a novelty in reactor design technology. This technology can solve many problems of the conventional F-T reactors. For example, MTFBRs productivity is limited by their heat removal capacity since the reaction is highly exothermic and in case of micro-reactors heat removal is very efficient. Their biggest disadvantage is replacement of inactive catalyst and consequently big investments to solve this problem [14].

## 2.5. Reactor design

Reactor design is often not straightforward. In many cases various characteristics of a chemical process impose conflicting requirements on selection of a reactor. In F-T synthesis there are two popular reactor types interesting reactors with their own advantages and disadvantages. A reactor design is often a compromise, which is not optimal for all process characteristics [11, 15].

There are several considerations in reactor design: catalyst design, injection and dispersion strategies and hydrodynamics. An overview is given in Table 2.

*Table 2: Summary of objectives for FTS reactor design [11]*

Level	Requirements
Level 1: catalyst design	<ul style="list-style-type: none"><li>• High activity</li><li>• Open morphology</li><li>• Short diffusion length</li></ul>
Level 2: injection and dispersion strategies	<ul style="list-style-type: none"><li>• Concentration in plug flow</li><li>• Temperature mixed</li><li>• Staged feeding of reactants</li><li>• In situ water vapor removal</li><li>• Periodic operations</li></ul>
Level 3: hydrodynamic regime	<ul style="list-style-type: none"><li>• High catalytic holdup</li><li>• Good heat-transfer characteristics</li><li>• Moderate to good mass-transfer characteristics</li><li>• Suitable catalyst strength, stability and particle size</li></ul>

### 2.5.1. Catalyst design

Firstly, catalyst design is considered. Phenomena such as the reaction scheme and kinetics, diffusion characteristics, particle morphology, reaction rate and selectivity are the key parameters. The diffusion distance and porosity are the parameters available to tune catalyst performance. Short diffusion distances are almost always favored from a reaction-rate point of view. Also, selectivity benefits in many cases from short diffusion distance as reactive intermediates are often desired. The solutions for reaching desired diffusion distance are small particle size, thin layer of catalysts, etc [11].

### 2.5.2. Injection and dispersion strategies

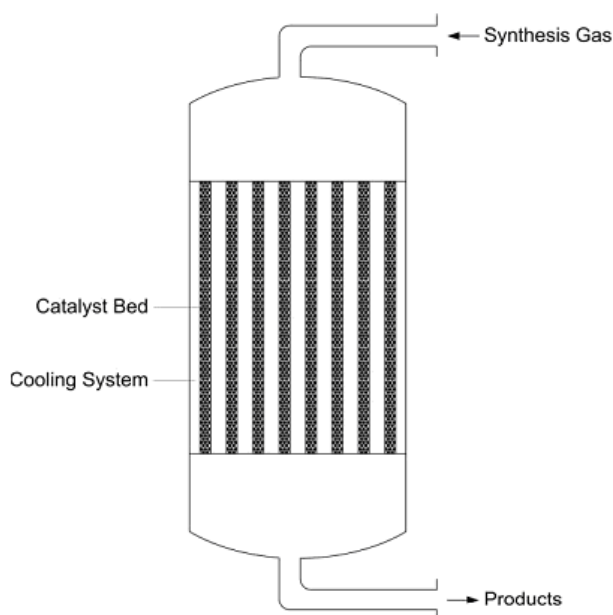
The next level is concerned with injection, dispersion and removal of reactants, products and energy. Options like batch or continuously operation, staged injection of reactants or heat and transient operations are considered. It should be noted that the desired state of mixing of concentrations and temperatures can be different. Strongly exothermal reactions require the removal of heat in order to keep within reasonable and safety limits of reaction rate and selectivity [11].

### 2.5.3. Hydrodynamics

The third level, hydrodynamics, is strongly dependent on the other two levels. The requirements formulated in the first two levels should be combined with desired hydrodynamics characteristics such as productivity per unit reactor volume, heat and mass-transfer behavior and catalyst strength and stability. In my case heat transfer is the most important reactor design parameter [11].

## 2.6. Multi-tubular fixed bed reactors

A bigger description about MTFBRs is located in section 2.4.2. The design of a MTFBR F-T (Figure 3) reactor requires a careful balance between conversion, pressure drop and heat transfer. In MTFBR catalyst is placed inside small-diameter tubes which are surrounded by circulating boiling water [7]. The boiling water acts as a coolant and removes the heat of reaction. A high linear gas velocity is applied and unconverted syngas is recycled. The MTFBR is appropriate for operation at low temperature. There is an upper temperature limit of about 530 K, above which carbon deposition would become extensive, leading to blockage of the reactor. This reactor can be considered a trickle-flow reactor, since a large part of the products formed at relatively low operating temperatures are liquid.



**Figure 3: Multi-tubular fixed bed reactor [16]**

## 2.7. Heat transfer

Heat transfer is transition of thermal energy from hotter mass to a cooler mass [17]. When an object is at a different temperature than its surroundings (or another object), transfer of thermal energy occurs in such a way that the body and the surroundings reach thermal equilibrium. Heat transfer always occurs from higher temperature object to a cooler temperature object (Second law of thermodynamics). In my case heat transfer is happening between fluid and gas inside the reactor and the reactor wall. The wall of the reactor consists of cooling jacket in which cooling water is circulating.

Heat transfer consists of three physical phenomena. Those are conduction, convection and radiation.

Conduction is a flow of internal energy from a region of higher temperature to one with lower temperature by interaction of the adjacent particles (atoms, molecules, electrons, etc.) in the intervening space.

Convection is the transfer of internal energy into or out of an object by the physical movement of surrounding fluid that transfers the internal energy along with its mass.

Heat radiation is the transfer of internal energy in the form of electromagnetic waves. For most bodies on earth, this radiation lies in the infrared region of electromagnetic spectrum. Radiation is neglected in this study, since its contribution is only significant at temperatures higher than 800 K.

In non-adiabatic reactors, heat flows have to be considered in both radial and axial directions, but the heat flow in axial direction is often neglected due to its limited contribution to the heat transfer process [11]. Radial heat transfer consists of convection, radiation and thermal conduction through fluids and the solid structure of

the packed bed. In this work, I used a set-up using the constant wall temperature approach (more about this procedure is written in the chapter 3.1.1).

## Heat transfer calculation

Heat transfer is introduced with following the equation 1:

$$Q = U_o \times A \times LMTD \quad 1$$

where Q is total amount of heat transferred [W],  $U_o$  overall heat transfer coefficient [ $W/m^2K$ ], A surface area of the heat being transferred [ $m^2$ ] and LMTD is the logarithmic mean temperature difference or temperature driving force [K] [17, 18].

This equation is determining heat transfer in different reactors. To increase heat transfer inside MTFBRs one of these parameters has to be changed. Since A is constant and the inlet and cooling temperatures are fixed, the only solution for this is to study  $U_o$ . Different packings have different  $U_o$ . So the main idea of studying heat transfer is to experiment on different packing inside fixed bed reactor and consequently we may solve one of the biggest problems of MTFBRs. A more detailed description is given in chapter 3.4.

## 2.8. Packings

The main purpose of packings is catalytic activity (mostly Co is in use as a catalyst). Packings can be made in different shapes, size, structure, etc., because of different purposes and conditions inside the reactor. Different packings have different properties which could contribute to solving some problems or disadvantages in MTFBR technology.



### 2.8.1. Random packings

Nowadays, mostly randomly packed bed reactors are used in industrial processes. This is mainly because of their low production cost and high catalyst loading. But on the other hand, there are some disadvantages also (high pressure drop, not predicted flow dynamics, etc.).

One of the most important advantages of randomly packed catalyst is high catalyst loading, and that is also important reason for its common use in industry. Randomly packed beds have around 60 % of catalyst loading and if we compare it with structured packing, this is very high (for the currently studied structured packings the catalyst loading is around 20 %).

Particles for randomly packed beds can be made in different shapes, e.g. small particles, eggshell catalyst, and multi-lobe extrudates. Small particles are desired because of their small diffusion length but on the other hand this could cause problems with high pressure drop.

### 2.8.2. Structured packings

Process intensification draws a lot of attention and it has become clear that structured reactors will play a key role in the near future [19]. A structured reactor contains a structured internal which can be made out of ceramics, metals or carbon. It can be considered as an intensified form of a randomly packed bed reactor. The advantage of structured reactors is that it may be designed in full detail up to the local surroundings of the catalyst allowing ultimate precision and control over the process.

Structured packings are a relatively new idea in F-T process but they are being used in other processes for some time. Since the 1960s structured packings have been applied successfully in industrial distillation and absorption columns.

Structured packings have amazing advantages that may be used in the F-T process. They effectively allow the decoupling of intrinsic reaction kinetics, transport phenomena and hydrodynamics. Decoupling is extremely valuable because it allows independent optimization for all these three aspects, each of which has a significant influence on the behavior of catalytic reaction, giving rise to a reliable and excellent reactor performance. The best example where decoupling between hydrodynamics and reaction rates is needed is the requirement of small particles for high catalyst effectiveness whereas hydrodynamics is demanding a low pressure drop, and as a consequence, the particles should be large. These two are the classical conflicting demands in a packed bed. In such case structured internals can play a very important role and allow solutions that were previously impossible.

An attractive and promising structured packing for the F-T process is the cross flow structure (CFS).

### 2.8.3. Cross flow structures (CFS) or corrugated packings

This diploma thesis is focused on cross flow structure packing and their different properties.

The early corrugated packings were BX gauze (constructed by Sulzer) packing and they were used for the separation of heat-sensitive products [20]. In the 1970s Mellapak structured packings opened up a large field of application in chemistry, petroleum chemistry, refinery and absorption processes.

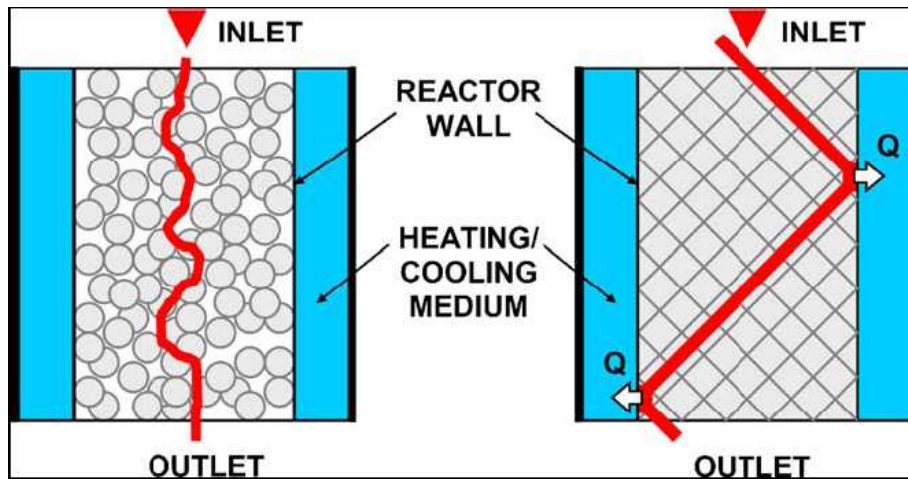


Figure 4: Flow paths inside randomly packed bed (left) and structured packed bed [21]

Radial heat transfer in tubular reactors can be significantly improved through the introduction of a geometry that allows for cross-flow in the reaction environment [21]. Cross-flow is convective flow of reactants that has a component perpendicular to the axial reactor direction, which improves the heat transfer by means of radial convective transport in addition to the generally small radial conductive heat transport. This can be realized by choosing a geometry that consists of slanted channels (see Figures 4 and 5). Depending on the type of cross-flow structure (CFS) mixing of the reactant flows from different channels can take place at various locations. Two types of CFS are distinguished (see Figure 5): (left) the open CFS (OCFS) and (right) the closed CFS (CCFS). Examples of these types of structures are Katapak-MK and Mellapak, developed and manufactured by Sulzer [21].

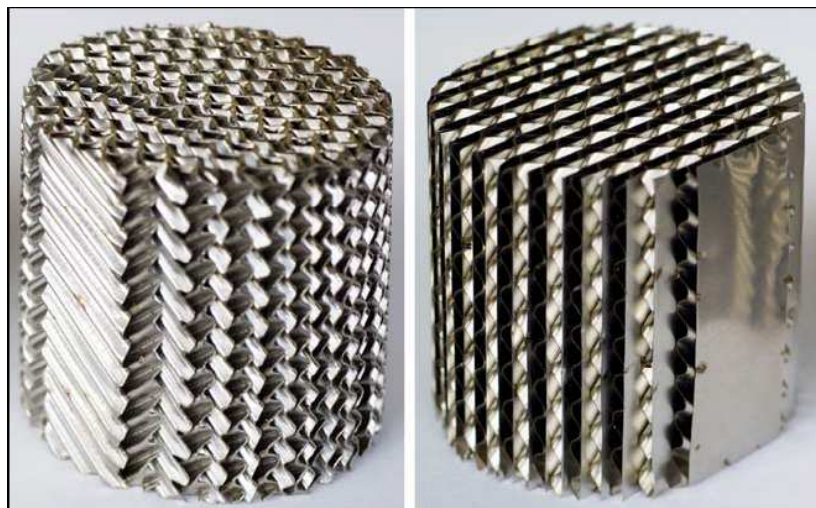


Figure 5: OCFS (left) and CCFS (right) [21]

An OCFS packing consists of a stack of corrugated plates with alternating angle configuration. The channels are formed by the corrugations in the sheets. In this case the reactants in the channels are allowed to mix with those of the channels from a neighboring plate at cross-sections and in the gap between the reactor wall and the packing structure (see Figure 5) [21].

In a CCFS geometry mixing between the channels of two neighboring plates is prohibited, due to the presence of flat sheets between the corrugated sheets (see Figure 6) [21].

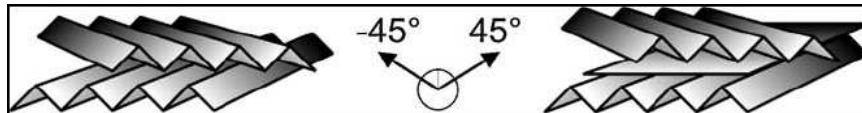


Figure 6: Corrugated plates inside OCFS (left) and CCFS packings (right) [21]

Because of their excellent properties on different fields, mainly heat transfer, CFS structures became an interesting solution for F-T synthesis.

## 2.9. Gas and liquid dynamics inside packings (flow dynamics)

Gas and liquid dynamics inside the packings is an important factor for heat transfer. It is important because if we can assure the desired flow dynamics this could assure better heat transfer. But to understand the influence of flow dynamics on heat transfer certain concepts have to be explained first.

### 2.9.1. Geometry of structured packings

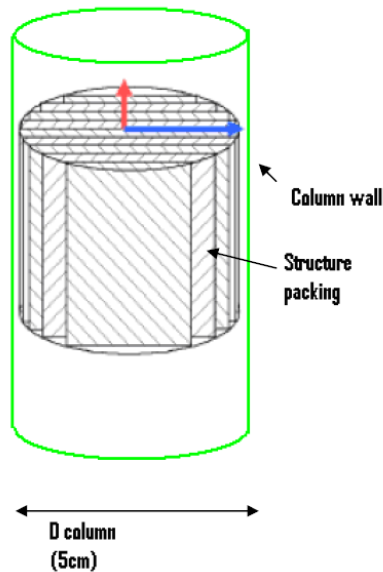


Figure 7: Structured packing inside column and geometry

On the Figure 7 we can see a structured packing inside a column. To understand certain problems connected to heat transfer, first we have to focus on some parameters inside the column.

In the Figure 7 we can see the position of the packing inside the column. Different packings have different properties and dimensions. Axial dimensions are the same for all packings (5 cm) but the radial dimensions are different (see Table 3). The space in between packing and column wall is called gap and most of heat transfer is taking place at the gap.

