SYNTHESIS OF HEXAFLUOROBENZENE THROUGH BATCH REACTIVE DISTILLATION

Jesita Reddy

[Bsc. Eng.]

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Supervisors: Doctor David Lokhat and Professor Deresh Ramjugernath

As the candidate's supervisor I agree to the submission of this thesis:

Dr. D. Lokhat

Prof. D. Ramjugernath

DECLARATION

I, Jesita Reddy declare that:

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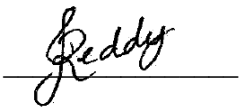
Signed: 

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ABSTRACT

South Africa is home to the second largest fluorspar (CaF_2) reserves in the world, outside China; and it is consequently integral to the international supply of CaF_2 to hydrogen fluoride producers. This is demonstrated by South Africa's position as the third largest exporter of CaF_2. But while it produces 5% of the world's total requirements (ca 4.55 million tons per annum), South Africa earns less than 10% of its final output value. As a result, a Fluorochemical Expansion Initiative (FEI) was established to increase the beneficiation of South African mined CaF_2.

Under the auspices of FEI, this dissertation describes the research and development of a method for the synthesis of a perfluorinated aromatic compound, hexafluorobenzene (C_6F_6). C_6F_6 is a product within the CaF_2 beneficiation value chain that has utility as a heat exchange fluid, lubricant, solvent and within the pharmaceutical industry.

The investigation was broken up into two phases: Firstly the equipment was validated by replicating the experiments and comparing results to the biodiesel reactive distillation experiments found in literature. Once the equipment was validated, the main experiment for improving the yield of hexafluorobenzene was carried out. This was undertaken by reacting hexachlorobenzene, dissolved in sulfolane under the action of various alkali metal fluorides (potassium fluoride (KF) and caesium fluoride (CsF)) and through variations in the ratio of the alkali fluoride to hexachlorobenzene. For both phases, the experiments were carried out in a glass, batch reactive distillation system. The quantities of the various products formed were determined via quantitative analysis using a gas chromatograph equipped with a flame ionization detector.

It was observed that the use of caesium fluoride increased the molar yield of C_6F_6 to 0.59% as to the 0.27% that was produced when potassium fluoride was used. The effect of temperature on the yield of C_6F_6 was also investigated and the results depicted that higher temperatures favoured higher yields of C_6F_6. The effect of varying molar quantity of KF on the molar selectivity of all fluorinated products was additionally examined and it was concluded that a change in amount of KF did not significantly affect the molar selectivity of the products. On the other hand, for increasing amounts of CsF an increase in molar selectivity's of the higher fluorinated compounds were observed. It was further noted that an increase in temperature resulted in an increase in

molar selectivity of fluorinated products. The opposite was observed for the lower fluorinated species.

A simplified kinetic model was developed for the KF and CsF system. The model comprised six reactions and the experimental data was used together with a nonlinear regression technique implemented in MATLAB® to identify the kinetic parameters. Using the kinetic parameters, a simulation was then performed to determine the effect of time on the moles of products and consumption of hexachlorobenzene using either KF or CsF as the fluorinating agent. It was observed that using KF resulted in a better conversion but poorer selectivity towards the highly fluorinated products as compared to using CsF. The better conversion may be due to the mixing efficiency due to the lower actual mass of solid KF in the reaction mixture than solid CsF. The poorer selectivity may be due to the slightly superior solubility of the CsF which promoted fluorination in the sulfolane medium.

TABLE OF CONTENTS

DECLARATION II

ACKNOWLEDGEMENTS III

ABSTRACT IV

TABLE OF CONTENTS VI

LIST OF FIGURES IX

LIST OF TABLES XII

LIST OF PHOTOGRAPHS XV

NOMENCLATURE XVI

GREEK SYMBOLS XVII

SUBSCRIPTS XVII

ABBREVIATIONS XVII

CHAPTER ONE 1

1. INTRODUCTION 1

1.1. BACKGROUND 1

1.2. OBJECTIVES 2

1.3 DISSERTATION OUTLINE 4

CHAPTER TWO 6

2. INTRODUCTION TO LITERATURE SURVEY 6

2.1. FLUOROCHEMICAL POLYFLUOROAROMATIC COMPOUNDS: A HISTORY 6

2.2. ALKALI METAL FLUORIDES 9

2.3. HEXAFLUOROBENZENE 10

2.4. USES OF HEXAFLUOROBENZENE 10

2.5. PREVIOUS METHODS OF HEXAFLUOROBENZENE SYNTHESIS 11

2.6. REACTION MECHANISM 13

2.7. BATCH REACTIVE DISTILLATION 14

2.8. GAS CHROMATOGRAPHY FOR QUANTITATIVE ANALYSIS 16

2.8.1. AREA NORMALIZATION METHOD 17

2.8.2. EXTERNAL STANDARD METHOD 17

2.8.3. STANDARD ADDITION METHOD 18

2.8.4. INTERNAL STANDARD METHOD 19

2.9. .. LITERATURE SURVEY: CONCLUSION 20

CHAPTER THREE 21

3. EXPERIMENTAL APPARATUS AND MATERIALS 21

3.1. MATERIALS 21

3.2..PRELIMINARY EXPERIMENTS/VALIDATION EXPERIMENT 22

3.3. HEXAFLUOROBENZENE SYSTEM: EXPERIMENTAL PROCEDURE 24

3.4. CALIBRATIONS – GAS CHROMATOGRAPHY 27

3.4.1. CALIBRATION – BIODIESEL EXPERIMENT 28

3.4.2. CALIBRATION – HEXAFLUOROBENZENE SYSTEM 28

3.4. ANALYTICAL TECHNIQUES 29

CHAPTER FOUR 30

4. RESULTS AND DISCUSSION 30

4.1. PRELIMINARY INVESTIGATION: VALIDATION EXPERIMENT – PRODUCTION OF BIODIESEL USING BATCH REACTIVE DISTILLATION 30

4.1.1. EFFECT OF MOLAR RATIO ON OLEIC ACID CONVERSION 31

4.1.2. EFFECT OF CATALYST AMOUNT ON OLEIC ACID CONVERSION 32

4.1.3. EFFECT OF REACTION TIME ON OLEIC ACID CONVERSION 32

4.1.4. EFFECT OF REACTION TEMPERATURE ON OLEIC ACID CONVERSION 33

4.1.5. COMPARISON BETWEEN LITERATURE AND EXPERIMENTAL RESULTS 34

4.1.6. VALIDATION EXPERIMENT: CONCLUSION 35

4.2. MAIN INVESTIGATION: SYNTHESIS OF HEXAFLUOROBENZENE THROUGH BATCH REACTIVE DISTILLATION 35

4.2.1. EXPERIMENTAL OBSERVATIONS 36

4.2.2. THE EFFECT OF USING KF AS THE ALKALI METAL FLUORIDE ON THE YIELD OF C_6F_6 37

4.2.3. THE EFFECT OF USING CSF AS THE ALKALI METAL FLUORIDE ON THE YIELD OF C_6F_6 38

4.2.4. The Effect of Using KF and a Varying Molar Ratio of KF: C_6Cl_6 on the Conversion of C_6Cl_6 38

4.2.5. The Effect of Using CsF and a Varying Molar Ratio of CsF: C_6Cl_6 on the Conversion of C_6Cl_6 39

4.2.6. Comparing KF and CsF as a Fluorinating Agent for the Synthesis of C_6F_6 40

4.2.7. Varying Temperature while Keeping The Ratio of KF:C_6Cl_6 Constant ..41

4.2.8. Varying Temperature while Keeping The Ratio of CsF:C_6Cl_6 Constant .43

4.2.9. The Selectivity of Products when Using KF or CsF 44

4.2.10 The Selectivity of Products when Varying Temperature 46

4.2.11. Comparison Between Literature and Experimental Results 47

CHAPTER FIVE 49

5. Mathematical Modelling of the Hexafluorobenzene System..... 49

5.1. MESH Equations 50

5.2. Simplified Model 56

CHAPTER SIX 63

6. Commercial Production of Hexafluorobenzene 63

CHAPTER SEVEN 70

7. Conclusions and Recommendations..... 70

7.1.Conclusions 70

7.1.1. Validation Experiment: Production of Biodiesel 70

7.1.2.Main Experiment: Synthesis of Hexafluorobenzene through Batch Reactive Distillation 71

7.2.Recommendations..... 73

References 75

Appendices 81

Appendix A: Gas chromatography calibration plots 81

A Validation Experiment 81

B Main Experiment 82

Appendix B: Raw data 84

APPENDIX C: SAMPLE CALCULATIONS 93

APPENDIX D: CHEMICAL DATA TABLE 100

APPENDIX E: HEXACHLOROBENZENE SAFETY AND HANDLING 101

APPENDIX F: MATLAB SCRIPTS 107

LIST OF FIGURES

Chapter 2:

Figure 2.1: Dewar Benzene, Perfluoro Dewar Benzene (Buckingham, 1996) 11

Figure 2.2: Schematic representation of lab-reactor set up used for the reactive distillation process (Metkar, et al., 2015) 15

Figure 2.3 Sample chromatogram of detector response versus retention time (Handley & Adlard, 2001) 16

Figure 2.4: Standard addition method – a, b and c represent concentrations of a component added to the sample (Gerhards, et al., 1999) 18

Figure 2.5: Illustrative example of calibration plot generated using an internal standard gas chromatography quantification method (mcnair and Miller, 2011). 20

Chapter 3:

Figure 3.1: Schematic representation of Vigreux column 24

Chapter 4:

Figure 4.1.1: Percentage average conversion of oleic acid versus methanol/oleic acid molar ratio, literature (red dots), experimental (black dots) with uncertainty estimates shown as error bars. 31

Figure 4.1.2: Percentage average conversion of oleic acid versus varying catalyst amount ratio of grams of sulphuric acid to grams of oleic acid, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars. 32

Figure 4.1.3: Percentage average conversion of oleic acid versus time, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars 33

Figure 4.1.4: Percentage average conversion of oleic acid versus temperature, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars 34

Figure 4.1.5: Re-run of experiment 1; percentage average conversion of oleic acid versus temperature, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars 35

Figure 4.2.1: Molar yield percentage of C_6F_6 versus varying molar ratio of KF: C_6Cl_6 with repeat experiments illustrated in red and uncertainty shown as error bars 37

Figure 4.2.2: Molar yield percentage of C_6F_6 versus varying molar ratio of CsF: C_6Cl_6 and uncertainty shown as error bars 38

Figure 4.2.3: Conversion percentage of C_6Cl_6 versus varying molar ratio of KF: C_6Cl_6 39

Figure 4.2.4: Conversion percentage of C_6Cl_6 versus varying molar ratio of CsF: C_6Cl_6 40

Figure 4.2.5: Conversion percentage of C_6Cl_6 versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6 42

Figure 4.2.6: Molar yield percentage of C_6F_6 versus varying temperature, using KF as the alkali metal fluoride with repeat experiments illustrated in red and uncertainty shown as error bars 43

Figure 4.2.7: Conversion percentage of C_6Cl_6 versus varying temperature while keeping a constant molar ratio of CsF: C_6Cl_6 43

Figure 4.2.8: Molar yield percentage of C_6F_6 versus varying temperature, using CsF as the alkali metal fluoride with repeat experiments illustrated in red and uncertainty shown as error bars 44

Figure 4.2.9: Molar selectivity percentage of fluorinated products versus varying molar ratio of KF: C_6Cl_6 (6:1; 9:1; 12:1) 45

Figure 4.2.10: Molar selectivity percentage of fluorinated products versus varying molar ratio of CsF: C_6Cl_6 (6:1; 9:1; 12:1) 45

Figure 4.2.11: Molar selectivity percentage of fluorinated products versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6 46

Figure 4.2.12: Molar selectivity percentage of fluorinated products versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6 47

Chapter 5

Figure 5.1: Schematic representation of experimental system 50

Figure 5.2: Predicted moles of hexachlorobenzene in the reaction still point versus the measured moles of hexachlorobenzene in the reaction still pot using KF as the fluorinating agent 61

Figure 5.3: Predicted moles of fluorinated products in the reaction still point versus the measured moles of fluorinated products in the reaction still pot using KF as the fluorinating agent 61

Figure 5.4: Predicted moles of hexachlorobenzene in the reaction still point versus the measured moles of hexachlorobenzene in the reaction still pot using CsF as the fluorinating agent 62

Figure 5.5: Predicted moles of fluorinated products in the reaction still point versus the measured moles of fluorinated products in the reaction still pot using CsF as the fluorinating agent. 62

Chapter 6

Figure 6.1: Simplified process flow diagram of the recycling of chlorofluorobenzenes 65

Figure 6.2: Total moles of hexachlorobenzene in reaction still pot versus time using KF as the fluorinating agent 66

Figure 6.3: Total moles of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 in reaction still pot versus time using KF as the fluorinating agent 67

Figure 6.4: Total moles of C_6F_6, C_6F_5Cl and $C_6F_4Cl_2$ in reaction still pot versus time using KF as the fluorinating agent 67

Figure 6.5: Total moles of hexachlorobenzene in reaction still pot versus time using CsF as the fluorinating 68

Figure 6.6: Total moles of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 in reaction still pot versus time using CsF as the fluorinating agent 68

Figure 6.7: Total moles of C_6F_6, C_6F_5Cl and $C_6F_4Cl_2$ in reaction still pot versus time using CsF as the fluorinating agent 69

Appendix A:

Figure A.1: Oleic acid gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = 1.3088x$ 81

Figure A.2: Hexafluorobenzene gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = 43.41x^2 + 0.70x + 8 \times 10^{-5}$ 82

Figure A.3: Pentafluorochlorobenzene gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = -2.31x^2 + 1.53x + 5 \times 10^{-5}$ 83

Appendix F:

Figure F.1: Chemical Structure of Hexachlorobenzene 101

LIST OF TABLES

Chapter 3

Table 3.1: List of materials used for equipment validation experiments 21

Table 3.2: List of materials used for experiments using hexafluorobenzene 22

Table 3.3: Orthogonal array used to design experiments 23

Table 3.4: Design experiments for the production of biodiesel 23

Table 3.5: Operating conditions for main experimental runs 27

Chapter 5

Table 5.3: Activation Energy constants and Pre-exponential factors for each reaction using KF as the alkali metal fluoride 60

Table 5.4: Activation Energy constants and Pre-exponential factors for each reaction using CsF as the alkali metal fluoride 60

Appendix A

Table A.1: Raw oleic acid (OA) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard. 81

Table A.2: Raw hexafluorobenzene (C_6F_6) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard. 82

Table A.3: Raw pentafluorochlorobenzene (C_6F_5Cl) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard 83

Appendix B

Table B.1: Gas-chromatograph raw data for the validation experiment on the production of biodiesel based on the conversion of oleic acid (OA). 84

Table B.2: Extended results for the preliminary experiments on the production of biodiesel based on the conversion of oleic acid. 84

Table B.3: Gas-chromatograph raw data for the main experiment on the synthesis of hexafluorobenzene and other fluorinated products in the reboiler flask 85

Table B.4: Gas-chromatograph raw data for the main experiment on the synthesis of hexafluorobenzene and other fluorinated products in the distillate 85

Table B.5: Extended results for the main experiments on the yield of hexafluorobenzene (C_6F_6) in the reboiler flask 86

Table B.6: Extended results for the main experiments on the yield of hexafluorobenzene (C_6F_6) in the distillate 87

Table B.7: Extended results for the main experiments on the yield of chloropentafluorobenzene (C_6F_5Cl) in the reboiler flask 87

Table B.8: Extended results for the main experiments on the yield of chloropentafluorobenzene (C_6F_5Cl) in the distillate 88

Table B.9: Extended results for the main experiments on the yield of dichlorotetrafluorobenzene ($C_6F_4Cl_2$) in the reboiler flask 88

Table B.10: Extended results for the main experiments on the yield of dichlorotetrafluorobenzene ($C_6F_4Cl_2$) in the distillate 89

Table B.11: Extended results for the main experiments on the yield of trichlorotrifluorobenzene ($C_6F_3Cl_3$) in the reboiler flask 89

Table B.12: Extended results for the main experiments on the yield of trichlorotrifluorobenzene ($C_6F_3Cl_3$) in the distillate 90

Table B.13: Extended results for the main experiments on the yield of tetrachlorodifluorobenzene ($C_6F_2Cl_4$) in the reboiler flask 90

Table B.14: Extended results for the main experiments on the yield of tetrachlorodifluorobenzene ($C_6F_2Cl_4$) in the distillate 91

Table B.15: Extended results for the main experiments on the yield of pentachlorofluorobenzene (C_6FCl_5) in the reboiler flask 91

Table B.16: Extended results for the main experiments on the yield of pentachlorofluorobenzene (C_6FCl_5) in the distillate 92

Table B.17: Extended results for the main experiments on the total yield of all fluorinated products 92

Appendix C

Table C.1: Data for the yield computation of hexafluorobenzene 93

Table C.2: Data for the mass computation of tetrafluorodichlorobenzene 96

Table C.3: Data for the calculation of $X_{calculated}$ 98

Appendix D

Table D.1: Chemical Data Table 100

Appendix E

Table E.1: Physical and Chemical Properties of C_6Cl_6 102

LIST OF PHOTOGRAPHS

Photograph 3.1: Experimental Set-up. 1: Condenser; 2: Vigreux Column; 3: Temperature Probe Inlet; 4: Round Bottom Flask (reboiler); 5: Receiving Flask; 6: Sample Inlet; 7: Heating Mantle 22

NOMENCLATURE

Symbol	Description	Units
A_0	Pre-exponential factor for Arrhenius equation	S^{-1}
A_i	Area of peak i	-, varied
C_i	Concentration of species i	$Mol \cdot m^{-3}$
Cp	Heat capacity	$J \cdot K^{-1}$
D'	Distillate rate	$Mol \cdot s^{-1}$
E_i	Activation Energy for reaction i	$J \cdot mol^{-1} \cdot K^{-1}$
F_F	Contribution of fluorine atom to ECN	-
G_{r^o}	Gibbs Energy of Reaction	$Kj \cdot mol^{-1}$
H	Height	Mm
H_{dissln}	Heat of dissolution	$Kj \cdot mol^{-1}$
H_{Lj}	Liquid enthalpy on tray j	$Kj \cdot mol^{-1}$
H_{rxn}	Heat of reaction	$Kj \cdot mol^{-1}$
H_{Vj}	Vapour enthalpy on tray j	$Kj \cdot mol^{-1}$
k	Rate constant	Min^{-1}
K_c	Equilibrium constant	-
L_j	Liquid molar flow rate on tray j	$Mol \cdot s^{-1}$
M_i	Mass of species i	G
MM_i	Molar mass species i	$G \cdot mol^{-1}$
n_i	Moles of species i	Mol
NT	Number of trays	-
R	Gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
r_i	Reaction rate expression for reaction i	$Mol \cdot ml^{-1} \cdot min^{-1}$
R'	Overall reaction rate	$Mol \cdot ml^{-1} \cdot min^{-1}$
R_L	Reflux rate	$Mol \cdot s^{-1}$
T	Temperature	K
V	Volume	M^3or cm^3 or ml
V_j	Vapour flow rate on tray j	$Mol \cdot s^{-1}$
x_{ji}	Liquid fraction of species i on tray j	-
y_{ji}	Vapour fraction of species i on tray j	-
Z	Calibration factor	-

GREEK SYMBOLS

Symbol	Description	Units
δ	Uncertainty	Varied
ρ	Density	$Kg \cdot m^{-3}$
$\emptyset_i$	Fugacity coefficient	-
γ_i	Activity coefficient	-

SUBSCRIPTS

av	Average
IS	Internal Standard
In	Initial
F	Final
St	Standard
B	Reaction pot
D	Distillate

ABBREVIATIONS

NECSA	South African Nuclear Energy Corporation
FEI	Fluorochemical Expansion Initiative
GC	Gas Chromatography
ECN	Effective Carbon Number
OA	Oleic Acid
IS	Internal standard
RRF	Relative response factor
HETP	Height equivalent to a theoretical plate

1

CHAPTER ONE

1. INTRODUCTION

1.1 BACKGROUND

The global fluorochemical industry is worth approximately R120 billion annually and is allegedly growing at between 3 and 6 % per annum (Pelchem, 2011). South Africa is second to China as home to the largest fluorspar (CaF_2) reserves in the world, and it is an international supplier of CaF_2 to hydrogen fluoride producers.