In the Figure 7 there are two arrows (blue and red). The blue arrow is representing flow along the channels, and is responsible for the major part of the heat transfer (convection). The heat transfer is bigger because there is more interaction with column (or reactor) wall where the heat transfer is taking place [18]. The red arrow is representing heat transfer by conduction which is much lower. For calculation of heat transfer ratio between convection and conduction, I used the Peclet number for heat transfer. The calculations were made for highest and lowest liquid velocities. For more information see Appendix A [22]. The ratios (convection/conduction) are 218.4 (for lowest liquid velocity) and 728 (for highest liquid velocity).

### 2.9.2. Flow paths inside the column

The main purpose of cross flow structures is to improve radial flow [18]. Different paths could be observed inside cross flow structures (see Figure 8).

Figure 8.c shows the most desired flow path. The flow is going through the channel ending up at the wall and entering another channel. This is the best possible path with good mixing and heat transfer. This path can be observed in OCFS and CCFS packings.

Two other paths can be observed in cross flow structures. One is only possible inside the OCFS packing (see Figure 8.a). A flow through the packings is moving to a neighboring channel at every cross section [18]. For this possibility the heat transfer is very low because gas and liquid can not reach the reactor wall.

The last possible path is possible for all cross flow structures that have enough big gaps (see Figure 8.b). The flow is going through channel ends up at the wall and continues its way through the gap. In this possibility the heat transfer is the best but on the other hand mixing is very low and also the contact with catalyst layer is very short (reaction can not take place).

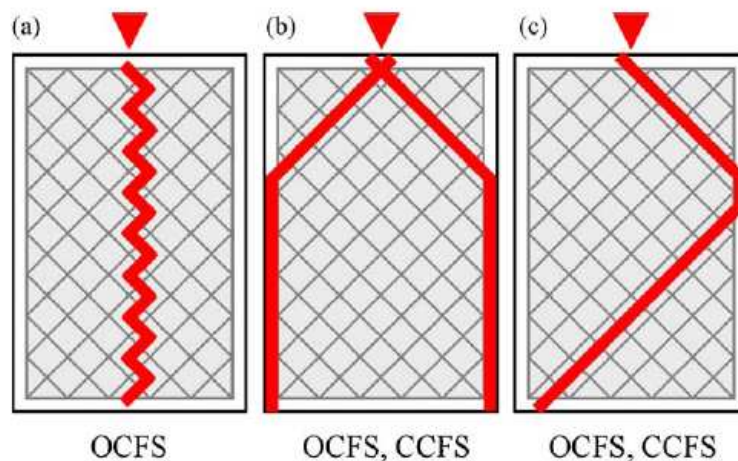


Figure 8: Possible flow inside structure packing [21]

### 2.9.3. The gap

The heat transfer is happening at the interface between gap and column wall that is why the gap size plays important role in overall heat transfer. For example, if we increase gap size, more gas and liquid is passing by and there is also reduction in mixing of liquid and gas. The result of bypassing is lower reaction rate and effectiveness of reactor. On the other hand, if the gap size is quite small, the contact between the reactants and reactor wall can become smaller leading to a decreasing the heat transfer. So the purpose is to find right gap size or to try some sort of device that could lead gas and liquid back to packing (increase mixing). For the second option there are some modifications that were tested and led us to some interesting results [23].

## 2.10. Maldistribution

Fixed bed reactors are extensively used in industrial processes. Gas and liquid distribution inside MTFBRs plays an important role in the efficiency of the process. Maldistribution inside multi-tubular reactor can be the cause of losses either in performance, selectivity or catalyst stability in fixed bed. The improved design of reactor internals and the bed structure all aim at achieving improved utilization of catalyst bed and better reactor performance. For instance, an optimized bed structure is developed to provide a homogenous gas-liquid distribution inside the catalytic bed.

The improvements of the contact between the three phases (gas, liquid and catalyst) enhance the transport phenomena and allow better overall reaction yields. Therefore it is important to have information on this flow dynamic behavior [23].

### 3. EXPERIMENTAL WORK

In this chapter all the equipment and procedures of experimental work are presented.

For studying and understanding the heat transfer phenomena in different packings a set-up was used to simulate a tubular fixed bed reactor for F-T synthesis. This set-up is not only used to study heat transfer but also for studying phenomena like mass transfer, pressure drop, liquid hold-up, etc. However, this diploma thesis is only focused on heat transport phenomena.

#### 3.1. Set-up

In Figures 9, 10 and 11 the set-up scheme is shown. In this case set-up was designed in order to measure heat transfer rates in structured packings.

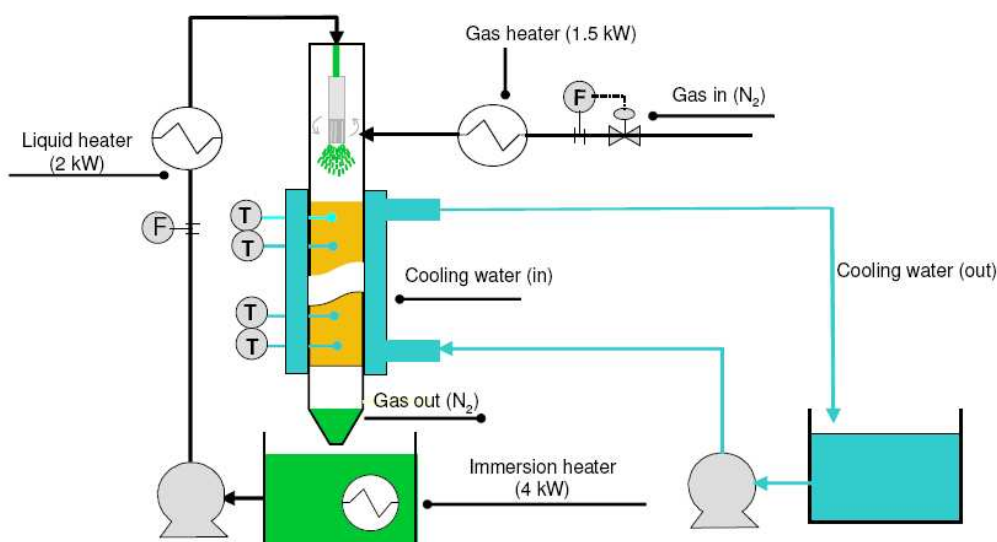


Figure 9: Scheme of experimental set-up

Gas ( $N_2$ ) and liquid (isopar-M) are heated with electrical heaters to approximately 60 °C.

After heating, gas and liquid enter the pre-column. The pre-column is designed for pre-mixing of gas and liquid phase before they are entering the cooling column. A pre-column of 80 cm in length is placed on top of the heat transfer column to stabilize the flow profile. No heat transfer takes place here.

A column of 60 cm in length is made from two aluminum tubes. The packings are placed in the inside tube and the purpose of the outside tube is for cooling. Inside the cooling elements there is a current of cooling water at room temperature (but never more than 25 °C). The column and cooling elements are made from 4 parts (2x10 cm, 2x20 cm).

Temperature profiles measured inside column and in the wall with support of more than 200 sensors. After gas and liquid are exiting column liquid is recycled and gas is released into atmosphere. Later on the whole procedure is repeated.

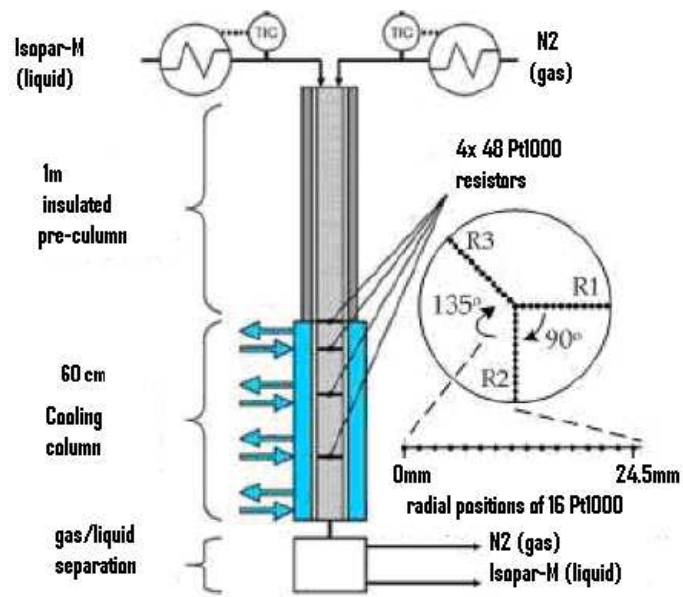


Figure 10: Column and pre-column of experimental set-up



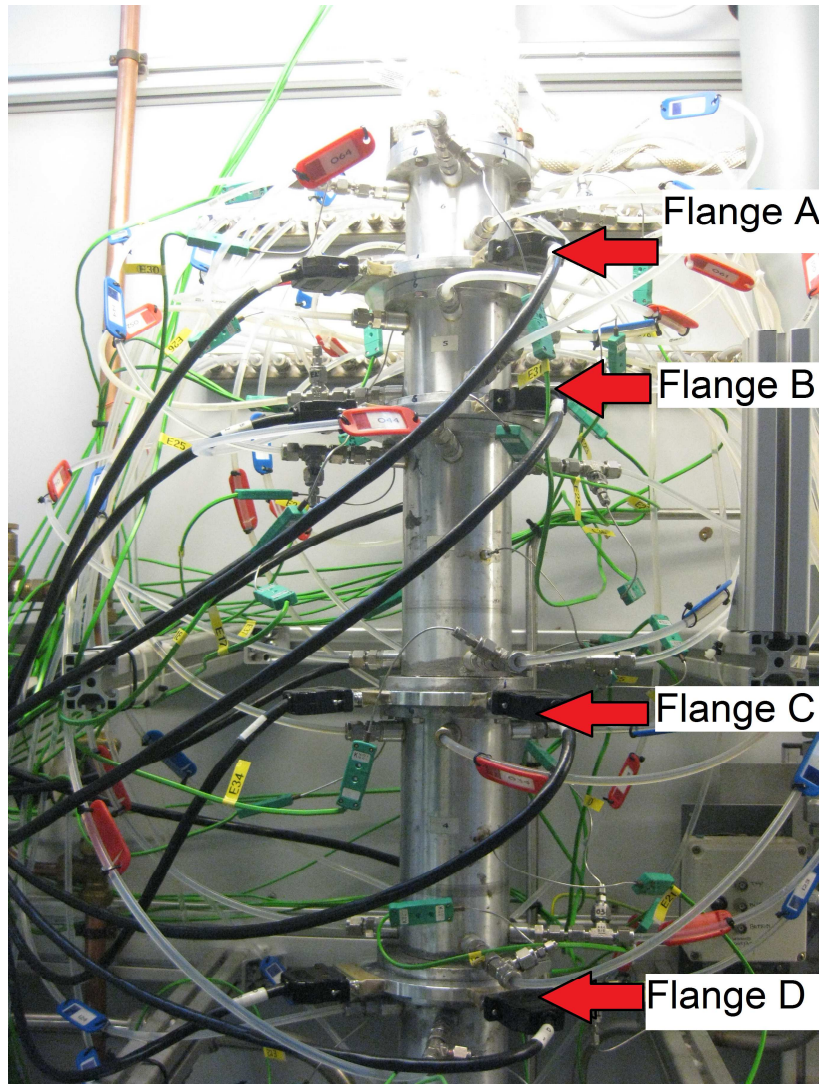


Figure 11: Column with flanges

### Constant wall temperature approach

In this work, I used a set-up using the constant wall approach. In this approach, the temperature at the wall of the heat transfer tube is maintained constant through the complete length of the column. This can be achieved by circulating heat transfer liquids at in the jacket of the heat transfer column. Depending on whether the heat transfer is achieved by heating or cooling (in my case cooling), either hot water or saturated steam or room temperature water can be used to circulate in the jacket. Care has to be taken that the heat transfer area is sufficient large to remove or supply the heat from or to the heat transfer column. Most importantly the circulation rates or the liquid in the jacket must be high enough to avoid any temperature variations in the wall along the length of the column.

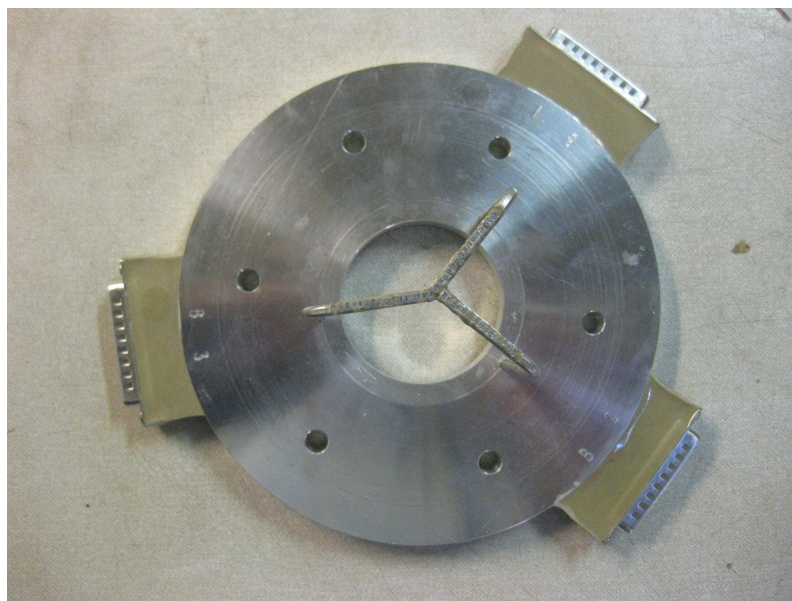
### 3.2. Temperature measurements

For studying and calculating heat transfer we have to know the temperature profiles inside the column. Heat transfer measurements were carried out by measuring the

radial and axial temperature profiles generated by cooling a heated mixture of Isopar-M (organic liquid consisting of C<sub>13</sub>-C<sub>16</sub> isoparafins) and nitrogen flowing co-currently downwards in a 60 cm long heat transfer column. That is why temperature measurements are taking place inside column (on 4 flanges, see Figures 10 and 11), inside the cooling wall and inside the cooling water tubes. Inlet gas and liquid, wall temperatures and cooling water temperatures are measured by thermocouples. All sensors are connected to a computer and are displayed and processed by program called LabVIEW.

### 3.2.1. Temperature profile measurements

Temperature measurements are done in the column. The column consists of 4 parts, each cooled with separated cooling elements (cooling jacket). In between column parts flanges are placed in 4 axial positions each between two parts (flange A, B, C, D- see Figure 11). On the inside of a flange there are 3 arms, in the 3 different radial directions, containing Pt1000 resistors (temperature sensors). In the Figures 10 and 12 you can see different arms and angles (0, 90 and 135 °). On every arm there are 15 or 16 Pt1000 resistors. Temperature measurements inside the column are taking place after 5 cm, 15 cm, 35 cm and 55 cm. These Pt1000 resistors (type SMD 0603 (V), produced by Heraeus, tolerance ±0.12 %) have a linear dependency on temperature, which makes it possible to measure temperature profiles.



*Figure 12: Flange for temperature measurements inside column [18]*

### 3.2.2. Wall and cooling water temperature measurements

The column tube which contains the packing is covered by a chamber called as a “jacket” used for a circulation of the cooling water. The cooling jacket is designed to contain 4 sets of channels, each set of channels has its own inlet and outlet for cooling water (see Figure 13). Wall temperature measurements are taking place inside every part of the column (4 column parts) in several axial positions (2 or 3), and water

temperature measurements are taking place on almost every cooling water inlet and outlet.