The mineral, CaF_2, is a key raw material in the production of refrigerants, high-end technology products (computer chips), plastics (Teflon), fuel, glass, steel, pharmaceuticals, aluminium, water fluoridation, and nuclear fuels. South Africa is the third largest exporter of CaF_2 and produces 5% of the world's total requirements (ca. 4.55 million tons per annum), but yet earns less than 10% of its final output value (Pelchem, 2011). As a result, the Fluorochemical Expansion Initiative (FEI) (a South African Government Initiative) was established by Pelchem, a subsidiary of the South African Nuclear Energy Corporation (NECSA), in order to improve the understanding of fluorochemical technology, to increase the beneficiation of South African mined CaF_2.

This dissertation was carried out under the auspices of the FEI, and the South African research chair in fluorine process engineering and separation technology, at the University of KwaZulu-Natal. It sets out to research and develop a method to improve the yield of the perfluorinated aromatic compound, hexafluorobenzene (C_6F_6). C_6F_6 is a product within the fluorspar beneficiation value chain that has utility as a heat exchange fluid, lubricant, and solvent. It is also valuable as an intermediate in the production of pharmaceutical compounds, as well as artificial fibres (Haszeldine, 1966).

Previously, C_6F_6 has been synthesized by means of the fluorination of benzene over cobaltic fluoride, followed by dehydrofluorination and defluorination treatments of the intermediates (Gething, et al., 1959); and through the pyrolysis of tribromofluoromethane (Birchall & Haszeldine, 1959). However, these methods have proved to be arduous, hazardous and expensive; with the latter method involving the liberation of a large amount of bromine, which must be recovered (Barbour & Pedler, 1965). There is, therefore, a need for an improved route for the synthesis of hexafluorobenzene that minimizes these disadvantages.

Attempts have been made to find a new means to synthesise C_6F_6. Maynard (1966) carried out the fluorination of chlorine-containing aliphatic and cycloaliphatic compounds using an alkali-metal fluoride, in a solvent having a boiling point of at least 423.15 K. But the production of hexafluorobenzene was not achieved. Holbrook et al. (1966) conducted an experiment involving the reaction of hexachlorobenzene with potassium fluoride in the solvent N-methyl pyrrolidone at 473.15 K. The fluorination was found to be straightforward until three chlorine atoms had been replaced, after which hydrogen substitution occurred.

Prior to 1971, no one had been able to use alkali metal fluorides to obtain chlorofluorobenzenes, with more than three fluorine atoms in the ring, using a halogen exchange reaction. In 1971, George Fuller discovered that tetrahydrothiophen-1,1-dioxide (commonly known as sulfolane), was preferable to other solvents for the halogen reaction of alkali metal fluorides with hexachlorobenzene. Yields of highly fluorinated products, higher than any other high-boiling aprotic solvent, such as hexafluorobenzene, were obtained by using sulfolane (Fuller, 1971).

1.2 OBJECTIVES

The aim of the Fluorine Expansion Initiative as a whole considers the macro-economics of the various fluorine derivatives; however, this was not within the scope of this project which was a feasibility study determining whether the chosen experimental method (batch reactive distillation using solid fluorinating agents) could be used to produce hexafluorobenzene in satisfactory quantities. The main objectives of the project were as follows:

- To synthesize hexafluorobenzene through batch reactive distillation using solid fluorinating agents;
- To determine the conditions under which hexafluorobenzene was synthesized (if synthesized);
- To determine quantities of hexafluorobenzene produced (if synthesized); and
- To generate performance data in order to develop a high level conceptual design of a commercial process.

This study picks up from where Fuller stopped in 1971. Fuller (1971) developed a simple one-stage method of preparing highly fluorinated aromatic compounds (such as dichlorotetrafluorobenzene, chloropentafluorobenzene and hexafluorobenzene) using simple glass equipment. He reacted hexachlorobenzene with potassium fluoride in the presence of sulfolane using batch reactive distillation. However, the yield of hexafluorobenzene (C_6F_6) was only 0.4%. C_6F_6 has widespread use within the biomedical field where it is used in investigating potential prognostic biomarkers of tumour oxygenation (Zhao, et al., 2009). It also plays a vital role in the preparation of pharmaceutical compounds and polymers. The inimitable properties of hexafluorobenzene allow it to be used as a non-inflammable anaesthetic and in the production of dyes and pigments (Cottrell & Hopkin, 1965). C_6F_6 also has a high resistance to degradation and a high chemical stability that make it useful as a cooling fluid in nuclear reactors (Bennett & Fuller, 1965).

The overall objective of this study was to improve the yield of the hexafluorobenzene synthesis process. This was achieved by varying operating conditions, and by using a more reactive alkali fluoride, i.e. Caesium fluoride. The primary hypothesis was that a satisfactorily yield of hexafluorobenzene could be obtained by indirect fluorination using caesium fluoride in a reactive distillation system. Although there is other methods of producing hexafluorobenzene, Fuller's experiments are cost effective and highly fluorinated aromatic compounds are produced using a simple one stage process.

Using Fuller's experiment as a basis, the current investigation was broken up into two phases:

- Phase 1: Equipment and experimental validation – During installation of new equipment, it is of integral importance to ensure that the experimental apparatus operates in the correct manner and, therefore, previously carried out experiments need to be replicated and the results compared in order to validate full functionality of the

equipment. The equipment for this investigation was validated by replicating the biodiesel production reactive distillation experiment undertaken by Nakkash and Al-Karkhi (2013). In this experiment, the esterification of methanol and oleic acid, using sulphuric acid as a catalyst to produce biodiesel (methyl oleate), was carried out. The results are compared to those produced by Nakkash and Al-Karkhi. The experimental apparatus used by Nakkash and Al-Karkhi is similar to the equipment used by Fuller; and, therefore, Nakkash and Al-Karkhi's experiments were used to validate the equipment.

- Phase 2: Improving the yield of the hexafluorobenzene synthesis process – This was achieved through modifications to the process conditions applied by Fuller (1971). Variations in process conditions were made in relation to temperature and pressure through the use of an alternative alkali fluoride, caesium fluoride, and through variation of the alkali fluoride - hexachlorobenzene ratio. Each variable was tested separately while keeping the other operating conditions constant. The results of these experiments were then used to determine how the collective effects of the variables impacted on the yield of hexafluorobenzene. Consequently, a set of optimum operating conditions could be gauged, on the basis of which, a novel method for the synthesis of hexafluorobenzene could be designed. This will in turn contribute to the Fluorochemical Expansion Initiative. The effect of the variables on the conversion of hexachlorobenzene as well as on the selectivity of all fluorinated products was additionally determined.

A detailed experimental plan was drawn up, based on the two phases outlined above. For both phases, the various performance criteria, such as conversion and yield, were determined via quantitative analysis on a gas chromatograph equipped with a flame ionization detector.

A simplified kinetic model was developed to identify the unknown kinetic parameters for both the hexafluorobenzene system using either potassium fluoride or caesium fluoride as the fluorinating agent. This was implemented on MATLAB® by least squares regression of the experimental data.

1.3 DISSERTATION OUTLINE

This dissertation is divided into five chapters, with the first chapter serving as a brief introduction to the topic, along with the motivation and objectives. A literature review is

presented in Chapter Two, encompassing the current state-of-the art for hexafluorobenzene synthesis, the need for an alternative method and the various uses of hexafluorobenzene. Chapter Three focuses on the experimental apparatus, procedure and design. The obtained results are presented, and subsequently discussed, in Chapter Four. Chapter Five presents the kinetic model of the system and regressed kinetic parameters while Chapter 6 details the viability of the presented experimental method for commercial production of hexafluorobenzene. Chapter 7 highlights the conclusions drawn, and associated recommendations needed to improve future work. The appendices incorporate the raw data, instrument calibration, sample calculations, MATLAB ® scripts and chemical data.

2

CHAPTER TWO

2. INTRODUCTION TO LITERATURE SURVEY

The review of literature will outline the various uses of the perfluorinated aromatic compound, hexafluorobenzene (C_6F_6), the history of, and current state-of-the art of hexafluorobenzene synthesis, and why there is a need to investigate an alternative method for its synthesis.

This study picks up from where Fuller stopped in 1971. The overall objective is to improve the yield of the hexafluorobenzene using batch reactive distillation. This is achieved by varying operating conditions, and by using a more reactive alkali fluoride, i.e. Caesium fluoride. It is instructive, however, to first provide a detailed background to the subject.

2.1. FLUOROCHEMICAL POLYFLUOROAROMATIC COMPOUNDS: A HISTORY

The first study on the chemistry of fluorochemicals was undertaken over 40 years ago, and since then, research has expanded into new areas of organic fluorine chemistry, followed by increasing commercial exploitation to the benefit of society (Godsell, et al., 1956). In 2010, the growing global market for fluorochemicals stood at R120 billion per year (Vocus, 2010). The key mineral, fluorspar (CaF_2), is used as raw material for the production of fluorochemicals.

Chlorofluorobenzenes, which are a class of fluorochemicals, have gained popularity due to their unique properties and characteristics that make them stable under thermal and high energy radiation changes (Fuller, 1971). These compounds are highly resistant to oxidation, and consequently, do not support combustion, thereby making them an ideal choice as a non-flammable hydraulic fluid lubricant in reactor coolants.

Prior to Fuller's ground-breaking work on chlorofluorobenzenes in the 1970s, they were inaccessible and little known (Fuller, 1971). Before this, Mcbee et al. (1947) synthesised chloropentafluorobenzene by treating hexachlorobenzene with bromine trifluoride; while Fielding (1965) looked at the use of molten salt mixtures to produce hexafluorobenzene and other fluorochlorobenzenes. Finger et al. (1975) synthesized 1, 3, 5-trichlorotrfluorobenzene through the reaction of hexachlorobenzene with potassium fluoride in dimethylformamide. Maynard (1963) carried out a similar experiment, but used N-methylpyrrolidone as the solvent instead of dimethylformamide, and obtained various amounts of 1,3,5-trichlorotrfluorobenzene, as well as dichlorotetrafluorobenzene, and chloropentafluorobenzene.

Early on, it was established that aryl halides need to be suitably activated (usually by the introduction of nitro-groups), before successfully participating in halogen exchange reactions with alkali metal fluorides (Bunnett & Zahler, 1951). These results were also previously represented by Gottlieb (1936), who produced 1-fluoro-compound from 1-chloro-2,4-di-nitrobenzene and potassium fluoride. In 1956, Finger et al. Extended this research, and carried out similar experiments with the polar aprotic solvents: dimethylformamide and dimethyl sulphoxide. However, only three, suitably placed chlorines could be replaced by fluorine, and the products were low in yield resulting in a 10% molar yield of trifluoronitrobenzene. At this time there was no proven method for using alkali metal fluorides to produce higher fluorinated chlorofluorobenzenes, i.e. Dichlorotertrafluorobenzene ($C_6Cl_2F_4$), chloropentafluorobenzene (C_6ClF_5), and hexafluorobenzene (C_6F_6) (Fuller, 1971).

Maynard et al. (1961), produced fluorinated compounds through the reaction of aliphatic and cycloaliphatic chlorine compounds and potassium fluoride dissolved in a solvent, having a boiling point of at least 423.15 K. In this patent there was no mention of the fluorination of aromatic compounds. However in 1963, Maynard was successful in using hexachlorobenzene with potassium fluoride in the solvent N-methyl pyrrolidone, to produce the higher fluorinated aromatic compounds dichlorotetrafluorobenzene and chloropentafluorobenzene. Unfortunately, it was not possible to substitute all chlorine atoms with fluorine and therefore hexafluorobenzene could not yet be produced.

It was only in 1971 that Fuller, albeit at low yields, succeeded in producing hexafluorobenzene (0.4% molar yield). This dissertation therefore adapts Fuller's

experimental procedure in order to produce higher yields of hexafluorobenzene using aromatic compounds and appropriate alkali fluorides and solvent.

Fuller (1971) discovered that out of all polar aprotic solvents, sulfolane (tetrahydrothiophen-1,1-dioxide) produces the best yields of highly fluorinated aromatic products, having more than three fluorinate atoms in the ring. He concluded that sulfolane promotes halogen-exchange reactions due to its high boiling point and good thermal stability. Additionally, other solvents require more severe conditions to achieve a higher degree of fluorination (Fuller, 1971).

The use of a solvent was found to accelerate the reaction rate, since dissolved solids are more mobile than molecules in the solid phase. Additionally, dissolved solids are able to access the fluorinating agent more easily. This was made evident when the reaction times of the fluorination experiments carried out, with and without solvents, were compared by Fuller (1971), and Vorozhtsov (1963), respectively. While Vorozhtsov (1963) worked at a temperature and pressure of 773.15 K and 50bar respectively, Fuller (1971) was able to implement his experiments at atmospheric pressure and at a temperature of 503.15 K. It can, therefore, be concluded that the use of a solvent reduces the severity of operating conditions.

This dissertation aims at improving the yield of hexafluorobenzene, using Fuller's system as a basis. Over and above its convenient operating conditions, the chosen experimental procedure offers the following advantages (Fuller, 1971):

(a) It is the only simple, one-stage method for producing highly fluorinated aromatic compounds;

(b) It is possible to regenerate the fluorinating agent (such as potassium fluoride or caesium fluoride) from the alkali metal fluoride (potassium chloride or caesium chloride) through the use of hydrogen fluoride;

(c) Its products are easily separated by distillation; and

(d) Its process may conveniently be carried out in a simple glass apparatus.

2.2. ALKALI METAL FLUORIDES

As mentioned above, aromatic compounds and appropriate alkali fluorides and solvents were investigated in this study to adapt Fuller's experimental procedure in order to produce higher yields of hexafluorobenzene.

It is generally accepted that alkali fluoride metals are required to activate the fluorination of perhalo-compounds (Bennett & Fuller, 1965). This is supported by Vorozhstov and Yakobsen (1963), who produced p-fluoronitrobenzene by reacting p-chloronitrobenzene with caesium fluoride. In British Patent 755,688, the conversion of 4-chlorophthalic anhydride to 4-fluorophthalic anhydride, in the presence of potassium fluoride, was carried out using an alkali metal fluoride. Therefore, it can be concluded that the fluorinating agent initiates and participates in the fluorination reaction in addition to the fluorination activation.

The efficiency of alkali metal fluoride as a fluorinating agent increases with surface area. The quantity used is dependent on the number of chlorine atoms that need to be substituted out in the starting material. It can be used in powder or pellet form. To convert hexachlorobenzene to hexafluorobenzene, at least one mole of alkali metal fluoride, per mole of chlorine to be replaced, is required. (Maynard & Hundred, 1966). The reactions can be carried out at sub-atmospheric, atmospheric, or super-atmospheric pressures.

In his fluorination experiments with the use of melts, Fielding (1962) tested a variety of fluorinating agents, from the least active lithium fluoride to the most active caesium fluoride. He found that under the action of lithium fluoride, the reaction proceeded slowly and only trace amounts of dichlorotetrafluorobenzene were achieved. The reaction proceeded more rapidly when sodium fluoride was used; however, no appreciable amounts of hexafluorobenzene were produced. It was only under the action of potassium, rubidium, or caesium fluoride that good yields, of highly fluorinated aromatic compounds, were achieved (Fielding, 1962).

2.3. HEXAFLUOROBENZENE

Hexafluorobenzene (C_6F_6) is a colourless liquid that possesses a sweet odour, and is popularly known for its good thermal stability (Boudakian, 2000). Research interest in hexafluorobenzene was sparked by its behaviour within the organic fluorine chemistry field, comparable to the usefulness of benzene within the aromatic organic chemistry field. Florin et al. (1960) concluded that C_6F_6 poses the same amount of resistance to gamma irradiation as benzene does.

Hexafluorobenzene is a polyfluoroaromatic compound derivative of benzene, in which all hydrogen atoms have been replaced by fluorine atoms. In the 1950's, it was discovered that hexafluorobenzene was unreactive toward electrophiles; the reagents used to initiate hydrogen substitution in benzenoid species. Electrophilic substitution would require the elimination of the fluoride ion; and therefore, this process was not pursued (Brooke, 1997).

In the 1950's it was discovered that hexafluorobenzene was reactive toward nucleophiles, which aroused much interest and led to a number of studies (Godsell, et al., 1956) (Burdon & Tatlow, 1957) (Pummer & Wall, 1958) (Forbes, et al., 1958).

2.4. USES OF HEXAFLUOROBENZENE

Hexafluorobenzene plays an integral role in the preparation of pharmaceutical compounds and polymers. It can also be treated with caustic potash in tert-butanol to form potassium pentafluorophenate (C_6F_5OK), which is a potent fungicide that could further be reacted with hexafluorobenzene, to produce halogenated diphenyl ethers (Fuller, 1971). These products are then utilised for their thermal properties in transformer oils.

C_6F_6 is also used as a precursor for the production of other highly fluorinated compounds containing the pentafluorophenyl group, such as pentafluoroaniline and pentafluorothiophenol that are resistant to heat, chemical attack, and radiation (Fuller, 1971). These properties make the compounds beneficial as heat exchange fluids and lubricants.

Due to its unique properties, hexafluorobenzene is also used as a non-inflammable anaesthetic and in the production of dyes and pigments (Cottrell & Hopkin, 1965). C_6F_6 also has a high resistance to degradation and a high chemical stability that make it useful as a cooling fluid in nuclear reactors (Bennett & Fuller, 1965).

The first perfluoro Dewar benzene was produced by irradiation of hexafluorobenzene with ultraviolet light (Markovskii, et al., 1977). Figure 2.1 shows the chemical structure of the Dewar benzene.

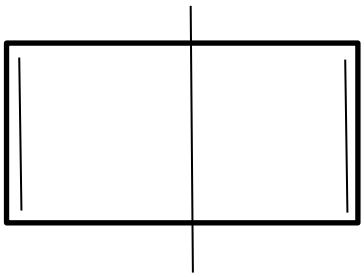


Figure 2.1: Dewar Benzene, Perfluoro Dewar Benzene (Buckingham, 1996)

Hexafluorobenzene, together with other fluorinated aromatics, have also been used in the production of drugs such as tranquilizers, anti-bacterial agents, and anti-inflammatory agents. Furthermore, the versatile properties of these fluoroaromatics have resulted in promising studies being carried out in the field of positron emission tomography (Boudakian, 2000).