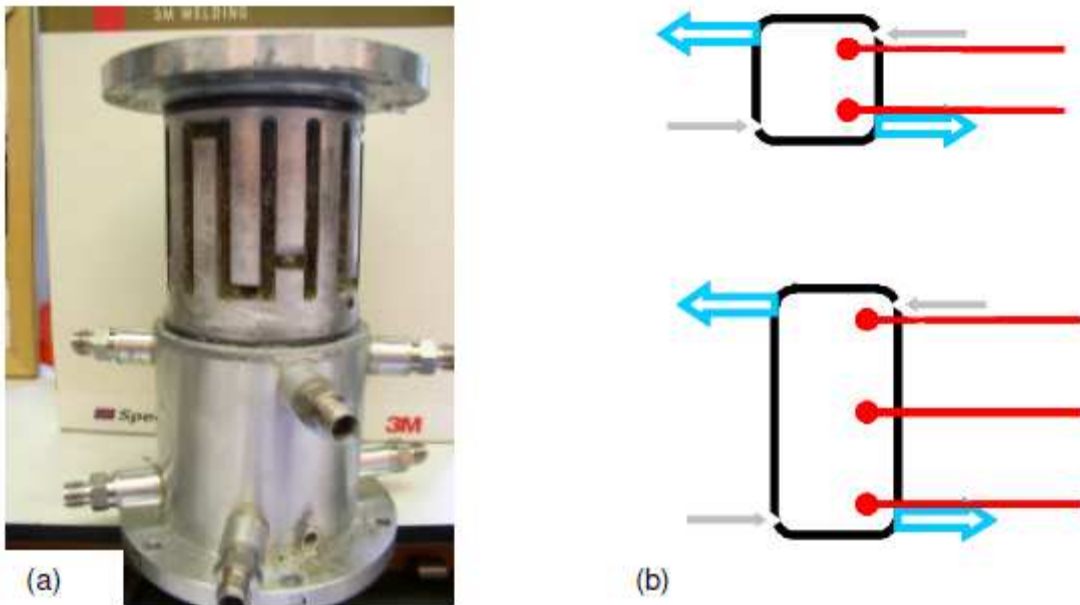


Figure 13: Picture (a) and scheme (b) of cooling jacket [20]

### 3.3. Packings used in experiments

To improve heat transfer properties my approach was to experiment on different packings that could be used in the F-T process. In Table 3 all the packings are presented that were used in the experimental work.

Table 3: Packings (and their properties) used in experiments [20, 22]

Packing	Material	Structure	$\epsilon$ [ ]	$D_{\text{packing}}$ [cm]	$d_h$ [mm]	Supplier
Glass beads [8]	Silica	Non-porous silica beads (random structure)	0.4	5.0	0.9	Fischer-Emargo
OCFS	Stainless steel	Corrugated sheets	0.84	4.85	1.98	Sulzer
CCFS	Stainless steel	Corrugated sheets	0.95	4.8	2.82	Sulzer
OCFS knitted wire with flaps	Stainless steel	Corrugated sheets made from knitted wire ( $d=0.1$ mm)	0.96	4.3 (with skirts to 5cm)	4.24	Sulzer

### 3.3.1. Glass beads

One of the experiments was made on glass beads (see Figure 14) because they represented the catalyst particles that are most common used in F-T industry. The results are used as a reference point for comparison to the other packings. Glass beads have very low heat transfer properties, but on the other hand, catalyst made in a same shape has a high catalyst loading ( $\epsilon=0.4$ -from the literature and  $\epsilon=0.375$  from calculation of experiment properties). The diameter of glass beads used in experiments was 2 mm and the hydraulic channel diameter is 0.9.



*Figure 14: Glass bead used which are representing randomly packed bed*

### 3.3.2. CCFS

Those packings were also used in previous experiments by K. Pangarkar, D Vervloet and B. T. Kuipers. They found out that if we use axial alternating 90° rotated orientation the heat transfer improves between 20-35 %. This is the approach used in all my experiments with structured packings.

CCFS packing is made from stainless steel corrugated sheets and pressed together to form a cylinder. In between two layers corrugated sheets there is also one layer of flat sheet which is preventing that gas and liquid can not leave the channel (Figure 15 right). The hydraulic channel diameter is 2.82 mm and porosity 0.95.

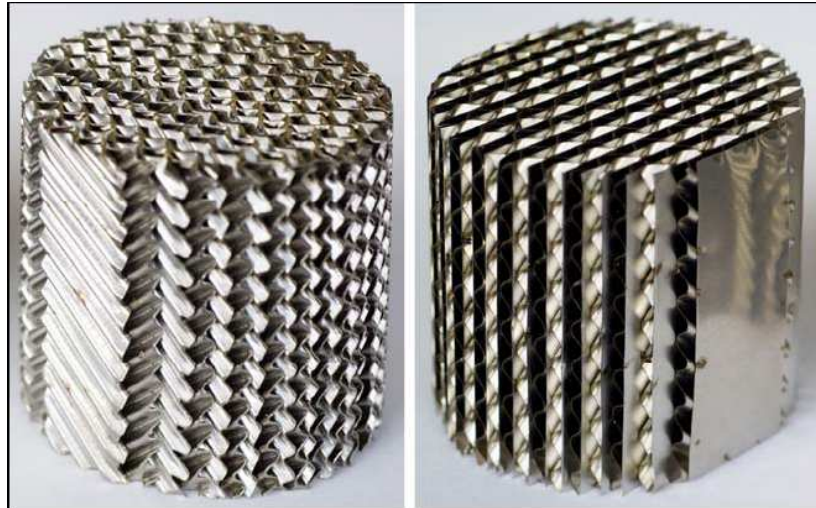


Figure 15: OCFS (left) and CCFS (right) [21]

### 3.3.3. OCFS

Another structured packing used in the experiments was OCFS. It is made from stainless steel corrugated sheets pressed together in the form of a cylinder (see Figure 15 left). The hydraulic channel diameter is 1.98 mm and porosity 0.84.

### 3.3.4. OCFS made from wire gauze with skirts

This structured packing is made out of 0.1 mm thick stainless steel wire formed into different corrugated sheets and pressed together to form a cylinder. The difference between that packing and other structured packing is that this has also some sort of “skirts” (see Figure 16). The purpose of the skirts is that gas and liquid are redirected from the gap into the inside of the packing where reaction can take place.



*Figure 16: Wire gauze packing with skirt*

### 3.3.5. Modifications (rings and skirts)

For better mixing and against bypassing of gas and liquid some modifications were used in the experiments. These were skirts and rings. The purpose was to lead gas and liquid from the gap back into the packing.

The skirts (see Figure 16 with wire gauze packing) are surrounding the packing and helping gas and liquid to reenter the packing. The result may be better mixing of gas and liquid, and reaction rate.

Rings or washers (see Figure 17) are causing a similar effect. Gas and liquid collected on the ring is forced to reenter the packing so that reaction can take place. Rings and washers are made from 0.1 mm thick stainless steel plate cut into a ring with outside diameter 5 cm (like the column tube) and inside diameter 4.2 cm. this was chosen arbitrarily.

The ring is placed on the top of every packing element (see Figure 17 right) so that gas and liquid can be collected after leaving the packing. After gas and liquid are collected they reenter the next packing.



Figure 17: Ring made from stainless steel (left) and the same ring on the top of OCFS packing like in experiments (right)

### 3.3.6. Experimental procedure

Different kinds of packing were tested in the set-up. Packings were tested at different gas (0.25 m/s, 0.75 m/s, 1.0 m/s and 1.5 m/s) and liquid velocities (6.0 mm/s, 10.0 mm/s, 15.0 mm/s and 20.0 mm/s). For every packing 16 experiments were made (see Table 4) and for most of them also duplicates. All experiments were 10 minutes long. After each experiment, average temperature was calculated.

In experiments with CCFS packing (without modifications) different gas velocities were in use (0.25, 1, 1.5 and 2m/s).

Table 4: table of experiments with different gas and liquid velocities

$V_g$ (m/s) \ $V_l$ (mm/s)	1 <sup>st</sup> gas velocity	2 <sup>nd</sup> gas velocity	3 <sup>rd</sup> gas velocity	4 <sup>th</sup> gas velocity
1 <sup>st</sup> liquid velocity	0.25 / 6	0.25 / 10	0.25 / 15	0.25 / 20
2 <sup>nd</sup> liquid velocity	0.75 / 6	0.75 / 10	0.75 / 15	0.75 / 20
3 <sup>rd</sup> liquid velocity	1 / 6	1 / 10	1 / 15	1 / 20
4 <sup>th</sup> liquid velocity	1.5 / 6	1.5 / 10	1.5 / 15	1.5 / 20

The packings inside the column were horizontally turned by a 90° angle on each other. This approach was used because of better mixing and consequently better heat transfer rate. This approach was tested by Bert-Jan Kuipers [18], among others, and his conclusion was that the overall heat transfer improves for 20-35 %. The mixing

effect of the alternation is redistributing the fluids, which keeps the temperature driving force optimal.

### 3.3.7. Start up

Before starting an experiment several things have to be done. To get steady-state conditions the set-up has to be heated to approximately 60 °C. Because of that relatively high gas and liquid velocities are chosen to obtain the desired temperature as soon as possible. But before starting liquid pump, gas has to be released inside the column because there is possibility that set-up will be under vacuum and liquid will not flow through the system. After starting with gas and liquid flow through the system, approximately 30-40 minutes had to be waited to reach steady state. After this is done the experimentation may start.

## 3.4. Heat transfer calculation and model

For calculating heat transfer calculation three steps were needed:

1. First step was to get all needed data for heat transfer calculation. For this approach I used program Lab view which monitored all temperatures inside set-up for approximately 10 minutes long experiments. These temperature measurements were:
  - Gas and liquid temperatures before entering the pre-column
  - Temperature profile measured inside cooling column
  - Reactor wall temperature measurements
  - Cooling water temperature measurements
2. Next step was to calculate heat transfer with help of using Microsoft excel. For this approach “master file” was used. Master file is calculating average temperatures inside set-up to get average temperature profiles. By using these temperature profiles and several equations I was able to calculate heat transfer. To define heat transfer properties for packings used in experiments I was calculating heat transfer coefficient ( $U_o$ ).
  - Equation number 2 was to calculate heat transfer rate ( $\dot{Q}$ )

$$\dot{Q} = \rho \times c_p \times \Delta T \times F \quad [W=J/s] \quad 2$$

$\dot{Q}$  -the total amount of energy transferred through heat transfer pre time

$\rho$ -density [kg/m<sup>3</sup>]

$c_p$ -specific heat capacity of material [J/kg K]

$\Delta T$ -temperature difference ( $T_1$ -temperature of gas or liquid at the beginning of set-up;  $T_2$ -temperature of gas or liquid at the end of set-up)

$F$ -flow rate of gas or liquid [m<sup>3</sup>/s or mm<sup>3</sup>/s]

With this equation I manage to calculate total amount of energy transferred from the cooling column which I used later on.



- Equation 3 was the log mean temperature difference (also known by its acronym LMTD)

$$LMTD = \frac{\Delta T_a - \Delta T_b}{\ln\left(\frac{\Delta T_a}{\Delta T_b}\right)}$$

3

$\Delta T_a$ -temperature difference between gas and liquid at the beginning of the column and cooling water temperature

$\Delta T_b$ - temperature difference between gas and liquid at the end of the column and cooling water temperature

- Equation 4 was for calculating heat transfer. For heat transfer estimation I used heat transfer coefficient overall ( $u_o$ )

$$\dot{Q} = u_o \times A \times \Delta T \rightarrow u_o = \frac{\dot{Q}}{A \times \Delta T}$$

4

A-surface [ $m^2$ ]

- Table of constant values

**Table 5: Values used for calculation**

	System	Isopar-M	Nitrogen (N <sub>2</sub> )
$\rho$ -density [ $kg/m^3$ ]	/	792	1.16
$c_p$ -specific heat capacity of material [ $J/kgK$ ]	/	2206	1007
A-surface [ $m^2$ ]	0.0785	/	/
$F_l$ or $g$ -flow rate for gas or liquid [ $mm^3/s$ ]	/	0.000012-0.00004	0.0005-0.003

- Heat transfer modeling-this was the last step. I used Matlab program for modeling the heat transfer. This approach was more detailed by using also temperature profiles to calculate heat transfer. For modeling I used two different models because of different flow inside cross flow structure and random packed bed (for more information see Figure 4 in chapter 2.8.3. which is explaining flow dynamics in different packings).

- Cross flow structure modeling

I was using model which was made by Bert-Jan Thomas Kuipers [18], previous student who was working at same set-up than me. He was using differential equation (5) to calculate  $h_{wall}$ .  $h_{wall}$  is local heat transfer coefficient, but in this case I am using it to determine heat transfer coefficient for the whole cooling wall. This was only possible by using dimensionless numbers like Peclet and Stanton numbers. To solve this differential equation I was using statistical method called "Sum of squared residuals" or  $SS_{RES}$ .

The anisotropic character leads to a different approach in modeling, where two radial directions, x (R2) and y (R1), are distinguished (see Figure 18) [18]. If a closer look is taken at the radial temperature profiles, it is noticed that the profile in R1 direction is almost flat over the entire range of R1 and suddenly drops at the wall where a drastic temperature difference occurs. In the R2 direction a more gradual temperature profile is observed.

To create starting point a uniform temperature is assumed over a slab into the y or R1 direction. In these slabs convective transport of heat takes place in the axial direction z, and conductive transport is happening at the reactor wall, and into direction x between slabs. Since more gradual temperature profile was observed into the x-direction there should be a temperature driving force for conductive transport. All heat transport terms are outlined in Figure 18 (b), and in 18 (a) the radial directions are outlined.

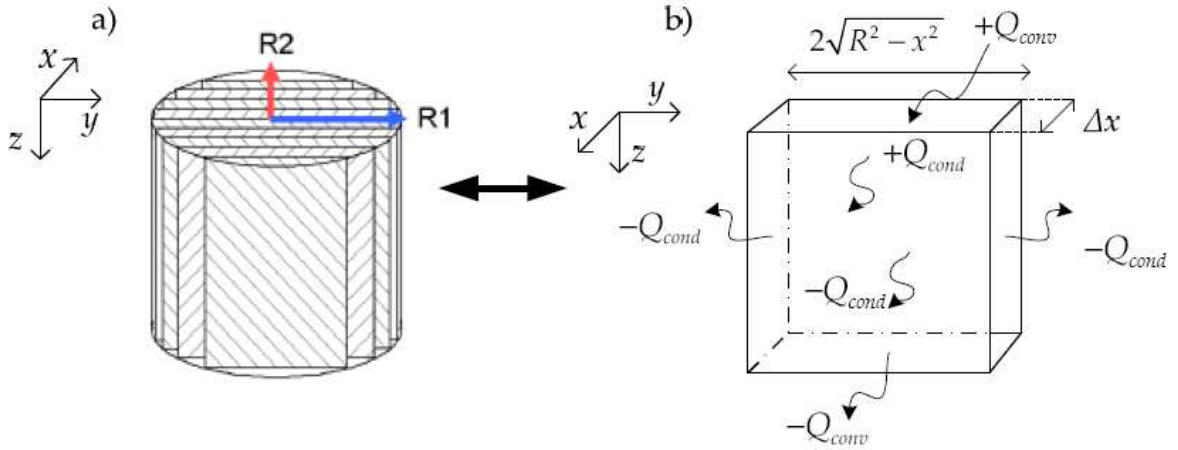


Figure 18: a. distinction between radial direction R1 and R2, b. heat transport terms over a slab I [18]

$$\frac{\partial \theta}{\partial \tilde{z}} = \frac{1}{Pe \sqrt{\tilde{R}^2 - \tilde{x}^2}} \frac{\partial}{\partial \tilde{x}} \sqrt{\tilde{R}^2 - \tilde{x}^2} \frac{\partial \theta}{\partial \tilde{x}} + \frac{St}{\sqrt{\tilde{R}^2 - \tilde{x}^2}} (\theta - 1) \quad 5$$

$\Theta$  - dimensionless temperature

Peclet number [/]

$$Pe = \frac{\text{convection}}{\text{conduction}} = \frac{\rho c_p v d_{tube}}{\varepsilon \lambda} \quad 6$$

Stanton number [/]

$$St = \frac{\text{heat\_transferred}}{\text{heat\_capacity\_fluid}} = \frac{h_{wall}}{c_p \rho v} \quad 7$$

- Random packings modeling (random walk model)

This model was done by Anthony G. Dixon [23]. This model can be used just for randomly packed beds and can not be used in a case of cross

flow structures because of the different flow dynamics inside packings. This model is using differential equation (8) which is estimating  $\alpha_{wall}$  and  $\lambda_r$ .  $\alpha_{wall}$  and  $\lambda_r$  are later used for calculating  $U_{est}$  (9) which is representing heat transfer. All numbers used in this model were the same then in previous model.

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\lambda_r}{\rho c_p} \frac{\partial T}{\partial r} \right) - v_0 \frac{\partial T}{\partial z} = 0 \quad 8$$

With following boundary condition:

- Inlet (z=0):  $T=T_0$
- Outlet (z=L):  $\partial T / \partial z = 0$
- Center (r=0):  $\partial T / \partial r = 0$
- Wall (r=R):  $\frac{\partial T}{\partial r} = \frac{\alpha_w}{\lambda_r} (T_w - T)$  9

$\alpha_w$  – wall heat transfer coefficient [W/m<sup>2</sup>K]  
 $\lambda_r$  – conduction coefficient [W/mK]

$$\frac{1}{U_{est}} = \frac{1}{\alpha_{wall}} + \frac{1}{4\lambda_r} \quad 10$$

### 3.5. Liquid flow measurements (maldistribution)

In this section the maldistribution experimental description is given. The main purpose was to see, how the flow regime and distribution of liquid inside different packings is changing. In this experiment CCFS and OCFS packings with modifications (rings or washers) or without them were tested, to see how modifications are affecting the flow dynamics inside packings. In the Figure 19 the set up for the maldistribution is shown.

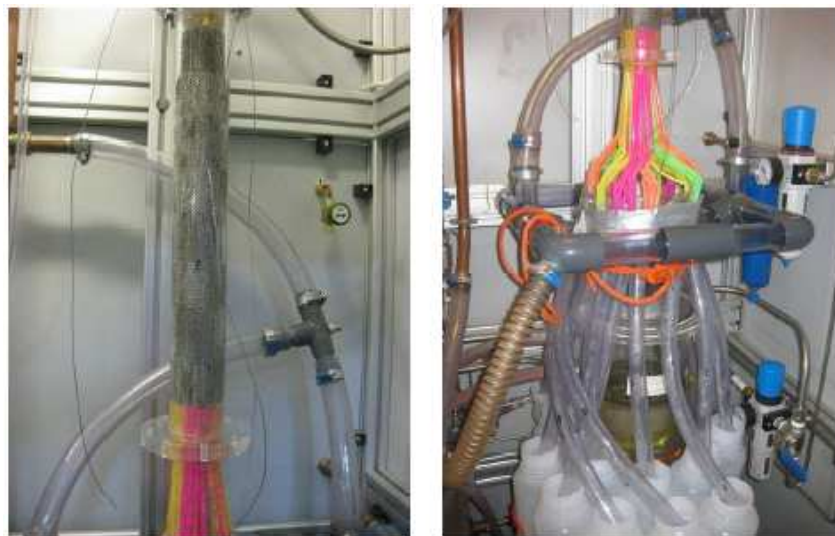


Figure 19: Set-up for maldistribution experiments. On the left is column made from plexiglass, and on the right is collector made from plastic tubes

## Experimental procedure for maldistribution

For measuring the distribution of the liquid flow, a collector was placed at the end of the plexiglass. This collector was designed from a system of plastic tubes to measure the distribution over the packings. The collector is directly placed against the last packing. The surface area of the collector was divided in 13 parts as you can see in the Figure 20a. Plastic tubes were collecting liquids and were leading it to the bottles. The liquid Isopar-M collected in these bottles was indicating a distribution over the packing. A similar concept was mentioned by A. Atta et al. when they studied maldistribution in trickle-bed reactors [24].

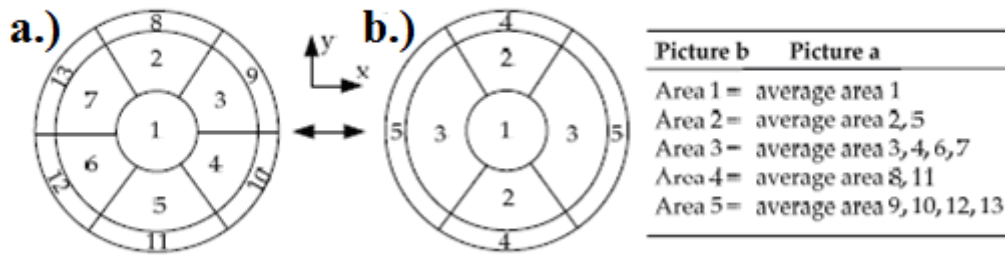


Figure 20: Surface areas in collector. On the left (a) is collector used in experiments, and on the right is collector used for calculation (b)

On every packing 6 experiments were done (see Table 6) on different gas and liquid velocities. Experiments were 2-3 minutes long (depends from liquid velocity).

Table 6: Experimental procedure

Experimental#/ Vl; Vg	1	2	3	4	5	6
Vl [mm/s]	6	6	10	10	20	20
Vg [m/s]	0.25	1.5	0.25	1.5	0.25	1.5

The experimental results were averaged per area (see Figure 20b) because of the symmetry of the packing.

## **4. RESULTS AND DISCUSION OF EXPERIMENTAL WORK**

In this chapter all the results are presented and discussed. This section is divided into two parts. Firstly, all the results form the experimentation and modeling are presented (1<sup>st</sup> objective), and secondly, the environmental research is presented (2<sup>nd</sup> objective).

### **4.1. Experimental results**

In this research two main experiments were performed:

- Heat transfer
- Maldistribution

The heat transfer experiments were done to see if the heat transfer can be improved by using CFS and modifications. All heat transfer results are presented with  $U_o$ . The maldistribution experiments were done to investigate the liquid flow distribution inside the packings.

### **4.2. Heat transfer results and discussions:**

Heat transfer measurements were done on 6 different packings:

- Glass beads
- Wire gauze OCFS packings
- CCFS
- OCFS
- CCFS+rings
- OCFS+rings

All results are presented in the following chapter in graphs and numbers are presented in Appendix C.

#### **4.2.1. Glass beads**

The first experimental results presented in this thesis are those of the glass beads. This is because glass beads are representing the catalyst particles that currently are in use in F-T industry and that is why this is a good reference point. The results are presented in Figure 21.

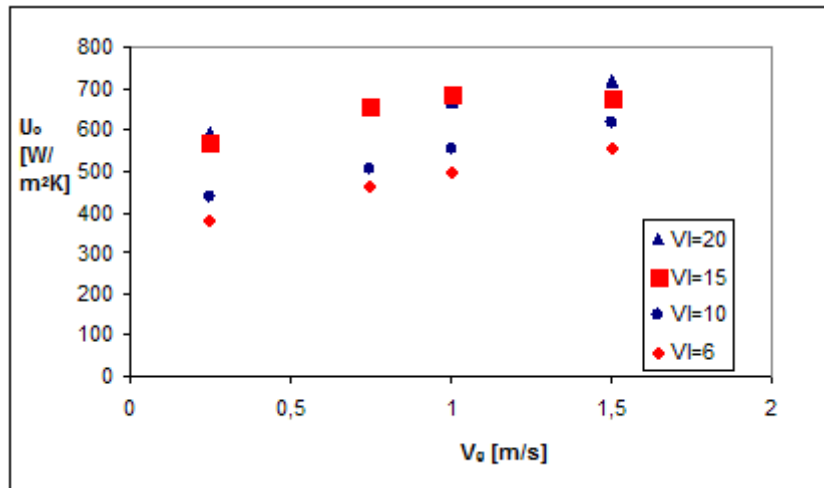


Figure 21: Results of  $U_o$  for experiment with glass beads

In the Figure 21 results for glass beads are presented. Several conclusions were made from observation:

- Glass beads (randomly packed bed) does not have best heat transfer properties,
- Heat transfer is mainly influenced by liquid velocity. This phenomena does not have much influence at higher liquid velocities (more than 15 mm/s),
- Gas velocity has small influence on heat transfer by lower liquid velocities.

Results for glass beads are used as a reference result for all following heat transfer results.

#### 4.2.2. Wire gauze OCFS packings

The next experiment was done on wire gauze packing which is a sort of CFS (OCFS packing) but with much larger channel diameter. The results are presented in Figure 22.

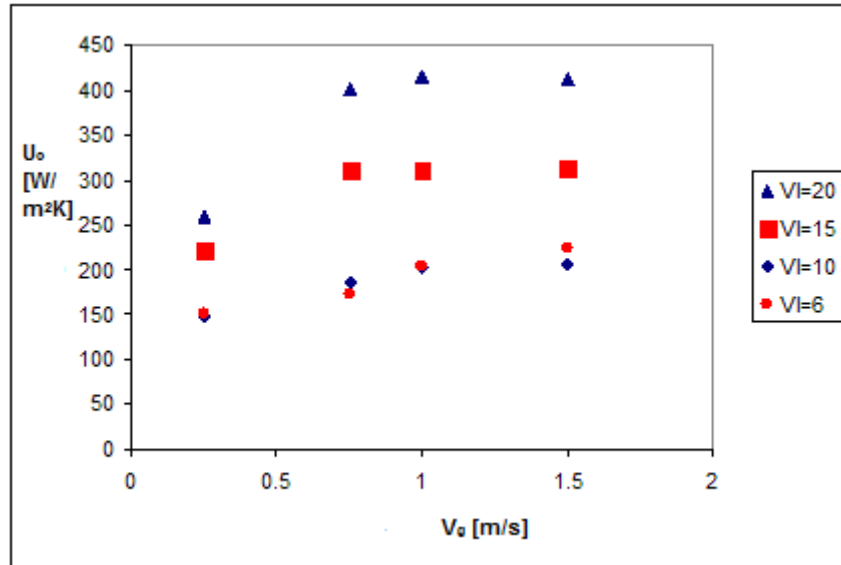


Figure 22: Results of  $U_o$  for experiments with wire gauze OCFS packings

The results for this experiment are surprising. The overall heat transfer of this packing is lower than that from the glass beads and this really was not the case that I was expecting. The overall heat transfer calculated from this experiment was so low (up to 63 % lower heat transfer compared to glass beads) that I decided not to spend more time on research of these packings.

The reasons for low heat transfer can be explained with the following arguments:

- The wire gauze packings have 3 skirts that are surrounding packing and collecting liquid at the reactor wall and forcing it back to the packing,
- The wire gauze packing is made from wire gauze and this material may be permeable, so that liquid may find a way through the material without passing through channels,
- The wire gauze packing has bigger channels than the OCFS packing and liquid flow can move through the packings to a neighboring channel at every cross section and never reach the reactor wall.

#### 4.2.3. CCFS

The next experiment was done on the CCFS packing. Two experiments were done in this section: one on just packings and one on modified packings (packings+rings). The first experiment was done on different gas velocities ( $V_g = 0.25, 1, 1.5$  and  $2$  m/s) then second ( $V_g = 0.25, 0.75, 1$  and  $1.5$  m/s). Results are shown in Figure 23.

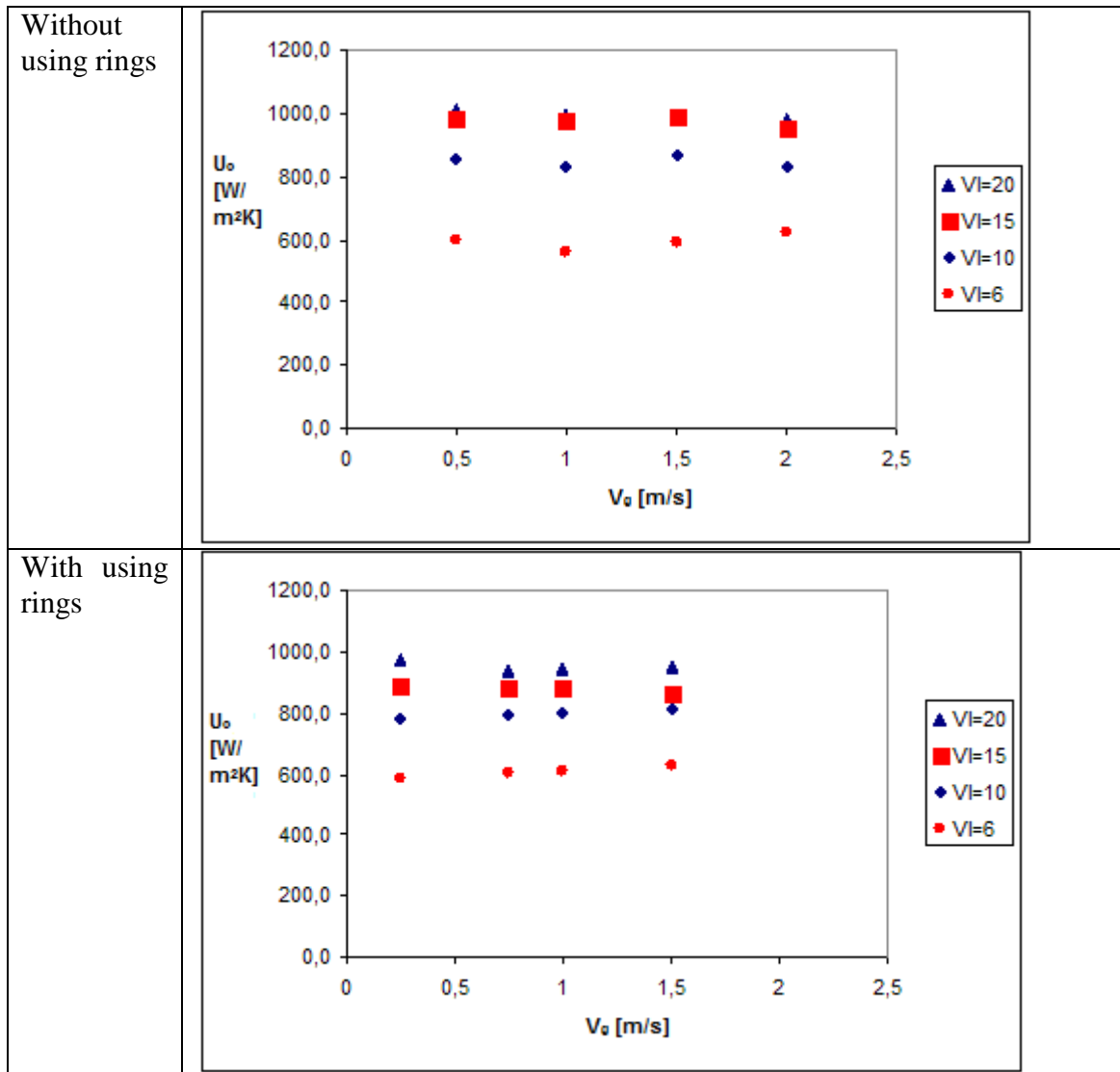


Figure 23: Results of  $U_o$  experiments with CCFS packings (with and without modifications)

Heat transfer properties from experiments with CCFS packings were following:

- CCFS packing have very good heat transfer properties compared to glass beads (up to 37.2 % larger heat transfer),
- From the Figure 23 it is seen that gas velocity does not influence a heat transfer properties and that is why these two results can be compared,
- From the experiment with rings it is seen that rings do not influence heat transfer significantly (up to 5.1 % lower heat transfer).