2.5. PREVIOUS METHODS OF HEXAFLUOROBENZENE SYNTHESIS

While hexafluorobenzene was little known until the 1970's, its first documented synthesis was disclosed in 1947, and was achieved through a two-step bromofluorination process followed by a dehalogenation reaction (Brooke, 1997). However, this method resulted in a low yield of hexafluorobenzene (5% molar yield), along with chloropentafluorobenzene (Wall & Hellman, 1960). Moreover, the process was hazardous and tedious (Equation 2.1):

$$C_6Cl_6 + BrF_3 \xrightarrow{SbF_5} [C_6Br_2Cl_4F_6]_{av} \xrightarrow{Zn} C_6BrCl_4F_7 \xrightarrow{EtOH} C_6F_6 + C_6ClF_5 \qquad 2.1.$$

In 1960, Stacey et al. (1960) used benzene and fluorine gas to produce hexafluorobenzene through a three-stage saturation-re-aromatization process. However, multiple setbacks were encountered, such as the complexity of the process and the high production cost of fluorine gas. Furthermore, the fluorine gas was poorly utilized, since nearly fifty percent of the fluorine introduced into the system was removed during the process (Boudakian, 2000).

Production of hexafluorobenzene through pyrolysis has also been carried out in a number of studies (Alsop, 1986), (Liotta & Harris, 1974), (Ellis & Musgrave, 1950), but this method has not been commercialized. Desirant (1955) carried out pyrolysis by passing tribromo-fluoromethane (cbr_3f) through a platinum tube at 903.15K – 913 K to achieve a yield of 45% hexafluorobenzene. In addition, 90% of the costly cbr_3f was lost as bromine (Equation 2.2):

$$6CFBr_3 \xrightarrow[\text{Pt tube}]{630\text{-}640^0\text{C}} C_6F_6 + 9Br_2 \qquad 2.2$$

In 1961, Wall was able to increase the yield to 55% by carrying out pyrolysis at an elevated pressure. However, this method was rendered obsolete when Tatlow et al. (1957) produced better yields of hexafluorobenzene through the aromatization of octafluorocyclohexadienes with nickel. Subsequently, in 1963, Vorozhtsov, the founder of Halex Fluorination in Russia, succeeded in producing appreciable quantities of hexafluorobenzene by reacting hexachlorobenzene with potassium fluoride, but in the absence of a solvent (Grigoriev, 2008).

An alternate method of synthesizing hexafluorobenzene was achieved through pyrolytic defluorination, over heated iron, of a mixture of octafluorocyclo-1,3- and 1,4-dienes (Patrick & Tatlow, 1960). However, the latter compounds are obtained through the dehydrofluorination of decafluorocyclohexanes, which is an onerous task.

Application Serial no. 982,625 describes the disproportionation reaction of tetrafluorodichlorobenzene and trifluorotrichlorobenzene at temperatures greater than

873.15 K, under the catalytic action of aluminium fluoride in a stream of nitrogen, through a heated tube. This method, however, produced low yields of hexafluorobenzene (not more than a molar yield of approximately 2.94 %) (Fielding, 1962). Following this invention, Fielding (1962) developed another method to increase this yield by heating fluorochlorobenzene in the presence of a mixture of molten salts. This was achieved by passing the fluorochlorobenzene over the molten salt mixture at temperatures ranging between 773.15 K and 1173.15 K. However, the results obtained were achieved under extreme conditions, and decomposition of products also occurred (Fielding, 1962).

The temperature at which fluorination of higher aromatics occurs is dependent on three factors, namely: the number of halogen atoms that need to be replaced (in this case chlorine); the alkali fluoride used; and the number of fluorine atoms originally present (Bennett & Fuller, 1965). The difficulty of chlorine replacement by fluorine, and the thermal stability of the perhalogenfluoroaromatics, is directly proportional to the fluorine content. Consequently, when no solvent is present, for total fluorination of hexachlorobenzene, temperatures between 773.15 K and 883.15 K are required (Bennett & Fuller, 1965).

2.6. REACTION MECHANISM

The superimposition of a reaction and distillation increases the complexity of the reaction mechanism, shifts equilibrium and prevents degradation of products but does not alter the reaction mechanism. However, no published work on the sequence of reactions for the synthesis of hexafluorobenzene, from hexachlorobenzene, under the action of an alkali metal fluoride, in the presence of a solvent, could be found.

The net chemical reaction, using potassium fluoride as the alkali fluoride, was suggested by Fuller (Fuller, 1971), and the yields are depicted in Equation 2.3. Hexachlorobenzene (C_6Cl_6) was reacted with potassium fluoride (KF) in the presence of a solvent to produce trichlorotrifluorobenzene ($C_6Cl_3F_3$), dichlorotetrafluorobenzene ($C_6Cl_2F_4$), chloropentafluorobenzene (C_6ClF_5) and hexafluorobenzene (C_6F_6).

$$C_6Cl_6 \xrightarrow[230\text{-}240^0C,\ 4\ h]{KF,\ sulfolane} \underset{0.4\%}{C_6F_6} + \underset{25\%}{C_6ClF_5} + \underset{24\%}{C_6Cl_2F_4} + \underset{30\%}{C_6Cl_3F_3} \qquad 2.3$$

Literature presents no data regarding the intermediate reactions therefore Fuller's equation was used as a means in determining the reactant quantities for this study.

2.7. BATCH REACTIVE DISTILLATION

Fuller (1971) carried out his experiments using batch reactive distillation. This is in keeping with Fielding's (1967) findings. Fielding (1967) conducted a similar experiment and concluded that it was imperative to distil out the hexafluorobenzene and other products as they were formed. He supported this deduction by stating that if the hexafluorobenzene was allowed to accumulate within the system, it would undergo a back reaction, with the fluorinating agent, to produce pentafluorochlorobenzene (Fielding, 1967).

Reactive distillation represents a process-intensification, by integrating chemical reactions and physical separation in a single vessel (Pappu, 2012). This combination concept is not new to the chemical engineering industry. The earliest record of commercial application of reactive distillation dates back to the 1860's, when ammonia needed to be recovered in the Solvay process for soda ash (Sundmacher & Kienle, 2003). Over the past three decades, the commercial application of reactive distillation has spanned an array of fields. This includes its use in the production of methyl tertiary butyl ether, a gasoline oxygenate additive (Zhu, et al., 2002). Reactive distillation has also been used as a process intensification technique for desulfurization, selective hydrogenation, dimerization and isomerization reactions (Murkute, et al., 2011). Today, there are over 200 licensed commercial applications of reactive distillation reported worldwide (Gaertner, 2009).

The application of reactive distillation, as a process intensification technique, reduces capital investment and operation costs, improves thermodynamic efficiency, and overcomes conversion limitations by driving the reaction toward completion through the

removal of volatile products (Erdem & Cebe, 2011). Furthermore, better reactor control is achieved through the elimination of hot spots within the system (Newman, 1956).

In batch reactive distillation, the chemical reaction takes place in the reboiler and the products are taken off at the top, as they form. Batch reactive distillation equipment is comprised of a reboiler (which also serves as the reaction still), a packed or trayed column, refluxing condenser, and a collecting still, in which condensed products are collected.

Thermodynamics plays a crucial role in understanding and designing reactive distillation, by providing the basic relations, such as, energy balances of equilibrium conditions (Sundmacher & Kienle, 2003). Figure 2.2 is a schematic representation of a lab-reactor used for reactive distillation processes (Metkar, et al., 2015).

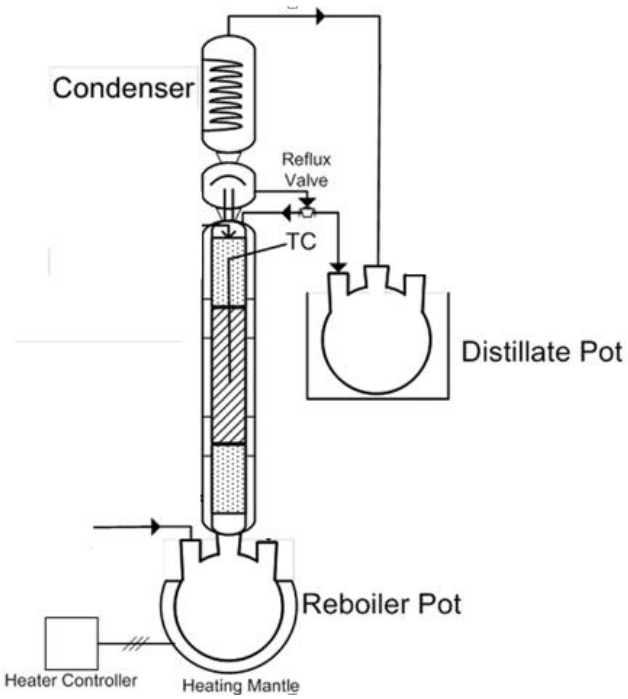


Figure 2.2: Schematic representation of lab-reactor set up used for the reactive distillation process (Metkar, et al., 2015)

2.8. GAS CHROMATOGRAPHY FOR QUANTITATIVE ANALYSIS

Chromatography plays a vital role in analysis as it allows for component separation in a sample mixture, which is subsequently used in sample quantification. In gas chromatography, a series of peaks are outputted when a solution is injected, as shown in Figure 2.3. Each peak represents a different component. Depending on the sample mixture under scrutiny, there exists various types of chromatography.

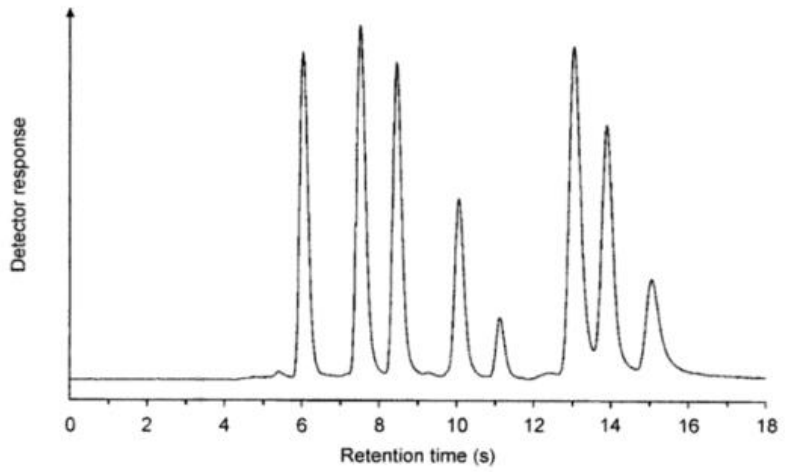


Figure 2.3 Sample chromatogram of detector response versus retention time (Handley & Adlard, 2001)

Gas Chromatography was applied in this study to undertake quantitative analysis (the mechanics of doing this will be described in Chapter 3). Here, the various methods that have been used, as shown in the literature, will be discussed.

Quantitative analysis by means of gas chromatography can be carried out using a variety of methods, such as the area normalization method, standard addition method, and the internal and external standard method. Some of the aforementioned techniques require calibration in order to quantify the results. A calibration is carried out by determining the relationship between the magnitude of a peak for a known amount of analyte in a standard solution and the amount of analyte injected into the chromatograph. That relationship, called the calibration curve, can then be used to determine the amount of analyte in a sample of unknown concentration.

2.8.1. AREA NORMALIZATION METHOD

The area normalization method is a straightforward analysis technique that requires no calibration. It is assumed that the weight percent of a component is equal to its corresponding peak area percentage, which is calculated by dividing individual component areas by the total area. However, this technique assumes the same response for all species in the sample. Samples vary significantly in volatility or functional group type, and will have different elution times, leading to erroneous results (Schirmer, 1991).

2.8.2. EXTERNAL STANDARD METHOD

The external standard method compares the analysis of an unknown sample with the analysis of a standard sample that has the same matrix, and contains the same analyte in known concentrations (Kolb & Ettre, 2006). Calibration curves are then generated, either via single point or multiple point calibrations. The single point calibration method makes use of a single standard prepared with a known concentration of the analyte (C_S). The calibration factor, Z, is then determined by Equation 2.4, where S_{stand} Represents the area or height of the peak.

The same analyte is present in both the unknown and the standard sample, and will therefore share the same calibration factor. Once the calibration factor has been calculated, the concentration of analyte in the unknown sample can be deduced (Harvey, 2000; mcnair and Miller, 2011):

$$Z = \frac{S_{Stand}}{C_S} \qquad 2.4$$

On the other hand, the multiple point method, as its name suggests, uses multiple standards of varying concentrations. The calibration curve is then generated. The response factor is represented by the gradient. If the calibration plot is linear, the response factor is easily quantifiable. However, in the event that the calibration plot is non-linear, an additional equation, depicting non-linearity, will need to be used (Harvey,

2000). In addition, in order to produce reliable results, the injection volume for every sample must be exactly the same.

2.8.3. STANDARD ADDITION METHOD

In the standard addition method, a definite amount of the component to be quantified is added to the sample, and the change in peak area caused by the increase in concentration is used to quantify the component (Gerhards, et al., 1999). The quantification can be improved by injecting various concentrations of the component, such that a straight line is produced when plotting the peak area against concentration, as seen in Figure 2.4 (Gerhards, et al., 1999).

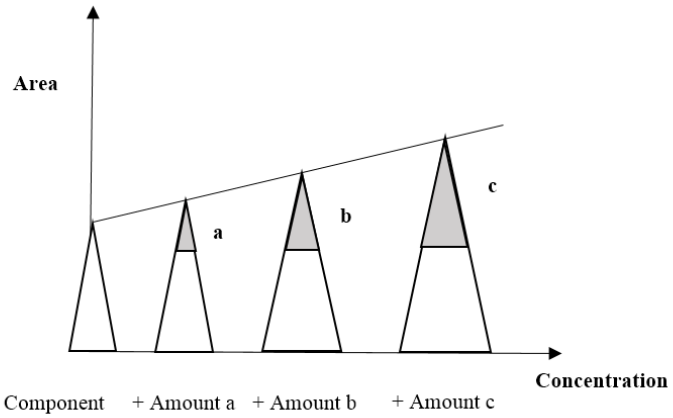


Figure 2.4: Standard addition method – a, b and c represent concentrations of a component added to the sample (Gerhards, et al., 1999)

The concentration of future unknown samples is then calculated using the following equation:

$$C = \frac{C_{st} \times A_0}{A_{st} - A_0} \qquad 2.5$$

Where,

C: Concentration of unknown sample (mol·m^{-3});

C_{st}: Concentration of the standard (mol·m^{-3});

A_0: Peak area of the component in the sample without addition; and

A_{st}: Peak area of the component in the sample with the standard.

2.8.4. INTERNAL STANDARD METHOD

An alternate, safer calibration technique is a method which utilizes an internal standard. An internal standard is a non-interfering compound with similar characteristics to that of the compounds of interest. An appropriate internal standard should meet the following criteria:

- It should be chemically similar to the species of interest but not interfere or merge with any of the components of interest;
- It should be of high purity;
- It should produce a sharp consistent peak; and
- It must have similar retention properties to the components of interest.

The internal standard is added to the sample and the quantification of the content is carried out based on the area ratio of the analytes and internal standard. Once an internal standard is identified, the area ratio between the two components on the chromatograph is determined, and a calibration curve is then plotted (as outlined in Appendix A). Figure 2.5 is an example of a chromatograph measurement where the area ratio is plotted on the y-axis and the known concentration ratio is plotted on the x-axis.

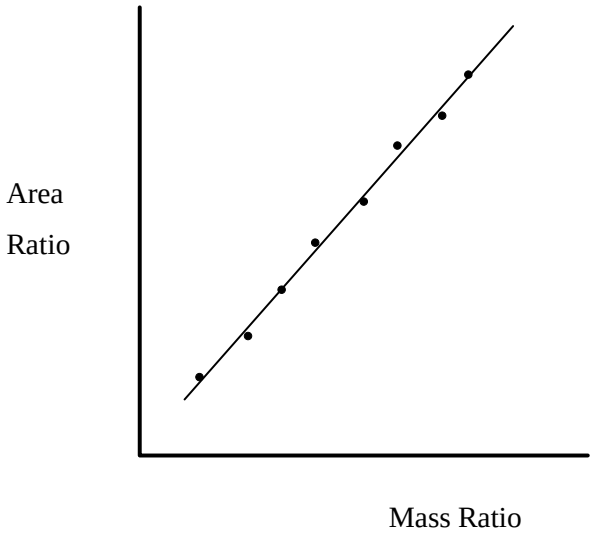


Figure 2.5: Illustrative example of calibration plot generated using an internal standard gas chromatography quantification method (mcnair and Miller, 2011).

The amount of analyte, M_A, of future samples can subsequently be determined using the equation of the curve, where a known mass of internal standard (M_{IS}) is added to the sample.

2.9 LITERATURE SURVEY: CONCLUSION

From the review of literature above, one can conclude that hexafluorobenzene is an important compound with a number of uses, and that there are several methods to produce it. The literature surveyed has shown that most of these methods are tedious and/or have limitations. Although the approach investigated by Fuller (1971) is cost effective, and carried out in a simple, one-step procedure, a low amount of hexafluorobenzene is produced (molar yield of 0.4 %). As a result, following Fuller's experimental methods, this investigation aims to develop an efficient technology to increase the yield of hexafluorobenzene, while using gas chromatography to quantify the results.

3

CHAPTER THREE

3. EXPERIMENTAL APPARATUS AND MATERIALS

3.1. MATERIALS

During installation of new equipment, it is of vital importance to ensure that the experimental apparatus operates in the prescribed manner to produce valid results. In order to validate full functionality of the equipment, if experiments were previously carried out and published, using equivalent equipment, these need to be replicated and the results compared.

As a result, the esterification of oleic acid with methanol, catalysed by sulphuric acid to produce biodiesel (methyl oleate) carried out by Nakkash and Al-Karkhi (2013), using a similar batch reactive distillation system to that required, was carried out. Table 3.1 summarizes the materials used for this experiment.

Table 3.1: List of materials used for equipment validation experiments

Material	Purity
Methanol	99.50%
Oleic Acid	90.00%
Sulphuric acid	95.00-99.00%

Table 3.2 summarizes the materials used for the main experiment (synthesis of hexafluorobenzene).

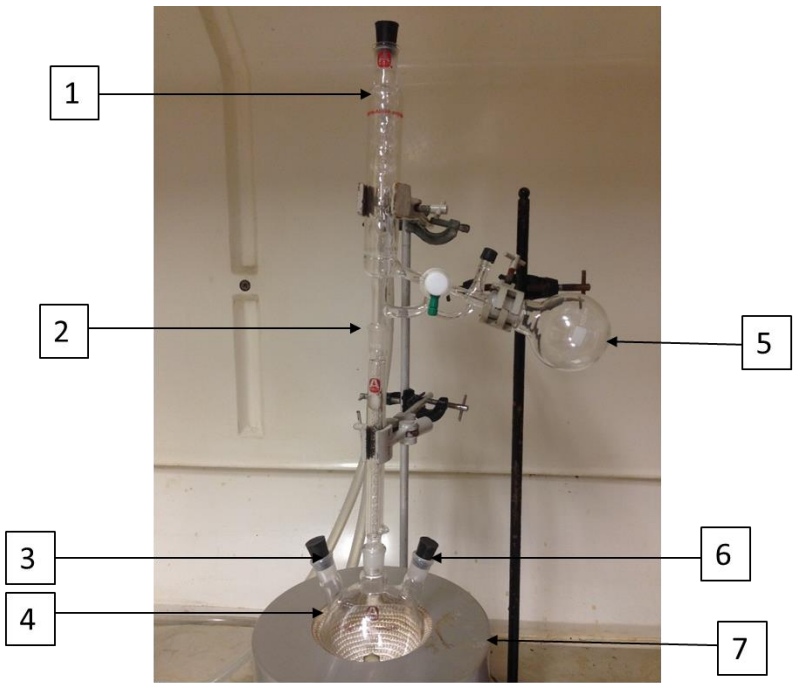
Table 3.2: List of materials used for experiments using hexafluorobenzene

Material	Purity
Sulfolane	99.00%
Hexachlorobenzene	99.00%
Potassium fluoride	99.00%
Caesium fluoride	99.90%

The means used to conduct the equipment validation is outlined in Section 3.2.

3.2. PRELIMINARY EXPERIMENTS/VALIDATION EXPERIMENT

As the means to conduct the experiments required testing the systems of interest, a new 250ml batch reactive distillation unit, consisting of a Vigreux column, as well as a refluxing condenser, was set-up, as shown in Figure 3.1.



Photograph 3.1: Experimental Set-up. 1: Condenser; 2: Vigreux Column; 3: Temperature Probe Inlet; 4: Round Bottom Flask (reboiler); 5: Receiving Flask; 6: Sample Inlet; 7: Heating Mantle

For the validation experiments, the biodiesel production experiment carried out by Nakkash and Al-Karkhi (2013) was replicated using the same experimental conditions. The molar ratio of methanol to oleic acid, catalyst amount, reaction time and temperature were varied, in order to determine the optimal conditions for biodiesel production through batch reactive distillation. Table 3.3 shows the orthogonal array used to design the experiments, while Table 3.4 shows the different design of experiments carried out for the production of biodiesel. Experimental conditions were chosen such that they were within range of literature values in order to draw a meaningful comparison.

Table 3.3: Orthogonal array used to design experiments

Experiment Number	Variables and their level			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	2	1	2	3
4	2	2	3	1
5	3	1	3	2
6	3	2	1	3

Table 3.4: Design experiments for the production of biodiesel

Variables	Levels		
	1	2	3
A Molar Ratio (OLAC/MEOH)	1:4	1:6	-
B Catalyst Amount (g sulphuric acid/g oleic acid)	0.6	1.2	1.8
C Time (min)	36	57	75
D Reaction Temperature (K)	373.15	393.15	403.15

The experiments were conducted using the apparatus depicted in Figure 3.1. A three-necked, 250ml, round-bottom flask (still-pot) was heated and stirred, using a heating mantle and magnetic stirrer, respectively. The Vigreux distillation column was assembled above the still pot, and was directly connected to a water-cooler condenser that condenses the vapour leaving the top of the column.

The Vigreux column, named after Henri Vigreux, is a simple column which has been modified with downward-pointing, orthogonal indentations projecting into the central

vapour space, thereby increasing the surface area per unit length of the column. The total length and diameter of the Vigreux column are 150mm and 15mm, respectively (shown in Figure 3.1). The vapours from the Vigreux column passed into a water-cooled, refluxing condenser.

Figure 3.1: Schematic representation of Vigreux column

Oleic acid was first charged into the 250ml round-bottom flask and continuously stirred. An acid catalyst, sulphuric acid, was added to methanol, and the mixture was charged to the still pot. The mixture was continuously stirred using a magnetic stirrer, and it was kept at the required reaction temperature and pressure.

For the duration of the specified reaction period, samples were taken and analysed using a Shimadzu 2010 Gas Chromatograph and a Shimdazu QP 2010 Plus Quadropole Gas Chromatograph – Mass Spectroscopy. Details regarding the analytical techniques used are discussed in detail in Sections 3.4 and 3.5.

3.3. HEXAFLUOROBENZENE SYSTEM: EXPERIMENTAL PROCEDURE

Once the experimental apparatus was validated, the experiments for the hexafluorobenzene system could be carried out. As previously mentioned, the experiments and findings of Fuller (1971) were used as the basis for the experimental procedure undertaken.

Fuller (1971) carried out his experiments in a 5 litre flask together with a thermometer pocket and a 1 foot column packed with glass helices connected to a Dean-Stark, take-

off head beneath a reflux condenser. He first dried a slurry of potassium fluoride (alkali metal fluoride) and sulfolane (solvent) with benzene, through azeotropic distillation. The benzene was then first removed through distillation at atmospheric pressure and again at reduced pressure. Hexachlorobenzene was then added to the system and the temperature was increased to 503.15 K. For the first five hours, distillation was carried out at atmospheric pressure and liquid product was taken off. Thereafter, distillation was carried out at reduced pressure and more liquid fraction and solid were recovered. Furin (2007) presented results of a similar experiment carried out at atmospheric pressure for 4 hours. Both experiments yielded the same amount of hexafluorobenzene.

Fuller carried out the experiments using large amounts of reactants in a 5 litre round bottom flask. Consequently, large amounts of the precursors (hexachlorobenzene, sulfolane and potassium fluoride) were also used. Due to the toxicity of hexachlorobenzene (a precursor), extreme precautions were required in terms of the safety and handling of the aforementioned compound (see Appendix E for a Safety and Handling Report).

Therefore, due to both the high cost of materials and safety concerns, in this study a smaller experimental apparatus was used. In addition, experienced researchers and PPE companies were consulted and the following safety gear was used to ensure minimal contact with hexachlorobenzene:

- Maxichem gloves – although PVC is a suitable option when dealing with hexachlorobenzene (as mentioned in the MSDS), Maxichem gloves were recommended as they provide excellent sensitivity and dexterity;
- 3M™ Full Face Mask Respirator 6000 Series – Hexachlorobenzene has been classified as extremely hazardous by the World Health Organization and the dust particles should not be inhaled;
- Tychem F Coverall – this overall was recommended by Dupont when working with hexachlorobenzene; and
- Dual density safety boots.

Once the equipment and safety factors were taken care of, the experimental work could begin. First, the required amount of sulfolane was measured and dried over calcium chloride to remove any traces of water. The alkali metal fluoride was subsequently dried by heating it to above 373.15 K. The sulfolane was added to the alkali metal fluoride and the mixture was transferred to the 250 ml round-bottom flask.

Hexachlorobenzene was then carefully added to the mixture and the temperature of the system was increased to 373.15 K using an MRC MNS-500 Laboratory Heating Mantle. The temperature of the system was monitored using a PHTC1/G Thermocouple. Loose-fill, rock-wool insulation was used around the round-bottom flask to ensure there were no heat losses. A heating coil was wrapped around the Vigreux column and the temperature was controlled using a Voltage Regulator $TDGC_2$-1kva. Once again this ensured there were no heat losses along the Vigreux column. The mixture was then continuously stirred using the magnetic stirrer and kept at the required reaction temperature and atmospheric pressure.

After 6 hours, samples were taken from both the round-bottom flask and distillate flask. The samples were analysed using the Shimadzu 2010 Gas Chromatograph (FID). However, it was discovered that hexachlorobenzene could not be quantified on the above mentioned GC due to its high boiling point.

After further research, it was found that a GC equipped with a thermal conductivity detector (TCD) is used to quantify hexachlorobenzene, as opposed to a GC equipped with an FID. Therefore, the Shimadzu 2010 Gas Chromatograph (with TCD) was used to quantify hexachlorobenzene. Details regarding the analytical techniques used are discussed in detail in Section 3.4 and 3.5.

An integral aim of the present work was to determine the effect of varying operating conditions on the yield of hexafluorobenzene. To this end, three operating conditions were chosen to be varied, these were: type of alkali-metal fluoride; fraction of alkali-metal fluoride in feed; and reaction temperature. In Experiments 1, 2 and 3, molar ratios of 1:6, 1.5:6 and 2:6 potassium fluoride (KF) (alkali-metal fluoride) to hexachlorobenzene were used while keeping the temperature at 503.15 K. In Experiments 5, 6 and 7 the same molar ratios of caesium fluoride (CsF) (alkali-metal fluoride) to hexachlorobenzene were used while keeping the temperature at 503.15 K. In Experiments 8 and 9 temperatures of 463.15 K and 483.15 K were used while keeping the molar ratio of $KF:C_6Cl_6$ constant. In Experiments 11 and 12 temperatures of 463.15 K, 483.15 K and 503.15 K were used while keeping the molar ratio of $CsF:C_6Cl_6$ constant. To ensure reproducibility of results, experiments 4, 10 and 13 were repeats of experiments 3, 9 and 12 respectively. Table 3.5 summarizes the experimental conditions.

Table 3.5: Operating conditions for main experimental runs

Manipulated Variables			
Experiment	Type of alkali metal fluoride	Molar ratio of alkali metal fluoride: hexachlorobenzene	Temperature (K)
1	KF	1:6	503.15
2	KF	1.5:6	503.15
3	KF	2:6	503.15
4	KF	2:6	503.15
5	CsF	1:6	503.15
6	CsF	1:6	503.15
7	CsF	1:6	503.15
8	KF	1:6	463.15
9	KF	1:6	483.15
10	KF	1:6	483.15
11	CsF	1:6	463.15
12	CsF	1:6	483.15
13	CsF	1:6	483.15

The cost of running these experiments was very high, as the reagents were expensive and difficult to acquire, with some of the reagents and standards being obtained from overseas suppliers. Furthermore, a number of precautions had to be taken with regard to working with the highly toxic hexachlorobenzene (as outlined in the above). These factors consequently limited the amount of experiments that could be carried out. Therefore, experiments were prioritized to determine the effect of the major operating variables on the process, particularly the temperature, type of fluorinating agent and ratio of reagents. Chapter 6 highlights additional factors which could be varied to determine its effect on the yield of hexafluorobenzene.

3.4. CALIBRATIONS – GAS CHROMATOGRAPHY

The different calibration techniques for gas chromatography are outlined in detail in Section 2.8, where it is concluded that an internal standard is the most advantageous method to use for our purposes. A disadvantage, however, of the aforementioned

method is, for the purpose of calibration, the need to find a suitable internal standard that meets all the criteria, as specified in Section 2.8.

3.4.1. CALIBRATION – BIODIESEL EXPERIMENT

For the validation experiments, i.e. The production of biodiesel, four internal standards were tested: acetone, ethanol, butanol and propanol. Based on the polarity of the analytes, these are common types of internal standards used when dealing with the above system. Butanol was chosen as the internal standard as it met all criteria, eluted within range of the compounds of interest and did not interfere with any other peaks.

A calibration procedure was conducted on completion of all experimental runs. This ensured that the obtained results fell within the calibration range. The minimum and maximum area ratio of analyte to internal standard for all experimental runs was noted before preparing the calibration samples. Samples of varying quantities of internal standard falling within the minimum and maximum area range were then prepared. The samples were then injected into the GC using a 0.5 microliter gas chromatography syringe. This procedure was carried out three times to ensure repeatability and consistency.

3.4.2. CALIBRATION – HEXAFLUOROBENZENE SYSTEM

Due to a mixture of polar and non-polar components being present in the analyte, non-polar, polar aprotic and polar protic internal standards were tested. For the hexafluorobenzene system, five internal standards were tested: acetone (polar aprotic), methanol (polar protic), butanol (polar protic), benzene (non-polar) and toluene (non-polar). Butanol was once again chosen as the internal standard as it met all criteria, eluted within range of the compounds of interest and did not interfere with the peaks of interest.

As with the validation experiment, the calibration procedure was conducted on completion of all experimental runs. The same procedure was followed as outlined in Section 3.4.1. However, the calibration (and quantification) of hexachlorobenzene was conducted on GC-TCD while the calibration (and quantification) for the rest of the components (for which standards could be obtained), was conducted on the GC-FID.

3.4. ANALYTICAL TECHNIQUES

Gas chromatography has the most widespread use in the field of quantitative analysis for the separation of gaseous and volatile substances due to the numerous advantages it offers (Scott, 1998):

- It only requires a small quantity of sample;
- It is designed to separate highly complex mixtures into components;
- Its results are obtained within a short period of time;
- It is highly precise;
- It is the only analytical method with the sensitivity to detect volatile organic mixtures having low concentrations; and
- It is user friendly and the gas chromatography analysis procedure is relatively easy to implement.

The gas chromatographic analyses were carried out using a Shimadzu 2010 GC, using a Restek® capillary column (30 m × 0.25 mm) coated in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. As previously mentioned, one of the factors affecting the quality of results is the temperature programme used. For the biodiesel system, the temperature program developed for the analytes started at 333.15 K. This temperature was held for 5 minutes. A heating rate of 293.15 K·min^{-1} was applied until a temperature of 523.15 K was reached and then held for a further 10 minutes. This resulted in a total run time of 24.50 minutes.

For the hexafluorobenzene system, the temperature program developed for the analytes started at 313.15 K and was held at this temperature for 5 minutes. A heating rate of 10 K·min^{-1} was applied until a temperature of 393.15 K was reached, and this temperature was held for a further 5 minutes. An additional heating rate of 20 K·min^{-1} was applied until a final temperature of 473.15 K was reached. It was held at this temperature for 7 minutes, resulting in a total run time of 29 min.

The temperature program developed for the hexachlorobenzene started at 313.15 K and was held at this temperature for 5 minutes. A heating rate of 10 K·min^{-1} was applied until a temperature of 393.15 K was reached, and then held for a further 5 minutes. Thereafter, a heating rate of 20 K·min^{-1} was applied until a final temperature of 523.15 K was reached and this was held for 20 minutes. This resulted in a total run time of 44.5 minutes.

4

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. PRELIMINARY INVESTIGATION: VALIDATION EXPERIMENT – PRODUCTION OF BIODIESEL USING BATCH REACTIVE DISTILLATION

A preliminary investigation was carried out to validate the batch reactive distillation system as presented in Chapter 3. Validation of the equipment was achieved by carrying out an esterification reaction of methanol and oleic acid to produce methyl oleate (biodiesel). The process conditions used were in agreement with those used by Nakkash and Al-Karkhi (2013) who carried out the same experiment. The results were then compared to those obtained by Nakkash and Al-Karkhi (2013) in order to establish the accuracy and reliability of the equipment and methods used.

Methanol and oleic acid were introduced into a 250ml round bottom flask in the presence of sulphuric acid which catalysed the reaction. The effects of varying molar ratio, catalyst amount, reaction time and reaction temperature on the conversion of oleic acid were determined. The internal standard method was used to quantify the amounts of products.

N-Butanol proved to be a suitable internal standard and was consequently used to quantify all product samples. The calibration plots for all components of interest are present in Appendix A. The results were quantified in terms of the conversion of oleic acid. They are depicted in sections 4.1.1 – 4.1.5.

4.1.1. Effect of Molar Ratio on Oleic Acid Conversion

The conversion of oleic acid was calculated based on the initial and final mass of oleic acid. This calculation is detailed in Appendix C, Section B. The conversion of oleic acid is affected by a number of variables, such as molar quantities of reactants, experimental temperature and experimental time. The molar ratio of methanol to oleic acid is an integral factor in this conversion. In the present experiment, molar ratios of 4:1, 6:1 and 8:1 of methanol/oleic acid were used to produce biodiesel. Theoretically, the stoichiometric ratio for the esterification requires that one mole of methanol be used to one mole of oleic acid. Practically however, this ratio is insufficient to complete the reaction and therefore a higher quantity of methanol was used to drive the reaction to completion (Nakkash & Al-Karkhi, 2014).

The conversion of oleic acid, with varying methanol/oleic acid ratios, is depicted in Figure 4.1.1. From the results it can be seen that the percentage average conversion of oleic acid is directly proportional to the molar ratio of methanol/oleic acid. The increase in methanol shifts the reaction equilibrium and favours the forward reaction and therefore results in an increase in oleic acid conversion. A comparison between the experimental and literature results is outlined in Section 4.1.5.

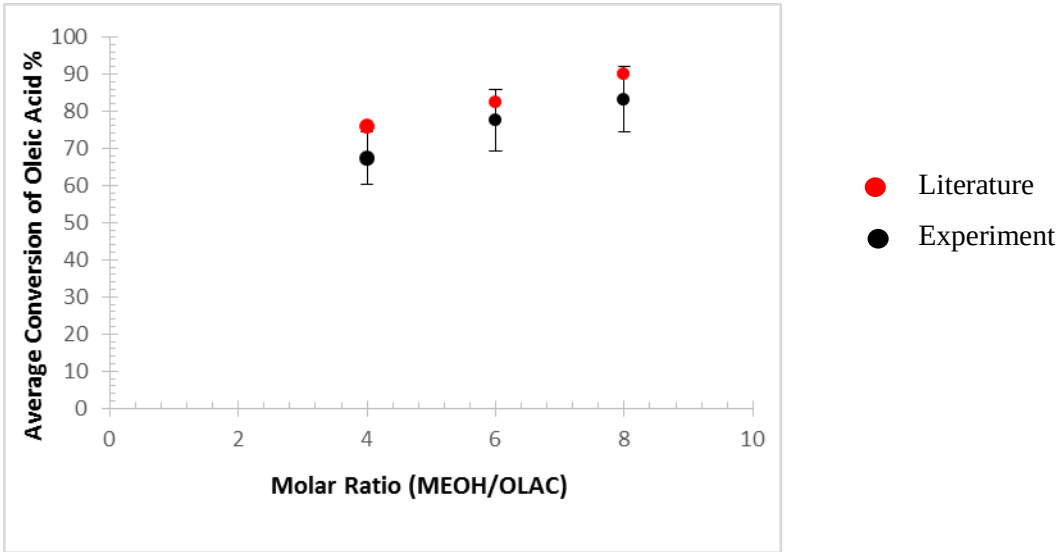


Figure 4.1.1: Percentage average conversion of oleic acid versus methanol/oleic acid molar ratio, literature (red dots), experimental (black dots) with uncertainty estimates shown as error bars.

4.1.2. Effect of Catalyst Amount on Oleic Acid Conversion

The quantity of catalyst used also plays a vital role in the conversion of oleic acid. Varying amounts of 0.6 and 1.2 grams of sulphuric acid/gram of oleic acid was studied and the results are presented in Figure 4.1.2. As depicted, an increase of sulphuric acid/gram of oleic acid from 0.6 to 1.2 grams resulted in an increase of oleic acid conversion from 72.9 % to 74.5 %. The amount of catalyst used is directly proportional to the esterification reaction rate and, therefore, a lower activation energy is achieved, thus reducing the time to achieve a high conversion (Nakkash & Al-Karkhi, 2014).

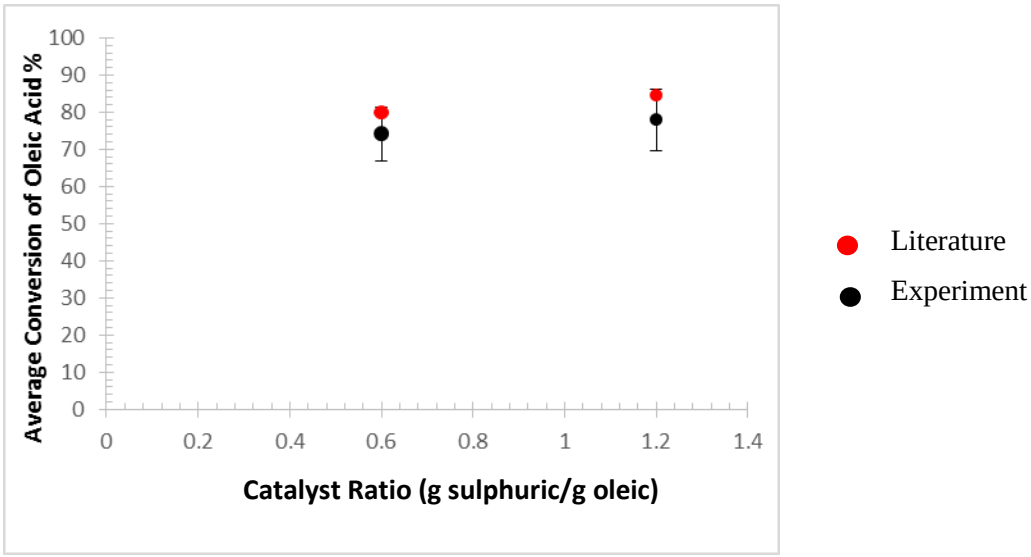


Figure 4.1.3: Percentage average conversion of oleic acid versus varying catalyst amount ratio of grams of sulphuric acid to grams of oleic acid, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars.