#### 4.2.4. OCFS

The next experiment was done on OCFS packing. Like by CCFS two experiments were done in this section: one was just using packings and one in which modified packings were used (packings + rings). Results are shown in Figure 24.



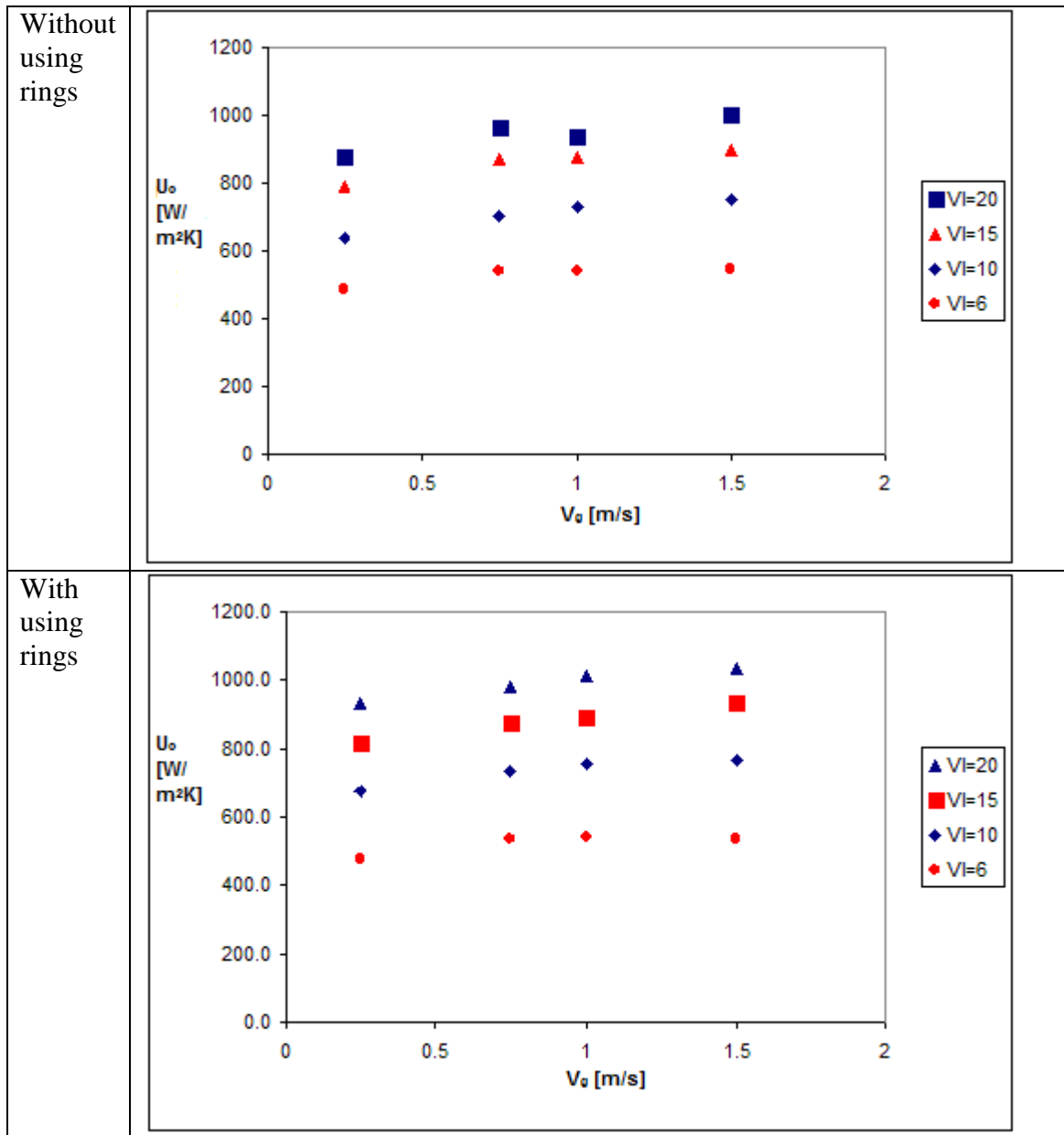


Figure 24: Results of  $U_o$  experiments with OCFS packings (with and without modifications)

Heat transfer properties from experiments with OCFS packings were following:

- OCFS packing have very good heat transfer properties compared to glass beads (up to 44.2 % larger heat transfer),
- From the Figure 24 it is seen that gas velocity does not influence a heat transfer properties a lot but we can see very weak trend (heat transfer is slightly increasing when we increase gas velocity),
- From the experiment with rings it is seen that rings do not influence heat transfer significantly (up to 5.1 % larger heat transfer).

### 4.3. Maldistribution experiments

In the Table 7 all results from maldistribution are presented. In this pictures inside table flow rates (dimensionless flow rates) inside last packing (bottom of the set-up) are presented.  $F_i$  means flow rate used at the top of the set-up. For better interpretation of results standard deviation was used. Several conclusions were made during experimental and results observation.

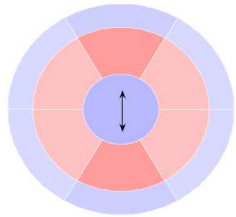
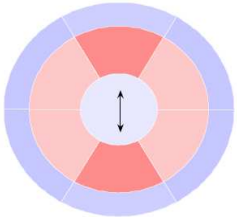
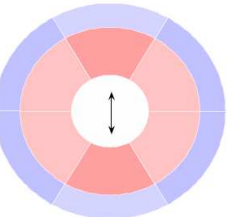
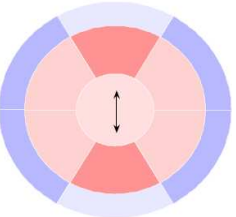
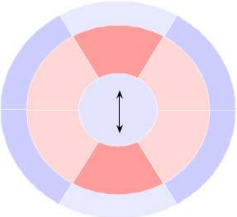
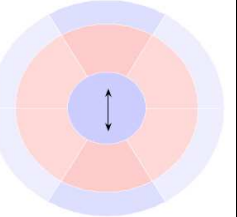
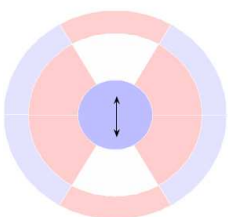
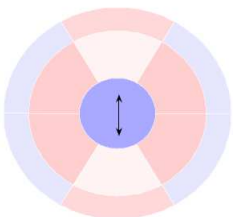
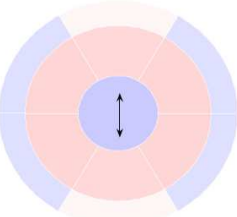
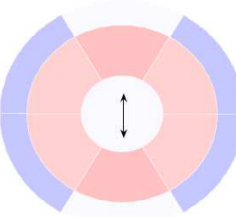
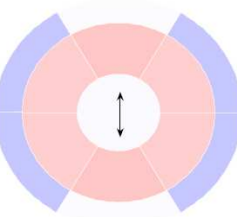
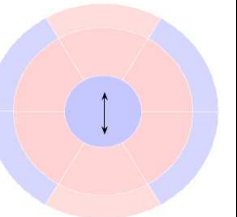
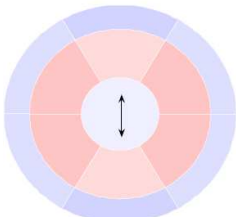
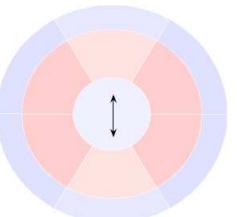
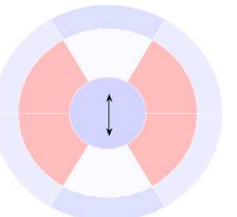
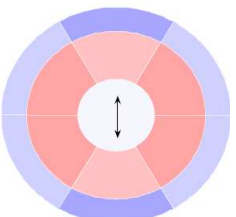
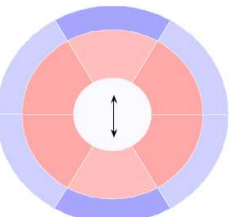
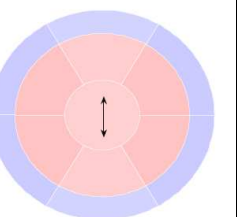
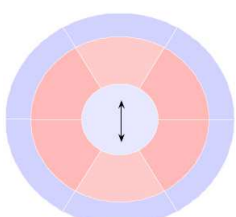
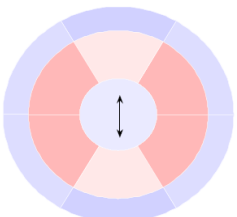
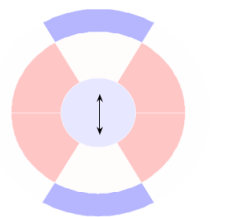
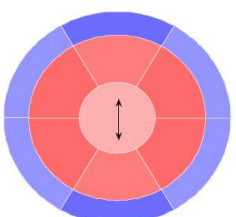
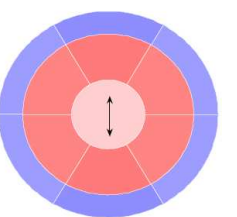
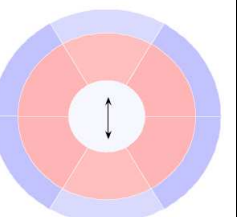
Experimental observation:

- When the gas flow was increased, this changed the flow regime inside the packings. At low gas velocities Taylor flow was observed. After change to a higher gas velocity the flow regime changed to annular flow regime
- During the experiments with modification accumulation of liquid was observed on the top of the column (which was not the case during experiments without modifications).

Results interpretation:

- The modification used on the CCFS packings were improving distribution inside packings,
- The modification used on the OCFS packings were causing maldistribution (bigger flow is observed on reactor wall) inside packings,
- Better heat transfer properties for OCFS packing with modifications can be explained because of bigger flow on the reactor wall. The opposite phenomena can be observed in CCFS packings and because of this, lower heat transfer.

Table 7: Results from the maldistribution experiments

	Low gas velocity (0.25 m/s)			High gas velocity (1.5 m/s)			Legend for flow rates inside the packings - $F_i$ [/]
VI [mm/s]	6	10	20	6	10	20	
CCFS							
Standard deviation	0.49	0.50	0.39	0.68	0.54	0.34	
CCFS+ rings							
	0.30	0.26	0.28	0.56	0.49	0.41	
OCFS							
	0.38	0.33	0.29	0.46	0.43	0.33	
OCFS+ rings							
	0.36	0.42	0.44	0.81	0.69	0.40	

#### 4.4. Results from heat transfer modelling

To investigate the results two models made in Matlab were in use. Two models were made because of the difference in flow dynamics inside randomly packed bed (glass beads) and inside structured reactor (CFS). These models were made by previous student that were working on similar project at the same set-up. For the glass beads I used pseudo homogeneous two dimensional plug flow model (PH2DPFM) and for CFS I used model made by Bert-Jan T. Kuipers who was also working at same set-up. All results that are not shown in this chapter, can be found in Appendix C.

#### 4.5. Comparison between modelling and experimental results (Pseudo homogeneous 2D plug flow model or PH2DPFM)

First modeling was made in PH2DPFM to value results from the experimental part made on glass (random packed bed). In the Figure 25 results from the experiments (red circles) and modeling (dashed black line) are shown. This figure is representing temperature profiles on different flanges. The first temperature profile (highest temperature) is flange A, the second is on flange B, the third is on flange C and the last one is flange D (with lowest temperatures).

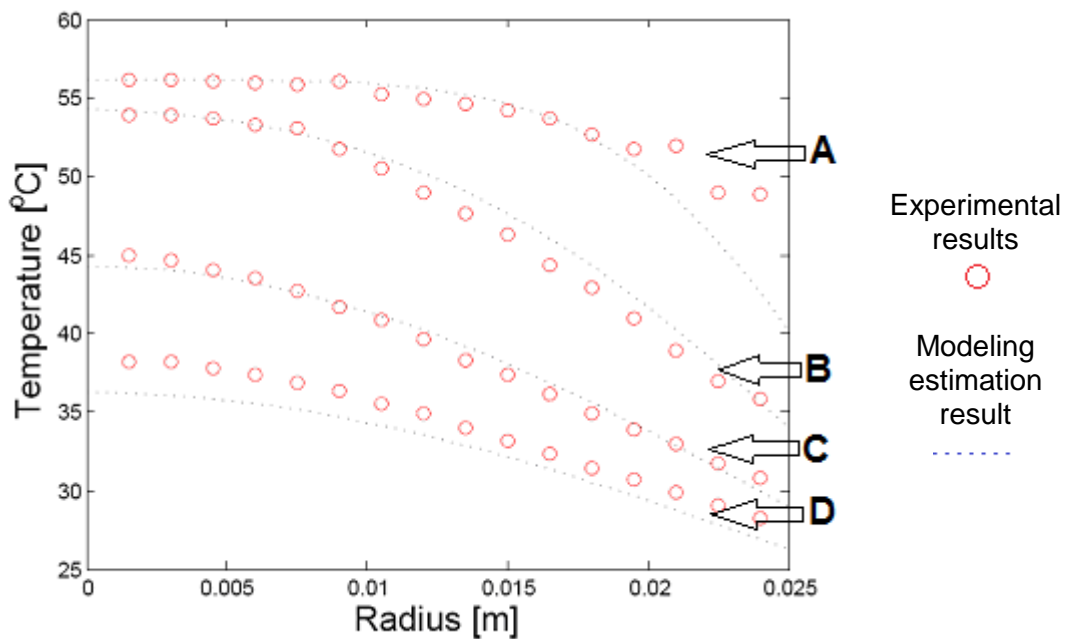
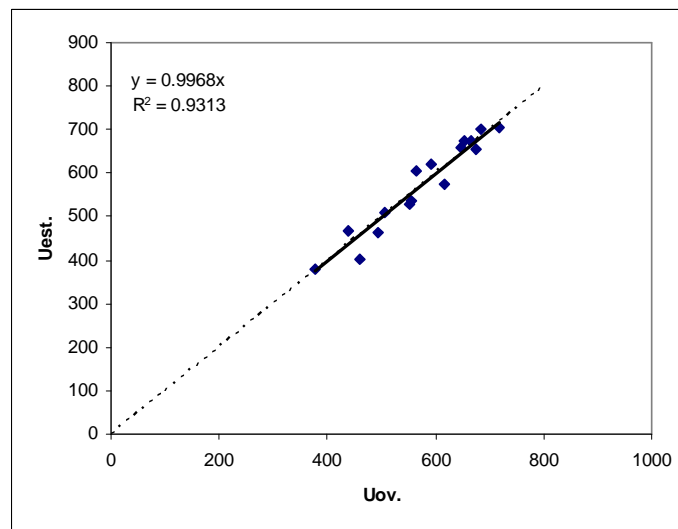


Figure 25: An example of comparison of results made in experiments and modeling for glass beads ( $V_I=10$  mm/s,  $V_g=0.75$  m/s)

##### 4.5.1. Glass beads

In this chapter a comparison is made between experimental and modeling results is made. From the Figure 26 it is seen that the model is very accurate and the results