4.1.3. Effect of Reaction Time on Oleic Acid Conversion

The effect of reaction time on the conversion of oleic acid is represented in Figure 4.1.3. In order to achieve adequate mixing between reagents, it is imperative that the reaction mixture must be stirred at a constant rate for the duration of the reaction. This was

achieved through the use of a magnetic stirrer set at a constant speed of 900 rpm for all experiments. Reaction times of 36, 57 and 75 minutes were implemented and the results show that the conversion increases up to a time of 57 minutes. Thereafter there is a decrease in the percentage average conversion. The percentage average conversion increases from 75% to 83% and then decreases to 75%. A possible explanation for this decrease is due to the loss of methanol from the mixture to the top of the distillation unit during the reaction (Nakkash & Al-Karkhi, 2014)

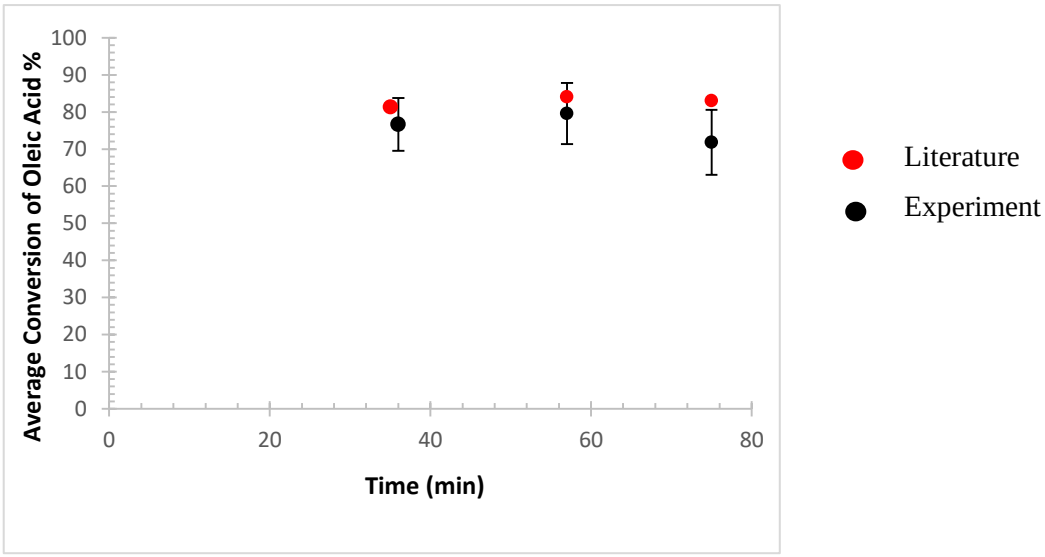


Figure 4.1.4: Percentage average conversion of oleic acid versus time, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars

4.1.4. Effect of Reaction Temperature on Oleic Acid Conversion

In this work, the column is operated at atmospheric pressure with varying temperatures of 373.15 K, 393.15 K and 403.15 K. The effect of varying temperatures on the average percentage conversion of oleic acid is depicted in Figure 4.1.4. From the results it can be seen that the reaction is endothermic, as the conversion of oleic acid is directly proportional to the reaction temperature. This is due to the fact that higher reaction temperatures favour reactions with higher activation energies.

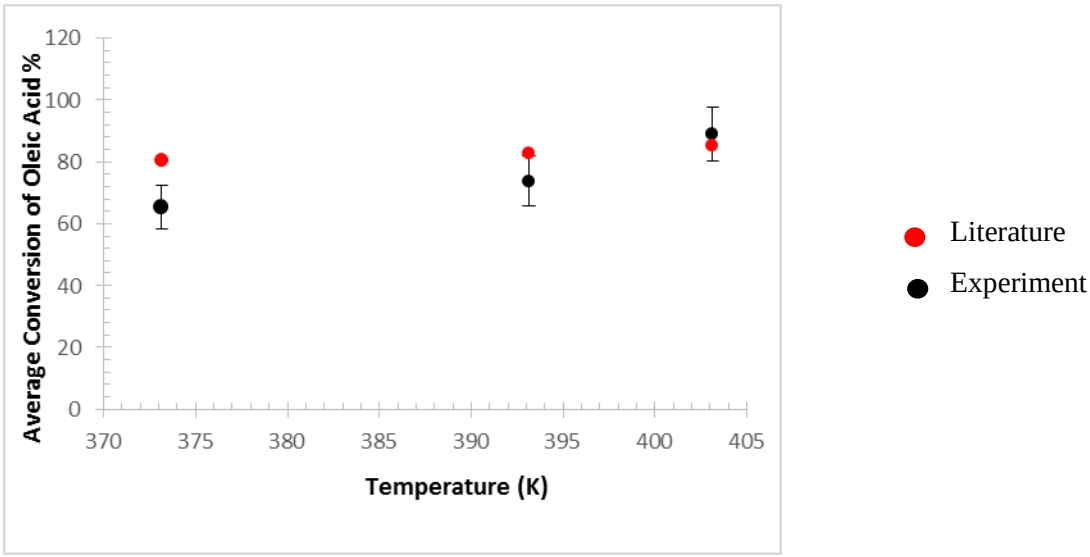


Figure 4.1.5: Percentage average conversion of oleic acid versus temperature, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars

4.1.5. Comparison Between Literature and Experimental Results

For all experiments carried out, it is noted that the experimental runs follow the same trends as depicted in literature. However, the conversion is slightly lower than that presented in literature. This is explained by the loss of heat during the reaction due to lack of insulation. In the esterification reaction, water is typically formed as a by-product and limits the reaction. Therefore, the water must be removed from the system in order to shift the equilibrium and increase the conversion of oleic acid. However, due to the loss of heating, products would condense on the walls of the round bottom flask and Vigreux column and fall back into the reaction pot. This problem was alleviated by the use of insulation and heating tape. Experiments depicted in Figure 4.1.4 were carried out again and the results presented in Figure 4.1.5 show an increase in conversion (as compared to the results in Figure 4.1.4).

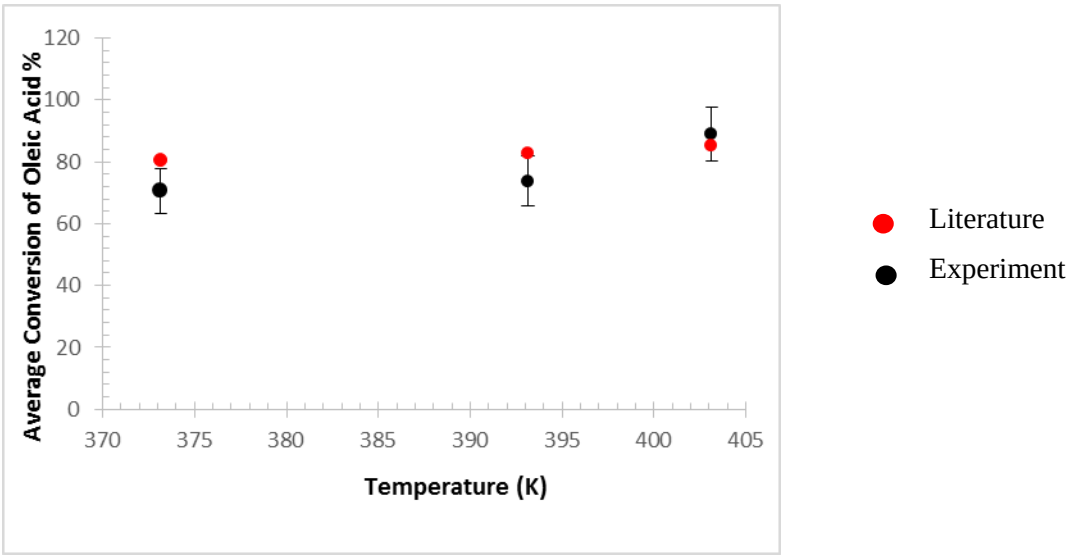


Figure 4.1.6: Re-run of experiment 1; percentage average conversion of oleic acid versus temperature, literature (red dots), experimental (black dots), with uncertainty estimates shown as error bars

4.1.6. VALIDATION EXPERIMENT: CONCLUSION

The principle aim of the above experiments was to validate the reaction unit. From the results outlined above, it was concluded that the batch reactive distillation unit operated satisfactorily, within experimental error, and could therefore be used to conduct the kinetic experiments for the main hexafluorobenzene system.

4.2. MAIN INVESTIGATION: SYNTHESIS OF HEXAFLUOROBENZENE THROUGH BATCH REACTIVE DISTILLATION

Once the experimental apparatus was validated, the main experiments could be carried out. Fluorination of chlorobenzenes occurs through the reaction of hexachlorobenzene with an alkali metal fluoride dissolved in a solvent. These fluorinated aromatics range from C_6Cl_5F (least fluorinated) to C_6F_6 (most fluorinated). The purpose of this investigation was to implement different process conditions in an attempt to increase the yield of C_6F_6 as well as determining the effect of different process conditions on the molar selectivity of the fluorinated products.

First, the required amount of sulfolane was measured and dried over calcium chloride to remove any traces of water. The alkali metal fluoride was subsequently dried by heating it to above a temperature of 373.15 K. Sulfolane was then added to the alkali metal fluoride and the mixture was transferred to the 250 ml round-bottom flask. Hexachlorobenzene was then carefully added to the mixture and the temperature of the system was increased to the required temperature. The mixture was then continuously stirred for a period of 8 hours through the use of a magnetic stirrer. This investigation only considered the effects of temperature and the type and mass of alkali metal fluoride used. Reaction time was kept constant for all experiments. Samples were then taken from both the round-bottom flask and distillate flask and analysed using gas chromatography. The results and trends are discussed in Sections 4.2.1 to 4.2.7 below.

Solubility limits of hexachlorobenzene in sulfolane could not be found in literature. However, the product samples were run through the GC-TCD and overall, the experimental results showed an unchanging quantity of hexachlorobenzene. As KF, CsF and hexachlorobenzene all have a low solubility in sulfolane, their respective concentrations in the liquid phase would all be at their respective solubility limits. This essentially illustrates that the conversion of hexachlorobenzene and yields of fluorinated products should not be significantly affected by changes in the amounts of these reagents added to the still pot.

4.2.1. EXPERIMENTAL OBSERVATIONS

Once the hexachlorobenzene was added to the mixture of sulfolane and potassium fluoride, a yellow-white slurry was formed. It was noted, that complete solubility of the potassium fluoride and hexachlorobenzene in sulfolane did not occur. After approximately 2 hours, a colourless condensate was taken off in the distillate flask. After a further hour, further condensate was taken off. At the end of 8 hours, it was noted that a very small portion of solid white product was taken off in the distillate. A similar result was observed by Fuller (1971) and he subsequently found that the white solid formed was trichlorotrifluorobenzene. Liquid samples were then taken from both the reboiler and distillate flask to run through the gas chromatograph.

4.2.2. THE EFFECT OF USING KF AS THE ALKALI METAL FLUORIDE ON THE YIELD OF C_6F_6

Figure 4.2.1 illustrates that as the molar ratio of KF: C_6Cl_6 increased, the yield of C_6F_6 likewise increased. Experiment 4 was a repeat of experiment 3 and shows a good degree of reproducibility (the experimental conditions for the various experiments are tabulated in Section 3.3., Table 3.5.). In the graph presented below, the repeat experiments are illustrated in red. The highest molar percentage yield achieved was 0.27% for a molar ratio of 12:1 for of KF: C_6Cl_6. This increase is explained by the shift in equilibrium which is caused by the excess KF. When an excess of KF is used, the effect of the reverse reaction becomes negligible. The presented results also support the notion that a series reaction is taking place. That being the case, a greater amount of KF would favour further fluorination of intermediate products to hexafluorobenzene. In addition, as C_6F_6 is produced, it is removed via distillation and therefore minimizes the effects of the reverse reaction.

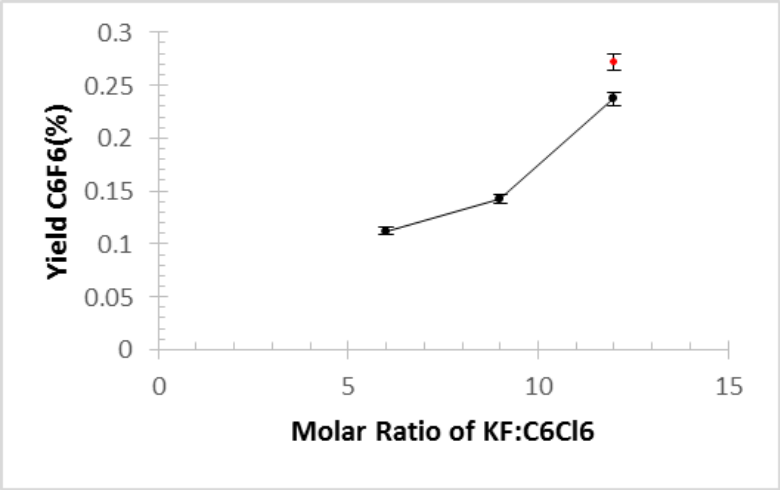


Figure 4.2.1: Molar yield percentage of C_6F_6 versus varying molar ratio of KF: C_6Cl_6 with repeat experiments illustrated in red and uncertainty shown as error bars

4.2.3. THE EFFECT OF USING CsF AS THE ALKALI METAL FLUORIDE ON THE YIELD OF C_6F_6

The same trend is depicted for CsF and C_6F_6 as for KF. Figure 4.2.2 also depicts that as the molar ratio of CsF: C_6Cl_6 increased, the yield of C_6F_6 correspondingly increased. The highest molar percentage yield achieved was 0.59% for a molar ratio of 12:1 for CsF: C_6Cl_6. Literature states that when the maximum substitution of fluorine is required, an excess of the alkali-metal fluoride is preferred (Blindinov, et al., 1999). The experimental results presented support this notion which illustrates that at higher ratios of CsF: C_6Cl_6, higher yields of C_6F_6 are produced.

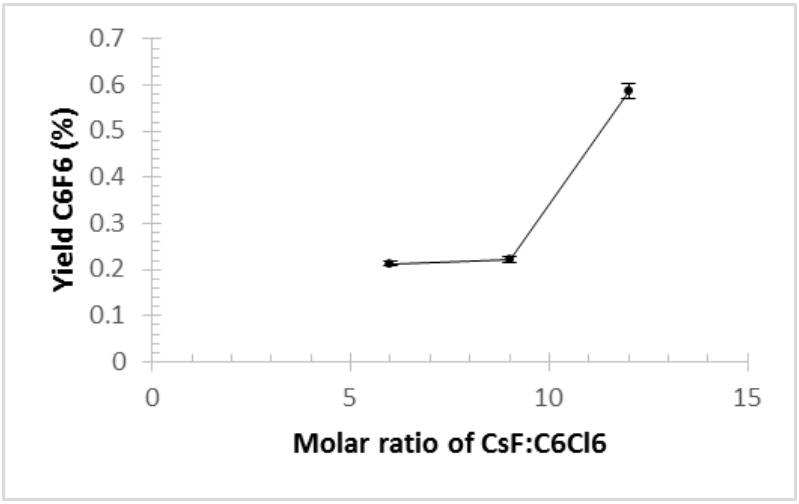


Figure 4.2.2: Molar yield percentage of C_6F_6 versus varying molar ratio of CsF: C_6Cl_6 and uncertainty shown as error bars

4.2.4. THE EFFECT OF USING KF AND A VARYING MOLAR RATIO OF KF: C_6CL_6 ON THE CONVERSION OF C_6CL_6

For the first 3 experiments (refer to Chapter 3, Table 3.5. For the different experimental conditions), the molar ratio of KF: C_6Cl_6 was varied at a constant temperature of 503.15 K. In the present work, hexachlorobenzene was converted to a range of fluorinated products including C_6F_6, C_6F_5Cl, $C_6F_4Cl_2$, $C_6F_3Cl_3$, $C_6F_2Cl_4$, and C_6FCl_5. Figure 4.2.3 exhibits the effect on the molar percentage conversion of C_6Cl_6 using molar ratios of KF: C_6Cl_6 of 6:1, 9:1 and 12:1. Figure 4.2.3 illustrates that as the molar ratio of KF: C_6Cl_6 increased the molar conversion percentage of C_6Cl_6 similarly increased. Once

again, this increase is explained by the shift in equilibrium which is caused by the excess KF which favours the forward reaction.

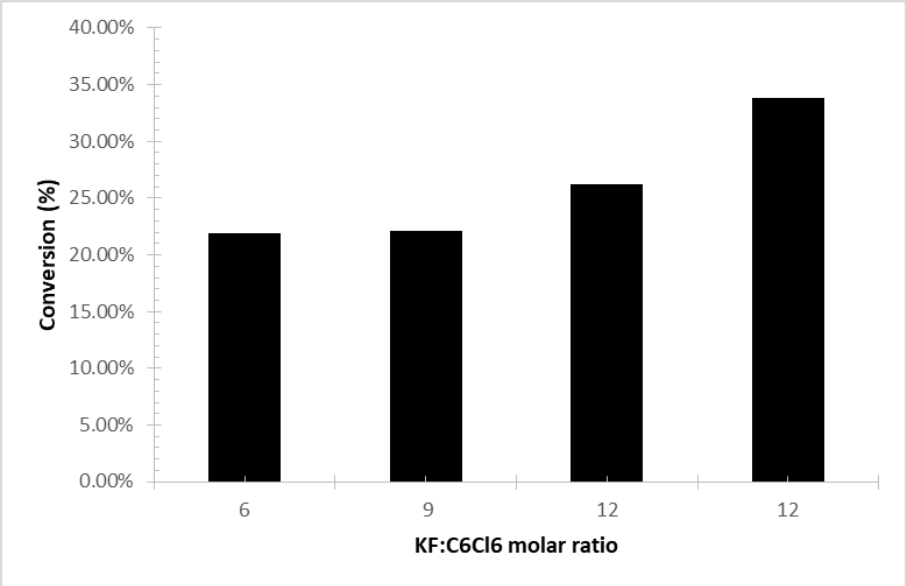


Figure 4.2.3: Conversion percentage of C_6Cl_6 versus varying molar ratio of KF: C_6Cl_6

4.2.5. The Effect of Using CsF and a Varying Molar Ratio of CsF: C_6Cl_6 on the Conversion of C_6Cl_6

For experiments 5 to 7, CsF was used as the alkali metal fluoride and the ratio of CsF: C_6Cl_6 was varied while keeping a constant temperature of 503.15 K. Literature does not provide extensive information on the reaction mechanism for this type of fluorination. Therefore, initially, a series reaction was assumed and 6 moles of CsF was used per mole of C_6Cl_6. For experiments 6 and 7 a molar ratio of 9:1 and 12:1 was used respectively. Figure 4.2.4 graphically represents the relationship between the molar ratio of CsF: C_6Cl_6 and the conversion of C_6Cl_6. As seen, the conversion of C_6Cl_6 decreased with an increasing molar ratio of CsF: C_6Cl_6. This is in contrast to the results highlighted in Section 4.2.2 using KF as the fluorinating agent. This suggests that a solubility limit of CsF in sulfolane had most likely been reached. Although solubility limits of CsF in sulfolane could not be found in literature, it is noted that the molar mass of CsF is 2.6 times greater than the molar mass of KF. Due to this difference, dissimilar masses of CsF and KF had to be used to achieve the same molar ratios of alkali metal fluoride to hexachlorobenzene. For experiments 1 to 3, masses of 29.14g, 43.72g and

58.28g of KF were respectively used. On the other hand, for experiments 5 to 7, masses of 76.19g, 114.29g and 152.39g of CsF were used which is more than double that of the KF used. Therefore, as the molar ratio of CsF: C_6Cl_6 increased, due to a solubility limit of CsF being reached, the amount of un-dissolved CsF also increased. This increased amount of un-dissolved CsF would, in all probability, impede a good degree of mixing resulting in inefficient contact of the hexachlorobenzene and fluorinating agent and hence causing a lower conversion of hexachlorobenzene.

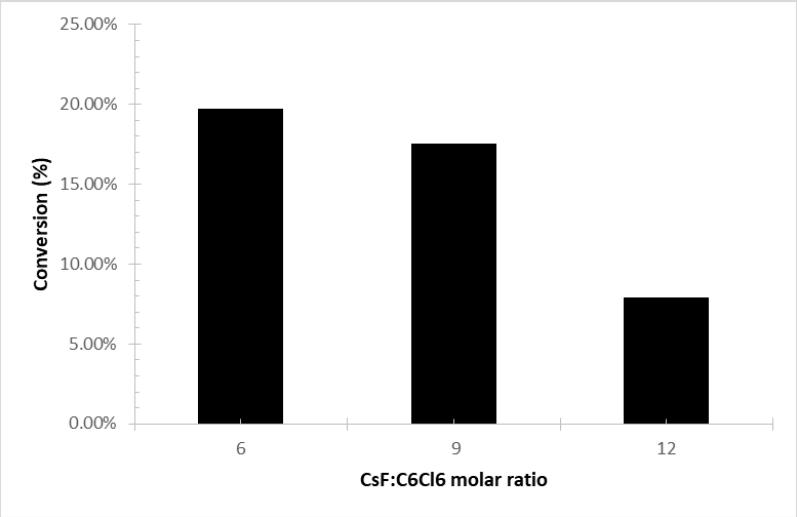


Figure 4.2.4: Conversion percentage of C_6Cl_6 versus varying molar ratio of CsF: C_6Cl_6

4.2.6. COMPARING KF AND CSF AS A FLUORINATING AGENT FOR THE SYNTHESIS OF C_6F_6

When comparing KF and CsF as a fluorinating agent, it is noted that CsF more than doubles the yield of C_6F_6. Alkali metal fluorides are the preferred fluorinating agents for the preparation of highly fluorinated fluorochlorobenzenes (George & Henry, 1967). These vary in activity from lithium fluoride (least active) to CsF which is most active (George & Henry, 1967). This is a possible explanation as to why CsF produces the highest yield of hexafluorobenzene, which is the most fluorinated species. Literature has also shown that although the fluorination reaction proceeds more rapidly when using sodium fluoride as the fluorinating agent, only traces of highly fluorinated fluorochlorobenzenes were produced. Conversely, using KF, CsF or rubidium fluoride

yielded much better yields of the higher fluorinated fluorochlorobenzenes (George & Henry, 1967).

An additional reason for CsF producing a higher yield of C_6F_6 than KF, is the surface area of the alkali metal fluoride. Bennet & Fuller (1967) showed that the efficiency of an alkali metal fluoride as a fluorinating agent is proportional to the surface area. Their results showed that the more finely crushed alkali metal fluorides produced a higher yield of the higher fluorinated products. The CsF used in the current investigation was a much finely ground powder compared to the KF that was used and therefore this postulates an additional reason as to why the use of CsF produced a higher yield of C_6F_6. In 2016, Lokhat et al., similarly found that the quality of KF used in reactions affects the yield of products. They observed that the more finely divided powder form of KF produced higher yields of products compared to the yield of products that were produced when larger clumps of KF was used. This is due to the hygroscopic nature of KF, which rapidly absorbs moisture from the atmosphere which in turn causes the salt to agglomerate and form large clumps (Lokhat, et al., 2016). Since a high surface area is required for KF to be sufficiently active, large clumps of KF will result in a decreased yield.

An additional factor which affects the yield of products is the solubility of the alkali metal fluoride in the solvent. In 1975, Henson found that the solubility of KF in a solvent is directly proportional to the yield of products (Henson, 1975). He observed that when the solubility of KF increases, the fluoride anion becomes less tightly paired with the cation and subsequently the reactivity of the fluoride ion increases thus producing a higher yield of products. Since CsF is much more soluble and reactive than KF, it makes for a better fluorinating agent. Conclusively, from the results depicted in Sections 4.2.2 and 4.2.3., it can be concluded that CsF is a better fluorinating agent for the production of C_6F_6 as compared to KF as it more than doubles the yield of hexafluorobenzene.

4.2.7. VARYING TEMPERATURE WHILE KEEPING THE RATIO OF KF:C_6Cl_6 CONSTANT

Figure 4.2.5 demonstrates the effect of increasing temperature on conversion of C_6Cl_6 while using a constant ratio of KF: C_6Cl_6 of 6:1. From the diagram it can be seen that as temperature increased, the conversion of C_6Cl_6 consequently increased. This trend is

supported by the findings of Maynard and Hundred (1966) who proved that at low temperatures (373.15 K – 423.15 K) the reaction proceeds too slowly and a low yield of fluorinated products were achieved. If temperatures higher than 503.15 K were used, thermal degradation of sulfolane would have occurred. This would have led to product decomposition and a reduced conversion of hexachlorobenzene. Therefore the highest temperature used in this investigation was 503.15 K.

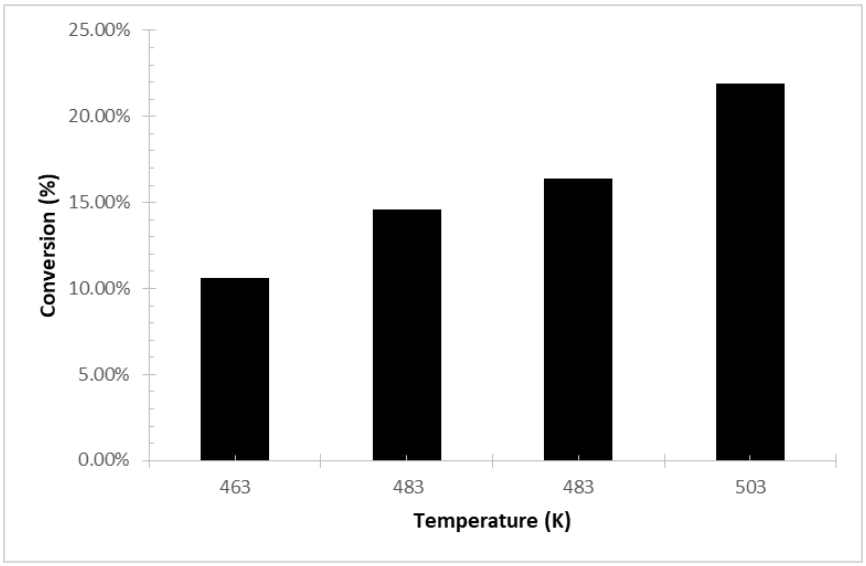


Figure 4.2.5: Conversion percentage of C_6Cl_6 versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6

Figure 4.2.6 below exemplifies the relationship between a varying temperature and the yield of C_6F_6 (using KF as the fluorinating agent). The figure demonstrates that an increase in temperature resulted in an increase in yield of C_6F_6. However, this increase in yield is very minimal. A plausible explanation for this occurrence could be due to the activation energies of the fluorination reactions which produce hexafluorobenzene. These fluorination reactions may possibly have high activation energies which would be favoured at temperatures higher than those used in this investigation. Moreover, Maynard (1966) also stated that when lower temperatures are used, the more volatile product (C_6F_6) yields are lower as compared to when higher temperatures are used.

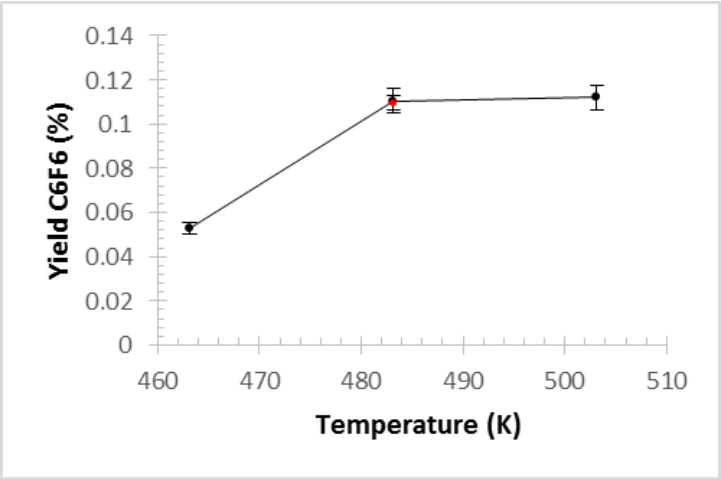


Figure 4.2.6: Molar yield percentage of C_6F_6 versus varying temperature, using KF as the alkali metal fluoride with repeat experiments illustrated in red and uncertainty shown as error bars

4.2.8. VARYING TEMPERATURE WHILE KEEPING THE RATIO OF CSF:C_6CL_6 CONSTANT

Figure 4.2.7 displays the effect of increasing temperature on the conversion of C_6Cl_6 while using a constant ratio of CsF: C_6Cl_6 of 6:1. With the exception of the experiment 12 carried out at the temperature of 483.15 K, a constant conversion of C_6Cl_6 was achieved. The lower conversion achieved for experiment 12 (at 483.15 K) could possibly be due to the localized area of lower temperature resulting from the lower level of mixing of CsF in sulfolane as explained in Section 4.2.5.

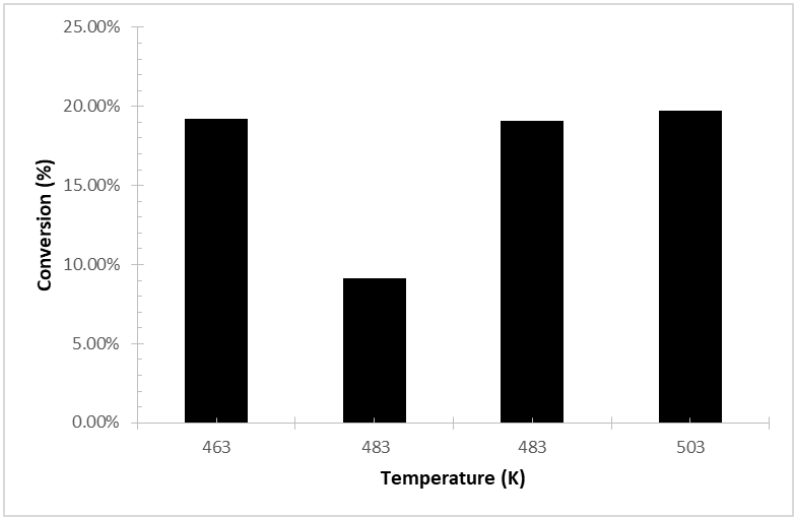


Figure 4.2.7: Conversion percentage of C_6Cl_6 versus varying temperature while keeping a constant molar ratio of CsF: C_6Cl_6

Figure 4.2.8 below represents the relationship between a varying temperature and the yield of C_6F_6 (using CsF as the fluorinating agent). The same trend as mentioned in Section 4.2.6 is observed when carrying out the same experiments with CsF and varying temperature. The highest yield of C_6F_6 produced occurred when a temperature of 483.15 K was used. A further increase in temperature resulted in a slight decrease in the yield of C_6F_6 (as opposed to the trend that is seen in Figure 4.2.7). This could be due to the fact that the temperature at which fluorination is carried out is dependent on the alkali metal fluoride used (Bennet & Fuller, 1967).

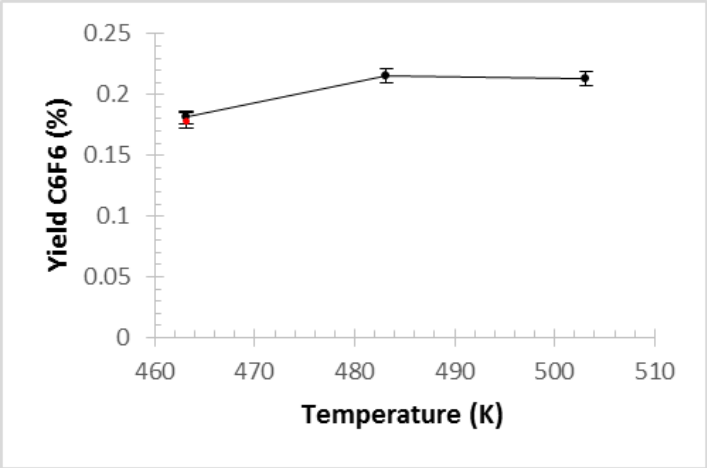


Figure 4.2.8: Molar yield percentage of C_6F_6 versus varying temperature, using CsF as the alkali metal fluoride with repeat experiments illustrated in red and uncertainty shown as error bars

4.2.9. THE SELECTIVITY OF PRODUCTS WHEN USING KF OR CSF

When hexachlorobenzene is reacted with an alkali metal fluoride, both submersed in a solvent, six fluorinated aromatics are produced. These include C_6Cl_5F (least fluorinated), $C_6Cl_4F_2$, $C_6Cl_3F_3$, $C_6Cl_2F_4$, C_6ClF_5 and C_6F_6 (most fluorinated). The selectivity for the aforementioned products was plotted for the varied amounts of KF as mentioned in Section 4.2.2. The results are graphically represented in Figure 4.2.9 below. As seen, the change in amount of KF did not significantly affect the selectivity products as similar molar selectivity's of products were achieved for varied amounts of KF.

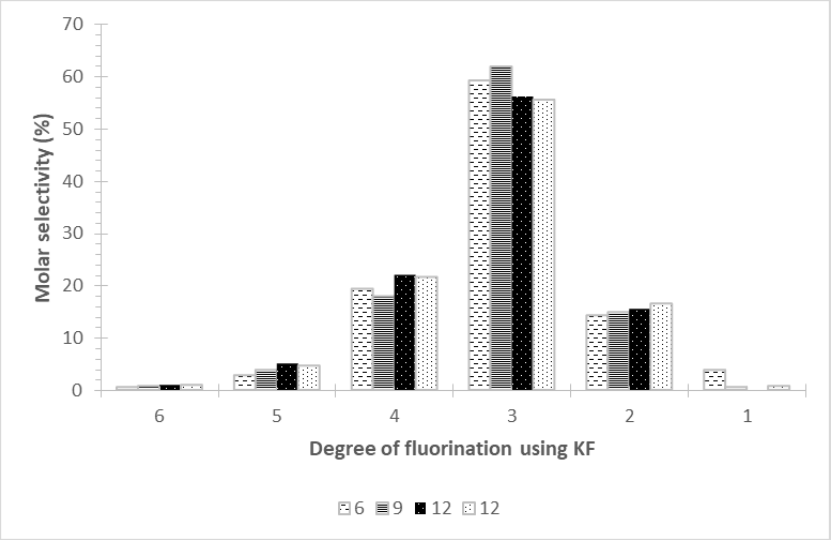


Figure 4.2.9: Molar selectivity percentage of fluorinated products versus varying molar ratio of KF: C_6Cl_6 (6:1; 9:1; 12:1)

The selectivity for the same products was plotted for the varied amounts of CsF as mentioned in Section 4.2.3. From the graph it is noted that there is an increase in molar selectivity's of the higher fluorinated compounds as the molar amount of CsF increased. The high molar selectivity achieved for $C_6Cl_3F_3$ when a CsF: C_6Cl_6 ratio of 12:1 was used is most likely due to the non-uniform reaction temperature due to poor mixing as mentioned in Section 4.2.7 above.

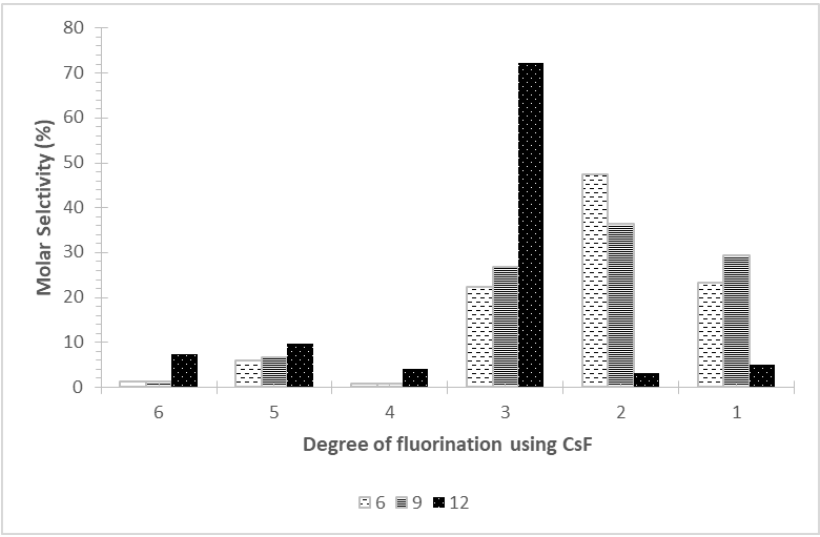


Figure 4.2.10: Molar selectivity percentage of fluorinated products versus varying molar ratio of CsF: C_6Cl_6 (6:1; 9:1; 12:1)

4.2.10 THE SELECTIVITY OF PRODUCTS WHEN VARYING TEMPERATURE

The selectivity's of products with varying temperature using KF and CsF as the alkali-metal fluoride is depicted in Figures 4.2.11 and 4.2.12 respectively. From the graphs, it is clear that the temperature had a larger impact on the selectivity's of the products as compared to varying the molar amount of alkali metal fluoride. When temperature was increased, it is noted that the higher fluorinated species increased in molar selectivity. The opposite is observed for the low fluorinated species. These results indicate that for low molar selectivity's of the highly fluorinated products, the less fluorinated product molar selectivity's are better. This supports the theory of a series reaction taking place. At low temperatures it was only possible to fluorinate to a low level thus producing high yields of the lower fluorinated compounds. Conversely, at higher temperatures, the lower fluorinated aromatics are consumed through secondary and tertiary fluorinations to produce better yields of the higher fluorinated aromatics; $C_6Fl_3F_3$, $C_6Cl_2F_4$, C_6ClF_5 and C_6F_6.