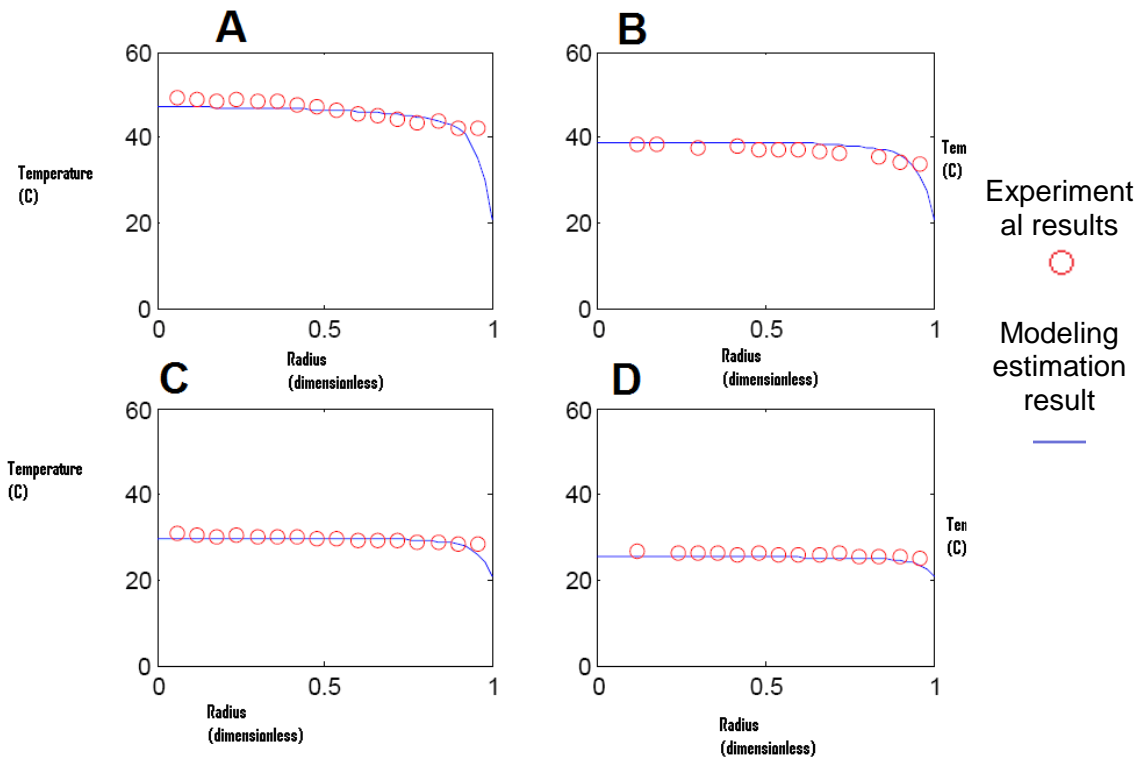
made in Excel and Matlab are almost equal. From this we can assume that model is perfectly adaptable for modeling random packed beds.



*Figure 26: Comparison between experiments and model for glass beads*

#### 4.5.2. Comparison between modeling and experimental results (Bert-Jans model for CFS)

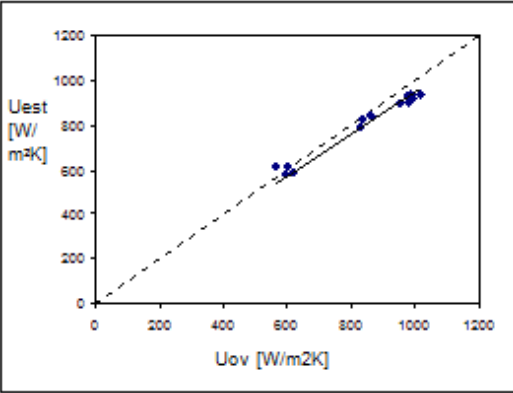
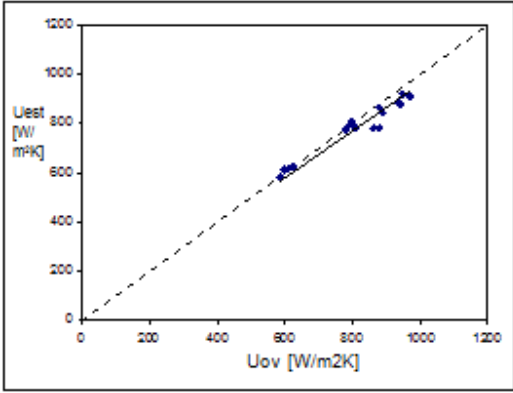
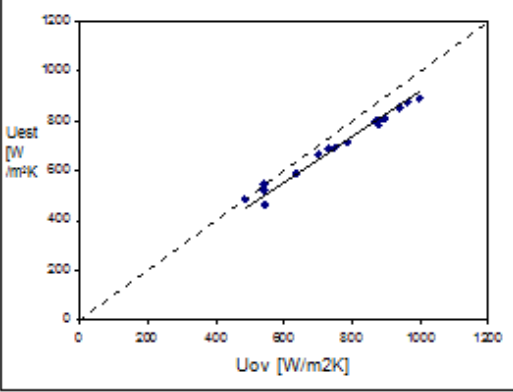
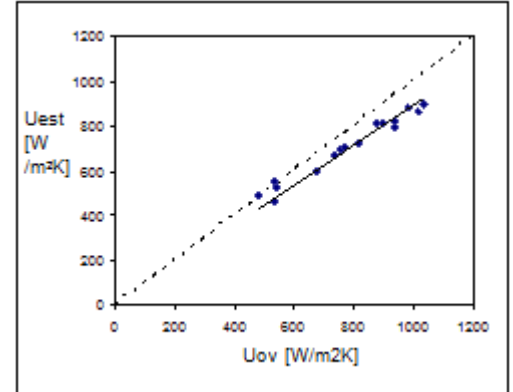
For the CFS a different model was used because of the flow dynamics inside CFS. Because of this I used model made by Bert-Jan T. Kuipers, a student that was working before me on the same set-up. He managed to develop a quite accurate model for CFS. In the Figure 27 modeling (blue line) and experimental (red circles) results are shown. The picture is presenting different temperatures on different flanges (A, B, C and D).



**Figure 27:** An example of comparison of results made in experiments and modeling for glass beads inside CCFS ( $V_I=10$  mm/s,  $V_g=1$  m/s)

In the Table 8 all the results from comparison between experimental results and modeling are presented. To get a better view on final results, I used excel graphs (on X axis are Overall and on y axis Uestimated results are presented).

**Table 8: Comparison between experiments and model for CCFS and OCFS packings with and without modifications**

Packing	Without using of modifications	With using modifications
CCFS		
	$y=0.9511x$ $R^2=0.9569$	$y=0.9619$ $R^2=0.9204$
OCFS		
	$y=0.9189x$ $R^2=0.9709$	$y=0.8956x$ $R^2=0.9399$

From the Table 8 several conclusions were made:

- The model made by Bert-Jan is very accurate and the results from modeling are quite similar to the actual results from the Excel calculations,
- The model is not fitting perfectly (the deviations become larger at higher  $U_o$ , i.e. higher liquid velocities),
- The model is more accurate for experiments with modifications (with using rings). This can be explained with a problem of liquid bypassing. With rings between packing the phenomena of bypassing is almost eliminated (bypassing is not included in this model).

To sum up, the predicted hypothesis of usage of rings is working quite good. I found a quick, easy, and cheap idea to eliminate bypassing without influencing heat transfer performance significantly.

## 4.6. Comparison of environmental treats between F-T fuels and conventional fuels (2<sup>nd</sup> objective)

The main idea for this chapter was to do small research (or literature review) and find some conclusions on emissions caused during syngas production, the F-T process and end-use to compare the emissions of the F-T process with those of the conventional fuel production from fossil fuels.

This chapter refers to the second objective of this diploma thesis and is just small part of the whole report. The idea for this task came when I first faced the main idea of this diploma thesis (heat transfer in structured packing used in the F-T multi-tubular fixed bed reactor) and I realised that this work is difficult to connect to my education and to the program that I am studying at my home university. At the first meeting with my mentors we together decided that this chapter should be sort of “bridge” between the main idea of the diploma thesis and my education.

### 4.6.1. LCA study for GHG emissions for F-T fuel and conventional fuels

In this chapter the study of J.J. Morano et al. was summarized [10]. Morano performed a life cycle analysis (LCA) for greenhouse gas (GHG) emissions for F-T fuels. The objective of this study was to conduct a full life-cycle inventory (LCI) for greenhouse gas emissions for synthetic fuels produced using the F-T process. As shown on Figure 28, the LCA is based on a “cradle-to-grave” approach and includes data identifications, collection and estimation of GHG emissions from upstream extraction/production, conversion/refining, transportation/distribution and end-use combustion of F-T fuels derived from three types of feedstocks: coal, biomass and natural gas.

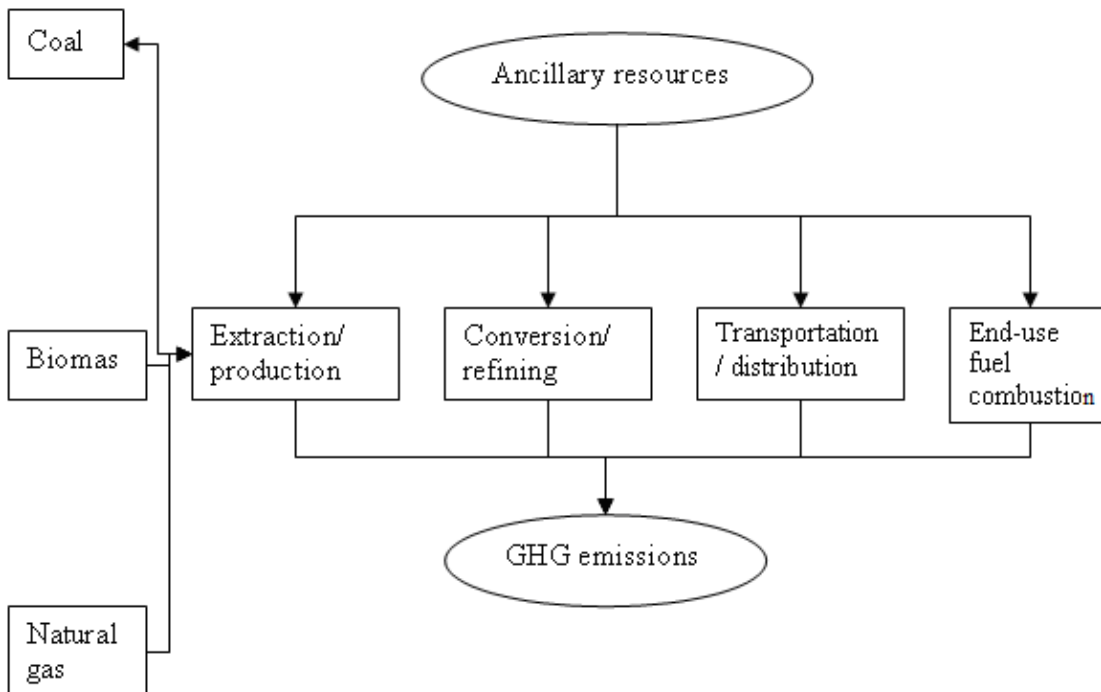


Figure 28: The block diagram of all processes used in LCA study (from feedstock to end product)



This analysis is limited to a LCA of airborne emission produced along F-T fuel product life cycle (it is not a complete inventory of all emissions). The impact of various GHG has been considered in relative terms by converting all GHG emissions to a CO<sub>2</sub> equivalency basis.

The greenhouse gases considered are CO<sub>2</sub> (carbon dioxide) from syngas production, F-T synthesis, fossil-fuel combustion along the life-cycle, and venting from natural gas production; CH<sub>4</sub> (methane) from fugitive plant and pipeline emissions, incomplete combustion or incineration (gas flaring), and coal-bed methane releases; and N<sub>2</sub>O (nitrous oxide) from fuel combustion and the cultivation of biomass. The weighting factors for CH<sub>4</sub> and N<sub>2</sub>O used in the CO<sub>2</sub> equivalency calculations are 21 and 310, respectively.

Assumptions relative to the geography of the product supply chain (fuel chain) are critical when comparing life-cycle emissions estimates. Since this study was made in U.S.A., the U.S. Midwest (southern Illinois) has been chosen as a reasonable location for the future siting of coal liquefaction plants, as well as biomass conversion plants. A Wyoming location was also chosen for a second coal scenario based on the conversion of sub-bituminous coal. For these scenarios, it was assumed that the F-T diesel fuel is supplied to an area in the vicinity of Chicago (southern Illinois) by pipeline and tank truck. Three locations were considered for siting a GTL plant: southern Illinois, Venezuela, and Alaska. The southern Illinois location has been included to allow direct comparison between coal, biomass and natural gas scenarios. For Venezuela, it is assumed that F-T syncrude is transported to the U.S. Gulf Coast by tanker and pipelined to the U.S. Midwest, where it is refined and blended into transportation diesel fuel near Chicago. It is assumed that GTL deployment on the North Slope of Alaska results in a syncrude that is transported via the Trans-Alaska pipeline to Valdez, transferred to a tanker, and shipped to the U.S. West Coast, where it is distributed in the San Francisco Bay area.

To compare GHG emissions from F-T fuel with conventional fuels also a small LCA study for conventional fuel was made. To compare those results they made a study on Wyoming Sweet crude oil, Arab light crude oil, Alaska Nord Slope (ANS) crude oil and Venezuela syncrude.

#### 4.6.2. Processes used for different feedstocks

In this research three different feedstocks were in use for syngas production:

- Biomass (maple wood from plantation placed in South Illinois),
- Coal (from Wyoming and South Illinois),
- Natural gas (South Illinois pipeline gas).

After syngas production they used bubble column reactor for F-T conversion. For catalyst mainly iron catalysts particles were in use. Only in case of natural gas they used Co as the catalyst. A list of all processes can be found in the Appendix B.

#### 4.6.3. Explanation for GHG emissions calculations

The basis for the full F-T fuel chain GHG emissions estimates reported here is vehicle-kilometre driven. This is the appropriate unit of measure for most, but not all, comparisons. Fuel economies in kilometre per litre (km/l) are from a recent analysis conducted by Argonne National Laboratory. This analysis considered a wide range of conventional, advanced, and electric hybrid gasoline and diesel powered vehicles. Since the emissions estimates will change based on the fuel economy used for the comparison, the calculations have been incorporated into a spreadsheet to facilitate analysis of various alternatives with different km/l ratings. The values presented here are for sport utility vehicle (SUV) conversion from conventional gasoline engines to conventional and advanced diesel engines. The average fuel economy for gasoline-powered SUVs is 8.5 km/l, and for light-duty diesel-powered vehicles it is about 16.5 km/l. In similar applications, diesel engines are 33% more efficient than gasoline engines. Therefore, converting all SUVs powered by gasoline to diesel would result in a fuel economy increase to 11.2 km/l. Fuel composition also plays a critical role in determining fuel economy. Substituting F-T diesel for petroleum diesel in SUVs would result in a decrease in fuel economy from 11.2 km/l to about 10.3 km/l, an 8 % decrease. This is a result of the inherent lower energy density per volume of F-T diesel relative to conventional petroleum diesel.

#### 4.6.4. Comparison of F-T and petroleum derived diesel fuels

To compare F-T and conventional fuels an additional analysis has been done for petroleum derived fuels. To estimate GHG emissions for conventional fuels they were using LCA for crude oil from an article published by T.J. McCann & Associate Ltd. Because of this in this diploma thesis there are no additional descriptions for all the processes that were taken for this study.

The fuel chain for petroleum is similar to that shown for F-T fuels (see Figure 28), the major difference being that petroleum crude oil may be transported distances prior to being refined into finished products. From Figure 29 it can be concluded that transportation of the crude oil is a significant source of GHG emissions.

For this study a comparison and analysis for 8 different crude oils was made. These were:

- Wyoming sweet,
- Canadian light,
- Brent North sea,
- Arab light,
- Alaska North slope,
- Alberta syncrude,
- Venezuela heavy oil,
- Venezuela syncrude.

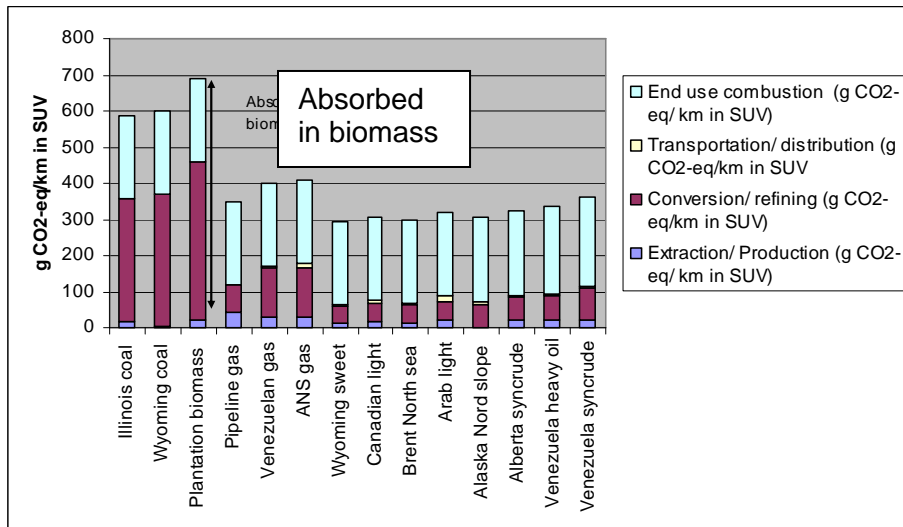


Figure 29: Sum of all GHG emissions for F-T diesel and diesel made from crude oil

#### 4.6.5. GHG emissions results interpretation

If we compare those two tables in Appendix B (see Tables 13 and 14), the production of F-T diesel from coal results in significantly higher GHG emissions than for petroleum derived diesel. GTL technology can achieve GHG emissions levels between those for coal liquefaction and petroleum refining, due to the higher hydrogen content of methane relative to petroleum. In fact, for the natural gas scenario, the GHG emissions for F-T diesel are lower than the emissions for Venezuelan syncrude, which requires several processes to make it suitable as a feedstock for refining. Also the emissions for transportations are bigger because longer transportation routes to refineries.

The scenario for biomass has the lowest GHG emissions due to the CO<sub>2</sub> necessary for photosynthesis which is calculated inside also. So I think this scenario is the best one to produce future F-T fuel, but we have to be careful with usage of fertilizers and other chemicals used in agriculture.

This study took all processes used in the late 1990s, so the overall emissions are higher than emissions from nowadays processes. F-T emissions are much lower because of the use of Co catalyst which has higher selectivity (less co-products) and activity (there is less syngas recycled).

#### 4.6.6. Comparison of combustion emission between F-T diesel and conventional fuels

This study was made for the Australian government [25]. The purpose of this study was to estimate emissions for alternative fuels. They were comparing different kind of diesel fuels (low sulphur diesel-LSD, ultra low sulphur diesel-ULSD and F-T diesel-FTD) emissions during combustion. This study was made for buses and trucks. Because those vehicles have different characteristics, they monitored emissions as emissions on an energy basis, as emissions on a per tonne-km basis for trucks, and on per passenger-km basis for buses. The energy used for calculations was for freight task (trucks) 1.2 MJ/tonne-km and for buses 1.06 MJ/tonne-km. In this study they made

estimations for emissions of CO<sub>2</sub>-equivalent, particulate matter with aerodynamic diameter less than 10 μm (PM<sub>10</sub>), nitrogen oxides (NO<sub>x</sub>), and non-methane hydrocarbons (HC).

The results are presented in the Figure 30.

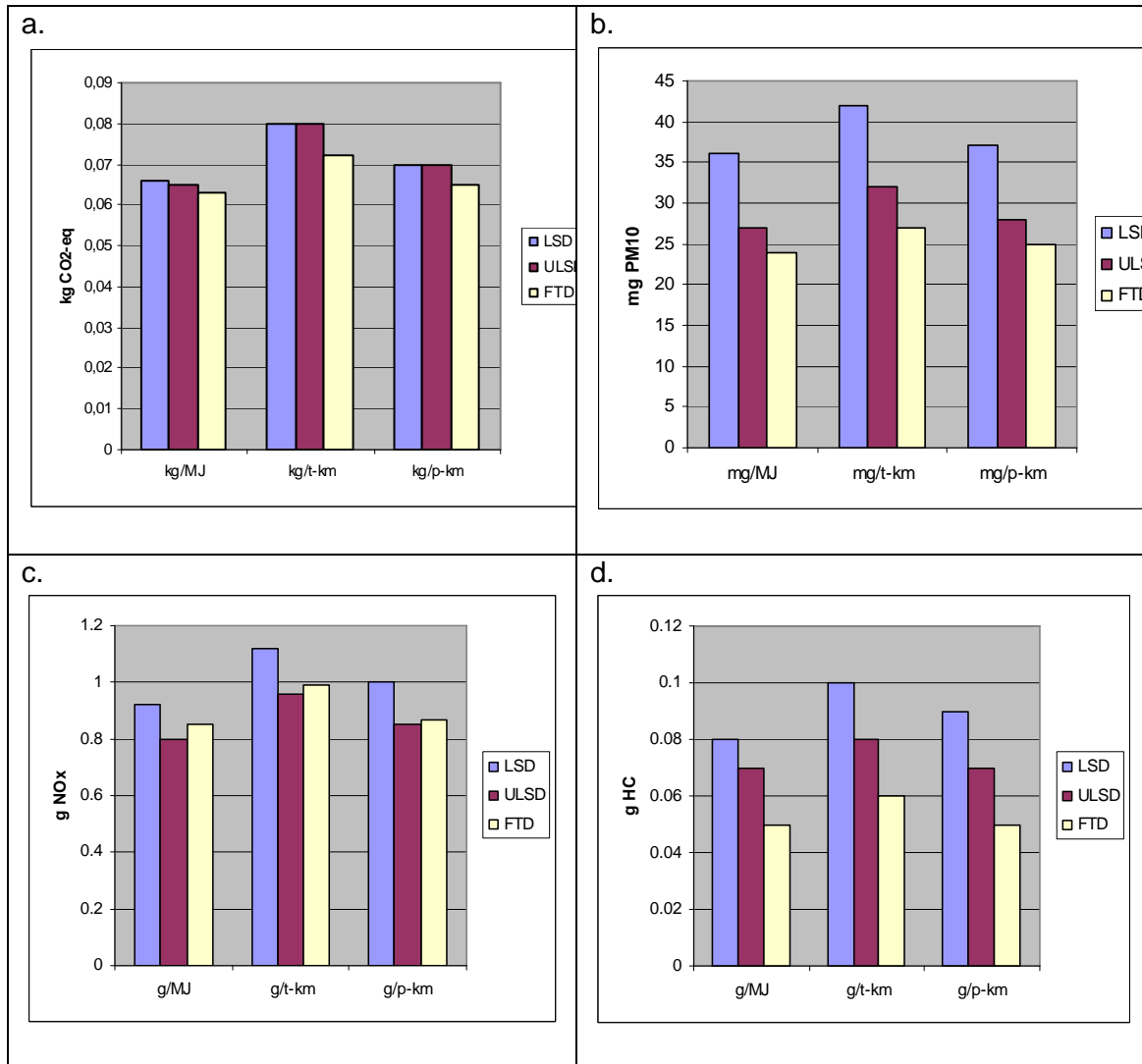


Figure 30: Emissions during combustion for different diesels (a. for CO<sub>2</sub>-eq, b. for PM<sub>10</sub>, c. for NO<sub>x</sub>, d. for HC)

#### 4.6.7. Conclusions for estimations of combustion emissions

Australian known reserves of natural gas are estimated to last for 90 years, ensuring a sustainable (in comparison with crude oil), and indigenous supply of natural gas as the feedstock for the F-T diesel process. That is why the Australian government also included F-T process to this study. In the previous graphs (see Figure 30 a, b, c and d) it is seen that almost all of emissions caused during combustion are lower than for other diesels (LSD and ULSD). The same is true for PM<sub>10</sub> emissions which is one of the most concerning problems connected to diesel fuels.

At the end of study they made a short conclusion of advantages and disadvantages:

Advantages of F-T diesel:

- F-T diesel contains virtually no sulphur or aromatics. In a properly tuned engine this is expected to lead to lower particle exhaust emissions,
- The absence of sulphur means that oxidation catalysts and particulate traps will operate at maximum efficiency,
- The existing diesel infrastructure can be used, unchanged, for F-T diesel,
- F-T diesel can be used in existing diesel engines,
- Diesel is one of the safest of the automotive fuels,
- An F-T plant does not produce any of the less desirable co-products from a refinery, such as heavy fuel or coke.

Disadvantages of F-T diesel:

- Diesel exhaust (including F-T diesel exhaust) is treated by US EPA as an air toxic,
- Because of the extra processing energy, F-T diesel produces more GHG than any of the conventional fuels (but most of GHG emissions can be absorbed in biomass),
- F-T diesel has slightly lower energy content.

#### 4.6.8. Other environmental problems

In those two previous studies (chapters 4.6.1. and 4.6.2.) only air emissions are presented. But if we want to do the whole LCA study, we have to present also emissions that concern water, soil, human health, etc.

In other articles authors are concerned about use of agricultural lands for production of biomass. This could lead to ethical and environmental problems.

For example, biodiesel (F-T diesel made from biomass) represents a higher contributing factor to acidification, eutrophication and formation of photochemical oxides [26, 27]. The contribution to acidification is primarily caused by nitrogen, sulphur oxides and ammonia which are released during the growing and some of them also during combustion. Likewise, biodiesel has a remarkably higher effect score concerning eutrophication (caused by intensive agriculture). Nevertheless, the contribution of the life cycle of biodiesel can be significantly higher than just GHG emissions are showing.

For the scenario for biomass there are many factors that are influencing the result. For instance climate, soil types (some are more sensitive than other), agronomic practices (including fertilizers and herbicides), and others [28].

Another issue is also food versus fuel. Many authors are concerned about idea that we will mainly use agricultural lands for producing biofuels instead of using it for food production in this critical time. In the article by Bruce Dale (Biofuels: Thinking clearly about the issue [29]), the author is not concerned about this problem. For example, about 75 % of corn consumed is fed to animals, not directly to people. Only 10 % of corn goes directly for human consumption [29]. So if we know that than we can not talk about food crisis. The problem with food is not the quantity but the distribution of it around the world. But this will not be discussed here.

If we want to do the whole LCA study, we have to present also emissions on other areas (soil, human health, etc.). In this diploma thesis this was not the main objective, and that is why my work was not focused on the entire LCA study. The objective was just to present a small part of emissions (air emissions) so the reader can imagine what are the differences between production of F-T and conventional fuels. But on the other hand, the reader should be aware of those issues.

#### 4.6.9. Syngas production in the future

In recent years, the quantity of municipal solid waste (MSW) has increased significantly in the industrialized and developing countries raising the question of its sustainable disposal management. The yield of MSW reaches approximately 900 million tonnes in the world each year, while over 200 million tonnes in China [30]. Recently, MSW increased at an annual rate of 8–10 %, and it reached  $150 \times 10^6$  tonnes in 2004 [30, 31]. Lots of energy and money were used for transportation, treatment, and final disposal of MSW, thus the disposal of MSW is one of the most important and urgent problems in environmental management in the world because of the decrease in the available space for land-filling and the growing concern about the living environment.

A waste management system consists of reuse/recycling or/and biological treatment of organic waste (e.g. landfilling, compost and thermal treatment (e.g. incineration, pyrolysis, gasification)). Some literature shows that thermal disposal especially incineration is a desired and viable option with energy recovery in forms of heat and electricity, and has the advantage of reduction of the amount of MSW by weight and volume compared with landfilling and compositing [30].

A possible solution is production of syngas from MSW. This could be done in different ways. For example, we could use anaerobic degradation of waste. By this process the main products are  $\text{CO}_2$  and  $\text{CH}_4$ . Ratios are depending on quality of waste. The most important component is organic matter. The most common ratio between  $\text{CO}_2$  and  $\text{CH}_4$  are around 32:68 (but the volume % for  $\text{CH}_4$  can be from 46-72 %) [32]. After cleaning of the landfill gas, methane gas can be used as a feedstock to produce syngas.

Other options can be more direct. One of those is direct two-stage gasification of MSW [31]. Stage one is a free-fall gasification reactor and stage two is a fixed-bed reformer.

I think waste as a feedstock can be very important for the future of the F-T process. By using waste as a feedstock we could eliminate two major problems (or make it less problematic). The first problem, that can be eliminated, is insufficient surface of lands used for garbage dumps. And the second problem, that can be eliminated, is end of use of natural gas (fossil fuel). Those characteristics are the main important characteristics of sustainable energy feedstock.

## 5. CONCLUSION

This chapter is divided into two parts:

- Experimental and modeling conclusions (1<sup>st</sup> objective)
- Research conclusions (2<sup>nd</sup> objective)

### **Experimental and modeling conclusions (1<sup>st</sup> objective)**

The main purpose of this thesis was to contribute ideas and results to help solving heat transfer in F-T process. This is a long lasting research which is including not only heat transfer, but also mass transfer, catalyst improvement, and other things which are needed to improve this process.

To improve heat transfer properties different CFS packings in tubular reactors were investigated and compared to a randomly packed bed. This investigation was mainly focused on experiments with heat transfer. The theory behind this was mainly made before this research by other students and PhD students.

To verify these theories two experiments were performed: heat transfer measurements and maldistribution experiments. The packings that were investigated were glass beads (randomly packed bed) and CFS packings (OCFS, CCFS and gauze wire packing). The purpose of the maldistribution experiment was to see how the flow dynamics change if I use additional modifications for packings (rings).

The following conclusions were made after investigation:

Heat transfer:

- Currently heat transfer properties for industrial reactors can be improved,
- The wire gauze packings have low heat transfer properties,
- From all packings investigated in this research, CCFS and OCFS packing have the highest heat transfer properties (up to 44.2 % larger heat transfer compared to randomly packed bed),
- The modifications (rings) are not influencing heat transfer properties much ,
- The modifications (rings) are contributing to lower liquid bypassing inside packings.

Maldistribution:

- The modifications (rings) on CCFS packings are causing improvement in distribution inside packings,
- The modifications (rings) on OCFS packings are causing improvement in maldistribution inside packings.

During the time spent on this research several conclusions were made. For example, better distribution may improve the usage of surface area inside packings which could lead to better conversion of syngas to liquid hydrocarbons. However, this idea has to be further investigated.

## **Research conclusions (2<sup>nd</sup> objective)**

Nowadays technology of hydrogen and electric driven vehicle is still not developed to the extend to be used as commercial ways and for the next coming decades this most likely stay an issue. Oil prices are still increasing and they have reached a price that is comparable to prices for F-T diesel.

During this research I came to several important concussions:

- F-T diesel has less emissions caused during the combustion which makes it more environmental friendly and causes less health issues,
- Syngas production from biomass is a good way to lowering GHG emission because biomass absorbs almost all CO<sub>2</sub> caused during the process F-T process,
- Waste can be sustainable feedstock for syngas production because of the quantity and consequently less garbage dumps.