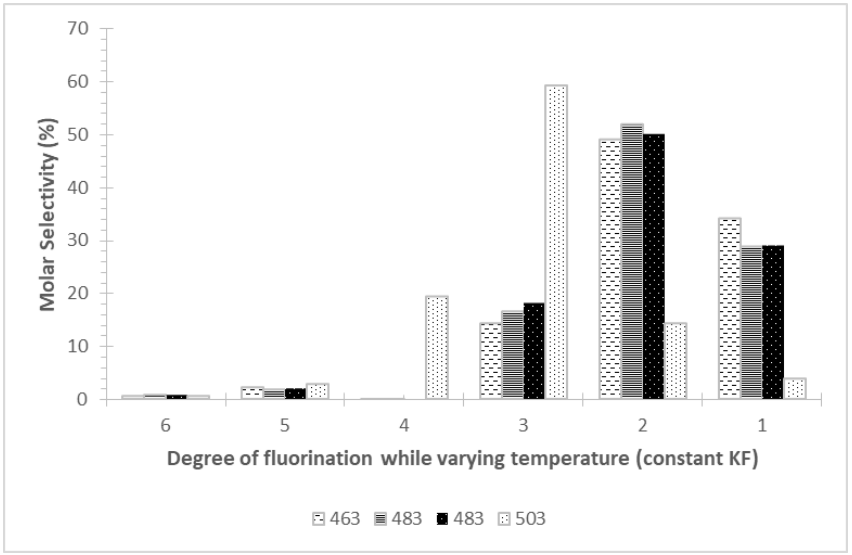


Figure 4.2.11: Molar selectivity percentage of fluorinated products versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6

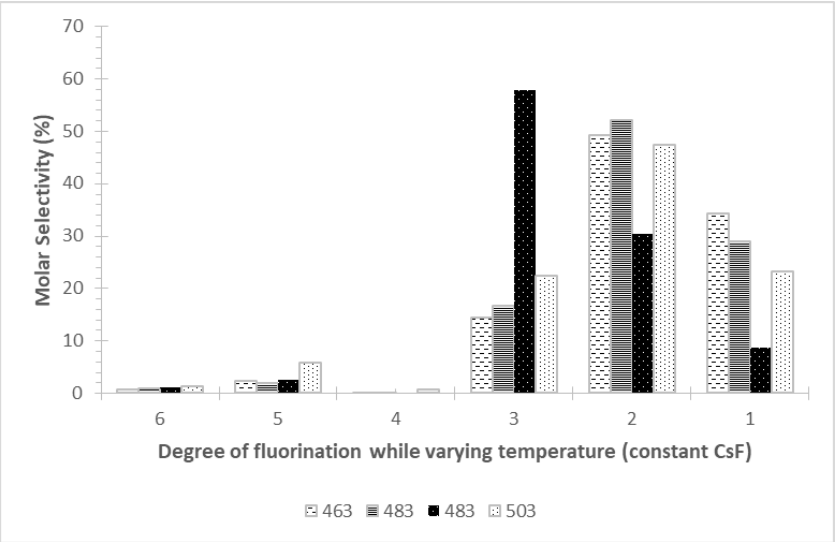


Figure 4.2.12: Molar selectivity percentage of fluorinated products versus varying temperature while keeping a constant molar ratio of KF: C_6Cl_6

4.2.11. COMPARISON BETWEEN LITERATURE AND EXPERIMENTAL RESULTS

This investigation followed Fuller's experimental methods and aimed to develop an efficient technology to increase the yield of hexafluorobenzene. Fuller's experiments showed a 0.4% yield of hexafluorobenzene when potassium fluoride was used as the alkali metal fluoride. The results presented in the current investigation show a maximum yield of 0.27% of hexafluorobenzene (using KF as the alkali metal fluoride). The obtained lower yield could be due to the nature of KF used. Fuller used azeotropic distillation using a Dean-Stark apparatus to dry the slurry of KF and sulfolane while the current investigation used heating and drying over calcium chloride. As explained above, the quality of KF used has an impact on the yield of products. The Dean-Stark apparatus is primarily used for water removal and therefore Fuller's experiments possibly resulted in a drier grade of KF and sulfolane compared to that used in the current investigation. It is worthwhile to note that, albeit low, the yield of hexafluorobenzene produced is supported by Fuller's results which likewise depicted a low yield of hexafluorobenzene (0.4%) using a similar experimental set-up (Fuller, 1971). The objective of this study was to ascertain whether the yield of hexafluorobenzene could be improved by varying the temperature, the type of alkali-metal fluoride or the ratio of alkali-metal fluoride: hexachlorobenzene. The motivation

behind selecting the presented experimental method has been highlighted in Section 2.1. Nevertheless, methods of improving the yield of hexafluorobenzene by extending the current experiment are listed in Chapter 6.

5

CHAPTER FIVE

5. MATHEMATICAL MODELLING OF THE HEXAFLUOROBENZENE SYSTEM

An additional objective of this study was to develop an appropriate kinetic model which best represents the synthesis of hexafluorobenzene through batch reactive distillation. The mathematical model was initially formulated using the following assumptions:

- Dynamics of the coolant were neglected;
- Vapour and liquid were in thermal equilibrium but not phase equilibrium;
- Pressure is constant and known on each tray;
- Dynamic changes in internal energies on the trays were much faster than the composition or total hold-up changes, therefore the energy equation for each tray is assumed to just be algebraic
- The vapour boil-up rate was constant
- The reaction took place in the still pot only
- No reflux took place

Figure 5.1 is a schematic representation of the experimental system.

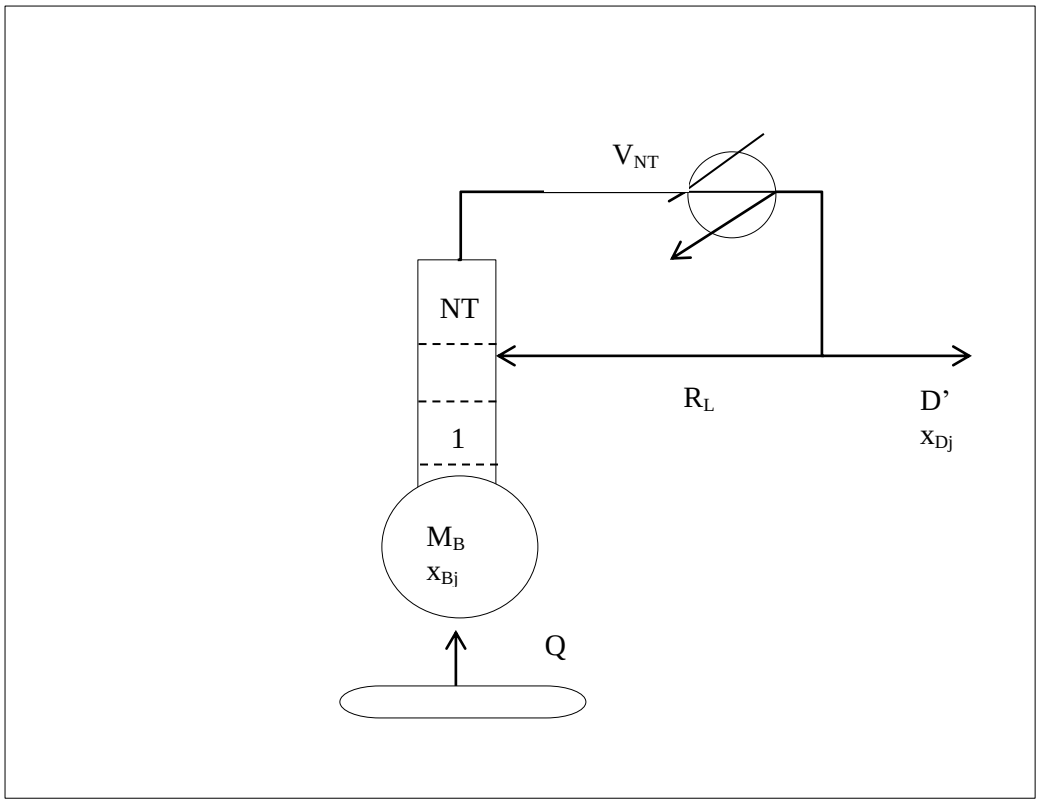


Figure 5.7: Schematic representation of experimental system

The typical height equivalent to a theoretical plate (HETP) for a Vigreux column is 100 mm (Pirrung, 2007). The length of the Vigreux column (H) was 150mm. Therefore the number of theoretical stages (N_t) was calculated to be:

$$N_t = \frac{H}{HETP} = \frac{150}{100} = 1.5\ stages \qquad 5.1$$

Based on the assumptions above, the following system of equations was formulated.

5.1. MESH EQUATIONS

The following equations represent the mass and energy balances occurring in the reaction still pot.

Material balance in still pot:

$$\frac{dM_B}{dt} = L_1 - V_B \qquad 5.2$$

Component balance in still pot:

$$\frac{d(M_{Bx_{Bi}})}{dt} = -V_B y_{Bj} + L_1 x_{1i} + R'_1 M_B + R'_2 M_B + R'_3 M_B + R'_4 M_B + R'_5 M_B + R'_6 M_B$$

5.3

Where $R'_1..R'_6 = \frac{r_i \rho_{av}}{MM_{av}}$ 5.4

Energy Balance for still pot:

$$0 = L_1 H_{L1} - V_B H_{VB} + Q$$ 5.5

$$Q = Q_R + H_{rxn} + H_{dissln}$$ 5.6

Where Q_R Represents the heat supplied and H_{dissln} Is calculated from the following equation:

$$H_{dissln} = n_{solute}(m_{solvent} Cp_{mixture} \Delta T)$$ 5.7

H_{rxn} is determined via the heats of formation.

The next set of equations represents the mass and energy balances taking place on the trays:

Material balance for tray 1:

$$\frac{dM_1}{dt} = L_2 + V_B - L_1 - V_1$$ 5.8

Component balance for tray 1:

$$\frac{d(M_{1x_{1i}})}{dt} = L_2 x_{2i} + V_B y_{Bi} - L_1 x_{1i} - V_1 y_{1i}$$ 5.9

Energy Balance for tray 1:

$$0 = L_2 H_{L2} + V_B H_{VB} - L_1 H_{L1} - V_1 H_{V1}$$ 5.10

Material balance for tray n:

$$\frac{dM_n}{dt} = L_{n+1} + V_{n-1} - L_n - V_n \quad 5.11$$

Component balance for tray n:

$$\frac{d(M_n x_{ni})}{dt} = L_{n+1}x_{n+1,i} + V_{n-1}y_{n-1,i} - L_n x_{ni} - V_n y_{n,i} \quad 5.12$$

Energy Balance for tray n:

$$0 = L_{n+1}H_{L,n+1} + V_{n-1}H_{V,n-1} - L_n H_{L,n} - V_n H_{V,n} \quad 5.13$$

Material balance on trop tray:

$$\frac{dM_{NT}}{dt} = R_L - L_{NT} + V_{NT-1} - V_{NT} \quad 5.14$$

Component balance on top tray:

$$\frac{d(M_{NT}x_{NT,j})}{dt} = R_L x_{Di} + V_{NT-1}y_{NT-1,i} - L_{NT}x_{NTi} - V_{NT}y_{NTi} \quad 5.15$$

Energy Balance for top tray:

$$0 = R_L H_{L,RL} + V_{NT-1}H_{V,NT-1} - L_{NT}H_{L1,NT} - V_{NT}H_{V,NT} \quad 5.16$$

The initial hold-ups in the reaction still pot were to be calculated as follows:

$$M_B = \frac{M_{VB} \times \rho_{av}}{MW_{av}} \quad 5.17$$

WhereM_{VB}: volumetric hold-up in still pot

ρ_{av}: average weighted density

MW_{av}: average weighted molecular mass

The initial hold-ups on the trays were to be calculated as follows:

$$M_N = \frac{M_{VN} \times \rho_{av,i}}{MW_{av,i}} \quad 5.18$$

The following assumptions were used when determining the vapour-liquid equilibrium (VLE) equations:

Assume ideal gas, $\emptyset_i = 1$

Assume ideal liquid, $\gamma_i = 1$

Therefore the VLE equation is represented as:

$$y_{i,j} P_j = x_{i,j} P_{i,j}^{sat} \quad 5.19$$

And

$$\sum y_{i,j} P_j = \sum x_{ij} P_{i,j}^{sat} \quad 5.20$$

$$\sum y_{i,j} P_j = P_i \sum y_{i,j} = P_j(1) = P_j \quad 5.21$$

Therefore,

$$0 = P_j - \sum x_{i,j} P_{i,j}^{sat} \quad 5.22$$

Using Antoine's equation:

$$lnP_{i,j}^{sat} = A_{i,j} - \frac{B_{i,j}}{T_j + C_{i,j}} \quad 5.23$$

A series reaction was assumed to be taking place through the following reactions:

$$C_6Cl_6 + KF \leftrightarrow C_6FCl_5 + KCl \quad 5.24$$

$$C_6F_5Cl + KF \leftrightarrow C_6F_6 + KCl \quad 5.25$$

$$C_6F_4Cl_2 + KF \leftrightarrow C_6F_5Cl + KCl \quad 5.26$$

$$C_6F_3Cl_3 + KF \leftrightarrow C_6F_4Cl_2 + KCl \quad 5.27$$

$$C_6F_2Cl_4 + KF \leftrightarrow C_6F_3Cl_3 + KCl \quad 5.28$$

$$C_6FCl_5 + KF \leftrightarrow C_6F_2Cl_4 + KCl \quad 5.29$$

The equilibrium constant (Kc) was defined as follows:

$$K_c = \frac{k_i}{k\_i} \quad 5.30$$

k_i and k_i represent the rate constants for the forward and reverse reactions respectively.

K_c Is related to Gibbs Energy:

$$K_c = \text{Exp}\left(\frac{-\Delta G_{r^o}}{RT}\right) \quad 5.31$$

Where,

$$\Delta G_{r^o} = \sum G^o_{products} - \sum G^o_{reactants} \quad 5.32$$

The Joback method could be used to solve the above equation.

The two alkali metal fluorides used in this study were potassium fluoride (KF) and caesium fluoride (CsF). It was found that the yield of hexafluorobenzene (C_6F_6) increased with an increase in KF:C_6Cl_6. The same trend was depicted when using CsF. This supports the hypothesis for a series reaction taking place; as a greater amount of alkali metal fluoride would favour further fluorination of intermediate products to hexafluorobenzene. Additionally, the yields for all the fluorinated products were evaluated against the independent variables mentioned in Section 3.3. It was noted that for low yields of the highly fluorinated products, the less fluorinated product yields were higher. Furthermore, at low temperatures and low masses of alkali metal fluoride it was only possible to fluorinate to a low degree. On the other hand, at higher temperatures and higher masses of alkali metal fluoride, the lower fluorinated aromatics produced better yields of the higher fluorinated aromatics. Conclusively, the experimental results and observations of this study support the hypothesis that a system of series reactions is taking place. Using this as a basis, the following system of reaction rates and constants were devised:

$$r_1 = k_1[C_6Cl_6][KF] - k_{-1}[C_6FCl_5][KCl] \quad 5.33$$

$$r_2 = k_2[C_6F_5Cl][KF] - k_{-2}[C_6F_6][KCl] \quad 5.34$$

$$r_3 = k_3[C_6F_4Cl_2][KF] - k_{-3}[C_6F_5Cl][KCl] \quad 5.35$$

$$r_4 = k_4[C_6F_3Cl_3][KF] - k_{-4}[C_6F_4Cl_2][KCl] \quad 5.36$$

$$r_5 = k_5[C_6F_2Cl_4][KF] - k_{-5}[C_6F_3Cl_3][KCl] \quad 5.37$$

$$r_6 = k_6[C_6FCl_5][KF] - k_{-6}[C_6F_2Cl_4][KCl] \quad 5.38$$

Overall reaction rates:

$$d[C_6Cl_6]dt = -r_1 \quad 5.39$$

$$d[C_6F_6]dt = r_6 \quad 5.40$$

$$d[C_6ClF_5]dt = r_5 - r_6 \quad 5.41$$

$$d[C_6Cl_2F_4]dt = r_4 - r_5 \quad 5.42$$

$$d[C_6Cl_3F_3]dt = r_3 - r_4 \quad 5.43$$

$$d[C_6Cl_4F_2]dt = r_2 - r_3 \quad 5.44$$

$$d[C_6Cl_5F]dt = r_1 - r_2 \quad 5.45$$

$$d[KF]dt = -r_1 - r_2 - r_3 - r_4 - r_5 - r_6 \quad 5.46$$

$$d[KCl]dt = r_1 + r_2 + r_3 + r_4 + r_5 + r_6 \quad 5.47$$

Literature presents limited data regarding the reaction rate constants and phase equilibrium data of the components involved in the reaction. Without this data, a large number of factors and constants are unknown and it is then quite challenging to simulate a rigorous model for this system. Knowledge of this information would improve the accuracy of modelling the reaction kinetics of the system and subsequently verifying the

reaction mechanism taking place. However, in the absence of these kinetic parameters and thermodynamic properties, a simplified model of the system is proposed in the following section.

5.2. SIMPLIFIED MODEL

The following assumptions were made when developing the simplified model:

- Only the forward reaction was considered as the volatile products were removed

- As C_6Cl_6, KF and CsF are all sparingly soluble in sulfolane, it was assumed that all 3 solubility limits were reached at the start of the experiment. Therefore, as the reaction proceeded and these reactants were consumed, more of the un-dissolved reactants took the place of the reacted component in the solution thus keeping the concentration of the aforementioned compounds constant.

As the concentration of C_6Cl_6 and KF were assumed to be constant and the reverse reaction negligible, equation 5.33 reduced to:

$$r_1 = k_1 \quad 5.48$$

Taking into account the assumptions mentioned above, the rate expressions were then redefined as follows:

$$r_2 = k_{-2}[C_6F_6][KCl] \quad 5.49$$

$$r_3 = k_{-3}[C_6F_5Cl][KCl] \quad 5.50$$

$$r_4 = k_{-4}[C_6F_4Cl_2][KCl] \quad 5.51$$

$$r_5 = k_{-5}[C_6F_3Cl_3][KCl] \quad 5.52$$

$$r_6 = k_{-6}[C_6F_2Cl_4][KCl] \quad 5.53$$

The concentration (C_i) can be expressed in terms of moles of species (i) and the reaction liquid volume as follows:

$$C_i = \frac{n_i}{V} \qquad 5.54$$

Due to excess sulfolane, the reaction volume was assumed to be that of the volume of sulfolane used. The DIPPR105 equation was used to determine the volume of sulfolane:

$$\rho = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^D}} \qquad 5.55$$

The values for the constants are as follows:

A = 137.4

B = 0.299035

C = 1062.19

D = 0.5299

Using equation 5.55, the volume of sulfolane was calculated to be 90cm^3.

Therefore, the general expression for the change in moles of species (i) in the reaction still pot over time can be defined as:

$$\frac{dn_i}{dt} = r_i V \left(\frac{n_{i,P}}{n_{i,D}+n_{i,P}}\right) \qquad 5.56$$

Let

$$\left(\frac{n_{i,D}}{n_{i,P}} = Fdist_i\right) \qquad 5.57$$

Therefore

$$\frac{n_{i,P}}{n_{i,D}+n_{i,P}} = \frac{1}{Fdist_i+1} \quad 5.58$$

Therefore, substituting equation 5.58 into equation 5.56 yields the following:

$$\frac{dN_i}{dt} = r_i V\left(\frac{1}{Fdist_i+1}\right) \quad 5.59$$

Hence, the change in moles in the reaction still pot for all components can be represented by equations 5.60 – 5.66 below:

$$\frac{dn_{C6Cl6}}{dt} = -r_1 V \quad 5.60$$

$$\frac{dn_{C6F6}}{dt} = r_6 V\left(\frac{1}{Fdist_{C6F6}+1}\right) \quad 5.61$$

$$\frac{dn_{C6F5Cl}}{dt} = r_5 V - r_6 V\left(\frac{1}{Fdist_{C6F5Cl}+1}\right) \quad 5.62$$

$$\frac{dn_{C6F4Cl2}}{dt} = r_4 V - r_5 V\left(\frac{1}{Fdist_{C6F4Cl2}+1}\right) \quad 5.63$$

$$\frac{dn_{C6F3Cl3}}{dt} = r_3 V - r_4 V\left(\frac{1}{Fdist_{C6F3Cl3}+1}\right) \quad 5.64$$

$$\frac{dn_{C6F2Cl4}}{dt} = r_2 V - r_3 V\left(\frac{1}{Fdist_{C6F2Cl4}+1}\right) \quad 5.65$$

$$\frac{dn_{C6FCl5}}{dt} = r_1 V - r_2 V\left(\frac{1}{Fdist_{C6FCl5}+1}\right) \quad 5.66$$

The rate constant for each reaction can be expressed in terms of the Arrhenius equation:

$$k = A_0 exp\left(\frac{-E}{RT}\right) \quad 5.67$$

However, the most recurrent difficulty related to the use of the Arrhenius equation is the suitable approximation of the pre-exponential factor (A_0) and the activation energy (E) from experimental data. The mathematical arrangement of the Arrhenius equation, relating the exponentiation of the reciprocal of the absolute temperature, presents a high

correlation between the two parameter estimates which consequently makes parameter estimation very challenging, predominantly during numerical minimization of the objective function which weighs the squared difference between the measured and calculated data (Schwaab & Pinto, 2007). With respect to the Arrhenius equation, the range of the independent variable is very large due to the absolute temperature scale, while the measurements are performed over a narrow range.