## **Final thoughts**

I believe biofuels are one important manifestation of a much larger trend. It appears we are at a crucial “tipping point”. The first decade or so of this century may eventually be regarded as the time when global society decided to stop mindlessly consuming our fossil carbon reserves and started thinking about how to rely more on renewable resources, in this case, renewable carbon-based fuels. To manage the transition to renewable fuels successfully, we will have to understand the issues. I offered some perspectives that I hope will help frame at least some of the related issues and help us think more carefully and clearly about biofuels and other petroleum alternatives.

We are going to need liquid fuels for a long time, and biofuels are the only renewable option that I know of to provide these fuels. That is why I think that we should support research on improvement of F-T fuel production to make it more competitive and environmentally friendly.



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## 7. APPENDICES

### Appendix A: basic calculations used in thesis

Hydraulic diameter [22]:

$$d_h = H\sqrt{2}$$

11

H-height of triangle channel

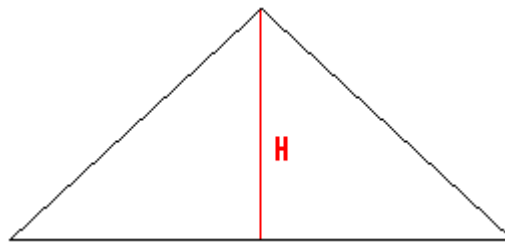


Figure 31: Hydraulic diameter

Peclet number [22]:

$$P_e = \frac{\text{convective\_heat\_transfer}}{\text{conductive\_heat\_transfer}} = \frac{\rho * c_p * v * d}{(1 - \epsilon_p) * \lambda} = [/]$$

12

Table 9: Parameters used for calculations

Name	Symbol	Stainless steel (25°C)	Isopar-M (25°C)
Density	$\rho$ [kg/m <sup>3</sup> ]	Not needed	792
Porosity of packing	$\epsilon_p$ [/]	≈0.85	/
Thermal conductivity	$\lambda$ [W/mK]	16	Not needed
Heat capacity	$c_p$ [J/kgK]	Not needed	2206
Tube diameter	$d$ [m]	0.05	/
Velocity	$v$ [m/s]	/	0.006 (lowest)-0.02 (highest)

## Appendix B: environmental par

**Table 10: Processes used to calculate GHG emissions using coal as a feedstock**

Area of process	Processes
Syngas generation area	<ul style="list-style-type: none"> <li>• Coal receiving and storage</li> <li>• Coal preparation</li> <li>• Air separation</li> <li>• Gasification</li> <li>• Syngas treatment</li> <li>• Syngas wet scrubbing</li> <li>• COS hydrolysis and gas cooling</li> <li>• Acid gas removal</li> <li>• Sulphur guard bed</li> <li>• Sulphur recovery</li> <li>• Sulphur water striping</li> </ul>
F-T conversion area	<ul style="list-style-type: none"> <li>• Syngas conversion</li> <li>• CO<sub>2</sub> removal</li> <li>• Dehydration and compression</li> <li>• Hydrocarbon recovery</li> <li>• Hydrogen recovery</li> <li>• Auto-thermal reforming</li> </ul>
F-T product upgrading area	<ul style="list-style-type: none"> <li>• Naphtha hydro-treating</li> <li>• Distillate hydro-treating</li> <li>• Wax hydro-treating</li> <li>• C<sub>5</sub>/C<sub>6</sub> isomerisation</li> <li>• Catalyst reforming</li> <li>• C<sub>4</sub> isomerisation</li> <li>• C<sub>3</sub>/C<sub>4</sub>/C<sub>5</sub> alkylation</li> </ul>
Offsite processes	<ul style="list-style-type: none"> <li>• Relief and blow-down</li> <li>• Tankage</li> <li>• Interconnecting piping system</li> <li>• Product shipping</li> <li>• Steam and power generation</li> <li>• Coal ash disposal</li> <li>• Catalyst and chemical handling</li> <li>• Sewage and effluent water treatment</li> <li>• Instruments and plant air facilities</li> <li>• Solid waste management</li> <li>• Acid gas removal</li> <li>• Syngas conversion</li> </ul>

**Table 11: Processes used for calculating GHG emissions using biomass as a feedstock**

Area of processes	processes
Syngas generation area	<ul style="list-style-type: none"> <li>• Wood receiving and storage</li> <li>• Wood preparation</li> <li>• Indirect gasification</li> <li>• Syngas treatment and compression</li> <li>• Syngas wet scrubbing</li> <li>• COS hydrolysis and gas cooling</li> <li>• Acid gas removal</li> <li>• Sulphur guard bed</li> <li>• Sulphur recovery</li> <li>• Sulphur water striping</li> </ul>
F-T conversion area	<ul style="list-style-type: none"> <li>• Syngas conversion</li> <li>• Hydrocarbon recovery</li> </ul>
F-T product upgrading	<ul style="list-style-type: none"> <li>• Naphtha hydro-treating</li> <li>• Distillate hydro-treating</li> <li>• Wax hydro-treating</li> <li>• C<sub>5</sub>/C<sub>6</sub> isomerisation</li> <li>• Catalyst reforming</li> </ul>
Offsite processes	<ul style="list-style-type: none"> <li>• Combined cycle power plant</li> </ul>

**Table 12: Processes used to calculate GHG emissions using natural gas as a feedstock**

Area of processes	Processes
Syngas generation area	<ul style="list-style-type: none"> <li>• Air separation</li> <li>• Sulphur guard bed</li> <li>• Heat recovery and syngas treatment</li> </ul>
F-T conversion area	<ul style="list-style-type: none"> <li>• Syngas conversion</li> <li>• CO<sub>2</sub> removal</li> <li>• Dehydration and compression</li> <li>• Hydrocarbon recovery</li> <li>• Hydrogen recovery</li> </ul>
F-T production upgrading	<ul style="list-style-type: none"> <li>• Naphtha hydro-treating</li> <li>• Distillate hydro-treating</li> <li>• Wax hydro-treating</li> <li>• C<sub>5</sub>/C<sub>6</sub> isomerisation</li> <li>• Catalyst reforming</li> <li>• C<sub>4</sub> isomerisation</li> <li>• C<sub>3</sub>/C<sub>4</sub>/C<sub>5</sub> alkylation</li> </ul>
Offsite processes	<ul style="list-style-type: none"> <li>• Relief and blow-down</li> <li>• Tankage</li> <li>• Interconnecting piping system</li> <li>• Product shipping</li> <li>• Steam and power generation</li> <li>• Coal ash disposal</li> <li>• Catalyst and chemical handling</li> <li>• Sewage and effluent water</li> </ul>

	treatment <ul style="list-style-type: none"> <li>• Instruments and plant air facilities</li> <li>• Solid waste management</li> <li>• Acid gas removal</li> <li>• Syngas conversion</li> </ul>
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**Table 13: GHG emissions converted into CO<sub>2</sub>-eq in a process using coal, natural gas and biomass as a feedstock**

Feedstock for F-T diesel	Extraction/ Production (g CO <sub>2</sub> -eq/km in SUV)	Conversion/ refining (g CO <sub>2</sub> -eq/km in SUV)	Transportation/ distribution (g CO <sub>2</sub> -eq/km in SUV)	End use combustion (g CO <sub>2</sub> -eq/km in SUV)	Total full chain (g CO <sub>2</sub> -eq/km in SUV)
Illinois coal	16.3	339.4	0.6	230	586.3
Wyoming coal	4.3	365.6	1.2	230	601.1
Plantation biomass	-605.6	439.4	0.6	230	64.4
Pipeline gas	44.4	75.6	0.6	230	350.6
Venezuelan gas	31.9	132.5	7.5	230	402
ANS gas	31.9	132.5	13.1	230	407.5

**Table 14: GHG emissions converted into CO<sub>2</sub>-eq in a process using crude oil as a feedstock**

Crude oil/ feedstock	Extraction/ Production (g CO <sub>2</sub> -eq/km in SUV)	Conversion/ refining (g CO <sub>2</sub> -eq/km in SUV)	Transportation/ distribution (g CO <sub>2</sub> -eq/km in SUV)	End use combustion (g CO <sub>2</sub> -eq/km in SUV)	Total full chain (g CO <sub>2</sub> -eq/km in SUV)
Wyoming sweet	14.4	46.3	5	227.9	293.6
Canadian light	18.8	50.6	6.9	230	306.3
Brent North sea	14.4	50.6	5	230	300
Arab light	21.9	50.6	16.3	230	318.8
Alaska Nord slope	17,5	63.1	8.8	236.2	325.6
Alberta syncrude	20	65	6.3	231.3	322.6
Venezuela heavy oil	20	67.5	8.1	238.8	334.4
Venezuela syncrude	20	89.4	6.3	244	359.7

## Appendix C: Modeling results

**Table 15: Heat transfer results (Excel results)**

VI [mm/s]/ Vg[m/s]	U <sub>o</sub> [W/m <sup>2</sup> K]					
	Glass beads	Wire gauze	CCFS	OCFS	CCFS+ rings	OCFS+ rings
6/0.25	377.6	150.1	598.7	486.3	586.9	478.1
6/0.75	459.4	173.2		541.5	601.4	535.7
6/1	493.8	203.5	563.2	541.7	610.8	539.4
6/1.5	552.8	224.2	593.0	543.8	625.6	535.7
6/2			620.4			
10/0.25	437.5	147.7	854.1	635.4	779.9	673.3
10/0.75	504.9	187.1		701.9	790.1	734.6
10/1	554.0	202.5	831.4	730.2	800.1	753.0
10/1.5	616.7	206.6	864.9	748.7	809.6	764.3
10/2			829.4			
15/0.25	564.9	221.4	982.0	789.5	887.8	815.1
15/0.75	653.7	311.1		867.7	877.9	872.6
15/1	683.1	309.8	973.1	877.6	877.8	891.6
15/1.5	673.9	313.4	984.1	896.0	862.8	931.1
15/2			951.2			
20/0.25	592.3	259.4	1013.9	876.9	970.7	930.3
20/0.75	648.5	400.6		963.3	937.0	980.2
20/1	666.8	413.5	991.9	937.6	940.6	1013.5
20/1.5	717.6	411.7	984.9	998.5	947.6	1034.5
20/2			982.1			

Matlab results:

**Table 16: Random packed bed results**

Vg/VI [mm/s]/[m/s]	U <sub>est</sub> [W/m <sup>2</sup> K]	α <sub>wall</sub> [W/m <sup>2</sup> K]	λ <sub>r</sub> [W/mK]	α <sub>wall</sub> (conf.inter.)	λ <sub>r</sub> (conf.inter.)	U <sub>est</sub> (conf.inter.)
6/0.25	379.34	616.24	6.19	581.5-782.5	2-10	206-524.5
6/0.75	400.39	686.3	7.14	658.5-842.5	3-11	278-570
6/1	464.9	688.12	8.96	654-768	5-13	359-561
6/1.5	527.0	968.15	7.23	906-1038	3-11	314-653
10/0.25	468.66	910.99	6.03	829-964	2-11	213-601.5
10/0.75	508.85	933.57	6.99	874-1010	3-11	310-642
10/1	537.75	1027.75	7.05	954-1150	3-11	319-696
10/1.5	575.95	1084.01	7.68	1008-1171	4-12	391.5-727
15/0.25	606.06	1209.48	7.61	1115-1286	4-12	406.5-770
15/0.75	674.99	1318.49	8.64	1226-1422	5-13	484-845
15/1	701.47	1401.37	8.78	1269-1495	5-13	491-870
15/1.5	656.73	1243.88	8.70	1154-1353.5	5-13	472.5-820
20/0.25	619.06	1125.92	8.59	1070-1192	5-13	458-758
20/0.75	659.03	1241.74	8.78	1172.5-1331.5	5-13	475.5-811.5
20/1	672.56	1238.89	8.83	1212-1384	5-13	482-831
20/1.5	705.43	1332.89	9.37	1253-1435	5-13	488-849



**Table 17: Results of CCFS packings**

VI [mm/s]; Vg [m/s]	Tw [°C]	T0 [°C]	Hw [W/ m <sup>2</sup> K]	SSres	Uov [W/ m <sup>2</sup> K]	Uab [W/ m <sup>2</sup> K]	Ubc [W/ m <sup>2</sup> K]	Ucd [W/ m <sup>2</sup> K]	Uad [W/ m <sup>2</sup> K]
6/0.25	18.55	48.7	1022	64.33	617.5	613.1	614.8	614.8	614.1
6/1	21.1	50.3	1012	67.3	612.2	607.6	609.4	609.4	609.0
6/1.5	21.15	50.0	952	47.7	577.1	572.6	574.3	574.3	574.0
6/2	18.7	48.7	972	36.7	589.3	584.7	586.4	586.4	586.1
10/0.25	18.8	53.2	1395	57.1	842.7	836.5	838.9	838.7	838.3
10/1	21.5	54.4	1367	51.9	826.6	820.3	822.8	822.7	822.3
10/1.5	18.7	53.0	1378	45.4	833.5	827.1	829.5	829.4	829.0
10/2	21.6	53.9	1303	29.9	788.3	783.1	785.5	785.4	784.9
15/0.25	20.2	57.6	1527	23.0	925.4	917.9	920.8	920.8	920.2
15/1	20.4	56.7	1544	28.0	935.9	928.2	931.1	931.2	930.6
15/1.5	20.7	56.8	1551	25.9	940.3	932.6	935.5	935.6	934.9
15/2	21.0	56.5	1480	21.5	898.3	890.8	893.6	893.7	893.1
20/0.25	21.5	57.6	1554	16.1	944.7	936.6	939.6	939.8	939.0
20/1	22.1	57.7	1525	23.8	927.7	919.6	922.6	922.8	922.1
20/1.5	20.5	57.2	1511	19.3	919.6	911.5	914.5	914.6	913.9
20/2	22.0	56.6	1490	20.4	907.3	899.2	902.2	902.3	901.6

**Table 18: Results of OCFS packings**

VI [mm/s]; Vg [m/s]	Tw [°C]	T0 [°C]	Hw [W/ m <sup>2</sup> K]	SSres	Uov [W/ m <sup>2</sup> K]	Uab [W/ m <sup>2</sup> K]	Ubc [W/ m <sup>2</sup> K]	Ucd [W/ m <sup>2</sup> K]	Uad [W/ m <sup>2</sup> K]
6/0.25	21.9	51.7	807	52.4	490.4	486.5	488.0	488.0	487.7
6/0.75	21.3	52.9	906	30.7	549.4	545.1	546.7	546.7	546.4
6/1	22.6	52.7	870	34.8	528.2	524.0	525.6	525.6	525.3
6/1.5	22.0	51.9	765	32.9	466.3	462.4	463.8	463.9	463.6
10/0.25	22.3	60.0	973	66.7	592.5	587.4	589.3	589.3	589.0
10/0.75	22.3	58.9	1102	22.4	669.9	664.5	666.6	666.4	666.1
10/1	22.5	58.0	1144	24.2	694.4	688.8	690.9	690.8	690.5
10/1.5	23.1	57.0	1154	18.7	700.6	694.9	697.1	697.0	696.4
15/0.25	22.2	60.6	1181	38.5	719.7	713.3	715.7	715.7	715.2
15/0.75	23.4	59.6	1324	14.5	804.9	798.1	800.6	800.7	800.1
15/1	22.6	59.4	1333	15.6	810.4	803.5	806.1	806.1	805.6
15/1.5	22.9	58.5	1342	18.4	815.9	808.9	811.6	811.7	811.1
20/0.25	22.4	60.1	1294	31.5	789.8	782.5	785.2	785.3	784.7
20/0.75	21.1	59.6	1448	20.4	881.8	873.9	876.8	877.0	876.3
20/1	21.9	59.7	1410	26.1	859.3	851.5	854.4	854.4	853.9
20/1.5	20.0	58.9	1468	27.6	894.0	886.0	888.9	889.1	888.4