The usual method to alleviate this problem is to rescale the independent variable so that the temperature is centred about the mean value, T, of the temperatures used in the experiments. This is known as reparameterization which enables convergence of the fitting procedure. For the Arrhenius equation, reparameterization results in the following equation:

$$k = A' exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \qquad 5.68$$

Where the reparameterized pre-exponential factor is described as:

$$A' = A_0 \,\mathrm{Exp}\left(\frac{-E}{RT}\right) \qquad 5.69$$

The model for the system of interest was developed and programmed in MATLAB®. For the model development, initial guesses of the kinetic parameters were passed into a function which implemented constrained optimisation. The MATLAB® function `lsqnonlin` was used to solve the nonlinear data regression problem. The function finds a minimum of the sum of squares of a function. The MATLAB® function `ode15s` (an integration solver) was then used to solve the system of ordinary differential equations which describe the component material balances of the system. Ode15s is an implicit integrator built on numerical differentiation formulas.

Ultimately, the goal of the model was to use the final moles achieved in the experiments to obtain the kinetic parameters using least squares regression. The MATLAB® scripts are attached in Appendix F (F1 and F2) and the results are depicted below.

Tables 5.1 and 5.2 respectively depict the predicted activation energy constants using KF and CsF as the alkali metal fluoride. The results presented indicate that the activation energies and pre-exponential factor for the series reaction involving CsF are in general much lower than that for the KF system. Some reactions appear to have a

near zero activation energy which could be related to their stereochemistry in the series fluorination mechanism (i.e. some of the reactions with very high activation energies may be sterically hindered by the molecular structure of the reactant aromatic and the attacking fluorine atom in solution). The particularly high activation energy for reaction 6 of 605550 $J \cdot mol^{-1}$ when using KF indicates that this specific reaction may not be possible at the lower temperatures.

The residual plots are illustrated in Figures 5.2 – 5.5. As seen, the KF model predicts slightly superior results as opposed to the CsF model and this is most likely due to the non-uniform temperature due to the inefficient mixing encountered with the CsF experiments (as discussed in Section 4.2.5).

Table 5.1: Activation Energy constants and Pre-exponential factors for each reaction using KF as the alkali metal fluoride

Reaction	Activation Energy Constant ($J \cdot mol^{-1}$)	Pre-exponential Factors (s^{-1})
1	54125	296.71
2	125660	5.69×10^{11}
3	187670	5.83×10^{17}
4	22109	0.640
5	5.03×10^{-8}	2.3×10^{-3}
6	605550	3.27×10^{60}

Table 5.2: Activation Energy constants and Pre-exponential factors for each reaction using CsF as the alkali metal fluoride

Reaction	Activation Energy Constant ($J \cdot mol^{-1}$)	Pre-exponential Factors
1	5699.4	1.80×10^{-3}
2	8.18×0^{-9}	1.94×10^{-2}
3	7.49×10^{-9}	1.09×10^{-2}
4	188140	2.39×10^{17}
5	36.425	2.53×10^{-2}
6	20360	0.79

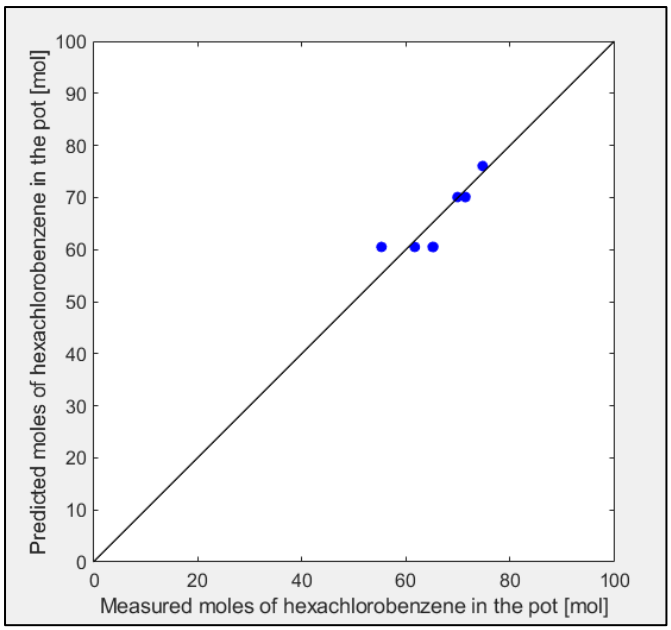


Figure 5.2: Predicted moles of hexachlorobenzene in the reaction still pot versus the measured moles of hexachlorobenzene in the reaction still pot using KF as the fluorinating agent

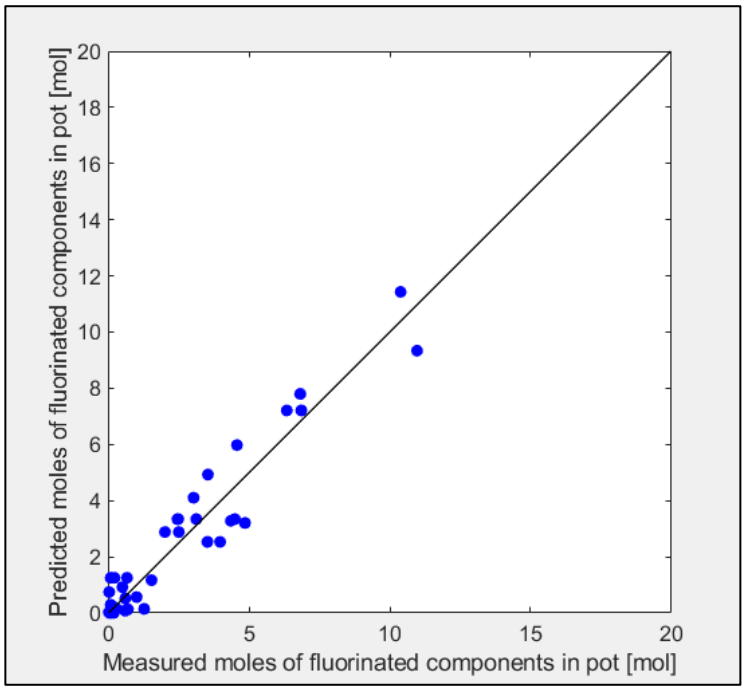


Figure 5.3: Predicted moles of fluorinated products in the reaction still pot versus the measured moles of fluorinated products in the reaction still pot using KF as the fluorinating agent

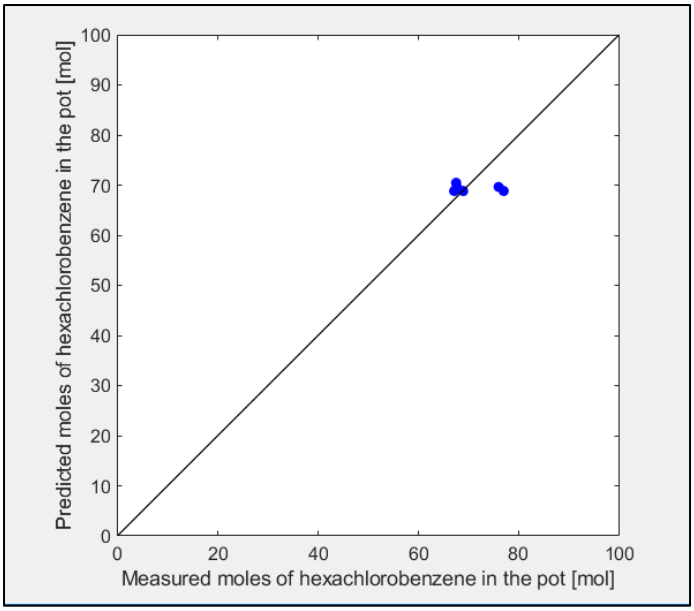


Figure 5.4: Predicted moles of hexachlorobenzene in the reaction still pot versus the measured moles of hexachlorobenzene in the reaction still pot using CsF as the fluorinating agent

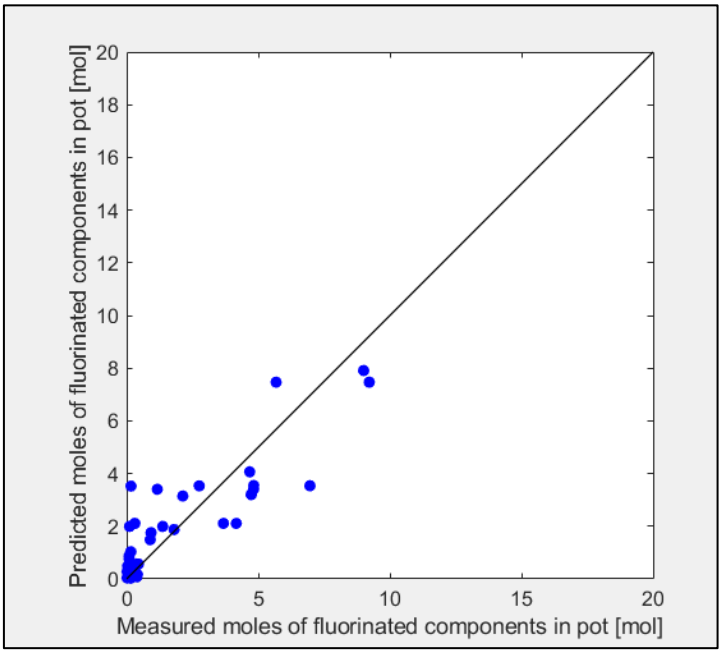


Figure 5.5: Predicted moles of fluorinated products in the reaction still point versus the measured moles of fluorinated products in the reaction still pot using CsF as the fluorinating agent.

6

CHAPTER SIX

6. COMMERCIAL PRODUCTION OF HEXAFLUOROBENZENE

This chapter presents a high level conceptual design of a process based on the presented method for commercial production of hexafluorobenzene. The various advantages of the presented method are first highlighted followed by modification recommendations to improve the yield of hexafluorobenzene. Literature presents inadequate data regarding the reaction rate constants and phase equilibrium data of the components involved in the reaction. Without this data, a large number of factors and constants are unknown and it is then quite challenging to simulate a rigorous model for this system. In the absence of these kinetic parameters and thermodynamic properties, a simplified model of the system was simulated based on the assumptions previously stated under Section 5 to regress for the kinetic parameters. Using these kinetic parameters, a simulation was modelled on MATLAB ® to determine the effect of time on the moles of products and hexachlorobenzene using either KF or CsF as the fluorinating agent. A starting quantity of 83.6 moles (25 kg) of hexachlorobenzene and a temperature of 230 K was used in the simulation. Based on the experimental findings and in the absence of phase equilibrium data, it is concluded that the developed model provides an adequate representation of the system.

When comparing the yield of hexafluorobenzene produced in the current investigation to the yields achieved using alternate methods, it is noted that the current investigation produced a lower yield;

Brooke (1997) produced, on average, a 15% molar yield of hexafluorobenzene through the direct fluorination of C_6Cl_6 followed by dehalogenation with iron filings in a cobalt fluoride reactor. The aforementioned is a two-step process and the use of fluorine gas is

highly toxic and dangerous as fluorine is explosive if it comes into contact with water. (Brooke, et al., 1964)

Fielding (1962) succeeded in producing a 38% yield of hexafluorobenzene by injecting the fluorochlorobenzene $C_6F_4Cl_2$ into a stream of nitrogen at atmospheric pressure which was then passed over a melt. The percentage molar composition of the melt was 20 molar % KF and 80 molar % KBF_4. However, the experiment was carried out a high temperature of 973.15K. Furthermore, the elevated temperature and action of the melt limits the choice of material that can be used to construct the reaction vessel (Fielding, 1962).

Wall and Hellman (1958) carried out the pyrolysis of tribromofluoromethane in order to produce 30% yield of hexafluorobenzene at a temperature of 923.15K and pressure of 20atm. As tribromofluoromethane could not be readily obtained, it was prepared by using stoichiometric amounts of tetrabromomethane and antimony trifluoride in the presence of bromine. Bromine is corrosive to human tissue and its vapours aggravate the eyes and throat. In addition, a complex experimental set-up is required for the pyrolysis (Wall & Hellman, 1960).

As previously mentioned, the chosen experimental procedure offered the following advantages:

(a) It is the only simple, one-stage method for producing highly fluorinated aromatic compounds;

(b) It is possible to regenerate the fluorinating agent (potassium fluoride/caesium fluoride) from the alkali metal fluoride (potassium chloride or caesium chloride) through the use of hydrogen fluoride;

(c) The products are easily separated by distillation; and

(d) The process was conveniently carried out in a simple glass apparatus

In its presented state, the experimental apparatus in this study operating under the chosen process specifications will not yield appreciable yields of hexafluorobenzene when used for commercial production. However, modifications to the process may be effected in an attempt to improve the yield.

The boiling points of the products $C_6F_3Cl_3$, $C_6F_4Cl_2$ and C_6F_5Cl are 196 °C, 156 °C and 115 °C respectively. These temperatures are below/similar the reaction temperatures used in this study. Consequently, as these products are formed, it will immediately leave the reaction mixture. This results in insufficient contact time for further reaction between the abovementioned products and reactants. Simply returning the refluxing fluorochlorobenzenes to the reaction unit will lower the temperature of the latter and will hence impede further fluorination. It is therefore suggested that the hexafluorobenzene be first separated from the remaining compounds followed by preheating of these compounds before being recycled to the main reaction unit. Alternatively, as $C_6F_4Cl_2$ and C_6F_5Cl are both valuable products, these products can too be separated from the mixture along with hexafluorobenzene. Once the hexafluorobenzene has been separated from the product mixture, the remaining partially fluorinated compounds are then to be pre-heated before being recycled to the main distillation pot. Figure 6.1 depicts the simplified process flow diagram of the aforementioned process.

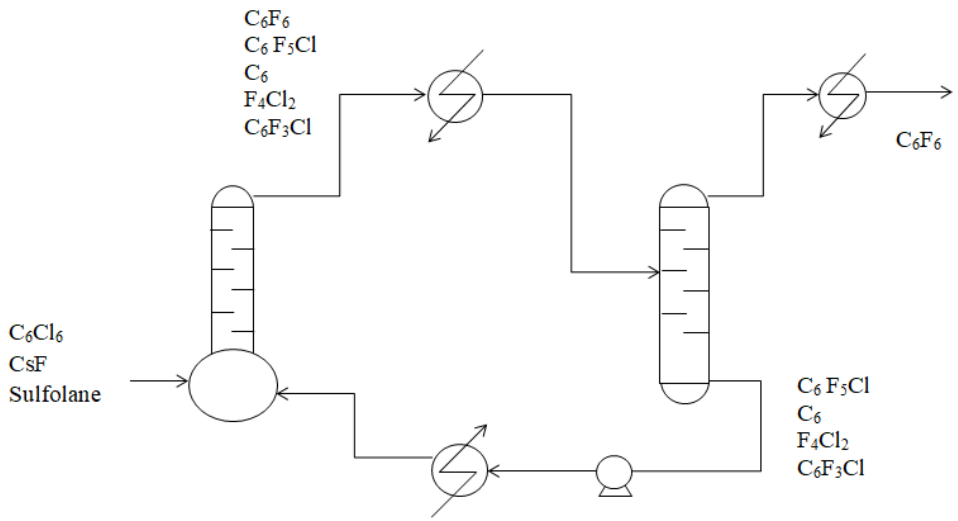


Figure 6.1: Simplified process flow diagram of the recycling of chlorofluorobenzenes

The high cost of running the experiments and toxicity of hexachlorobenzene limited the amount of experiments that could be carried out. Therefore, experiments were prioritized to determine the effect of the major operating variables on the process, particularly the temperature, type of fluorinating agent and ratio of reagents. The effect of time on the yield of products was not considered in this study. Although the factor of

time might not drastically increase the yield of hexafluorobenzene using the presented method (as shown by Fuller (1971) who ran a similar experiment for 18 hours and achieved a similarly low yield of hexafluorobenzene), it might, however, increase the yields of the other fluorinated aromatics which can in-turn be used to produce a higher yield of hexafluorobenzene. This is supported by the results of Fuller (1971) who reacted caesium fluoride with C_6F_5Cl in the presence of sulfolane to produce a molar yield of 78% of C_6F_6.

Using the kinetic parameters regressed for in Chapter 5, a simulation was modelled to determine the effect of time on the moles of products and hexachlorobenzene using either KF or CsF as the fluorinating agent. The MATLAB® scripts are attached in Appendix F (F3 and F4). A starting quantity of 83.6 moles (25 kg) of hexachlorobenzene and a temperature of 230 K was used in the simulation. From Figures 6.2 to 6.5, it is evident that using KF as the fluorinating agent slightly increases the rate of consumption of hexachlorobenzene as opposed to using CsF. Furthermore, the lower fluorinated products (C_6FCl_5, $C_6F_2Cl_4$, $C_6F_3Cl_3$ and $C_6F_4Cl_2$) are produced at a higher rate when KF was used. On the other hand, the higher fluorinated products (C_6F_6 and C_6F_5Cl) are produced at higher rates when using CsF as the fluorinating agent.

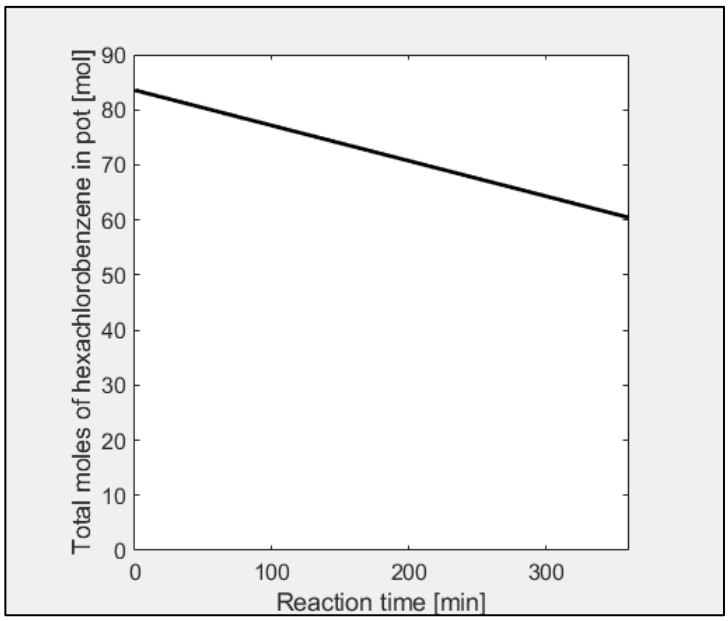


Figure 6.2: Total moles of hexachlorobenzene in reaction still pot versus time using KF as the fluorinating agent

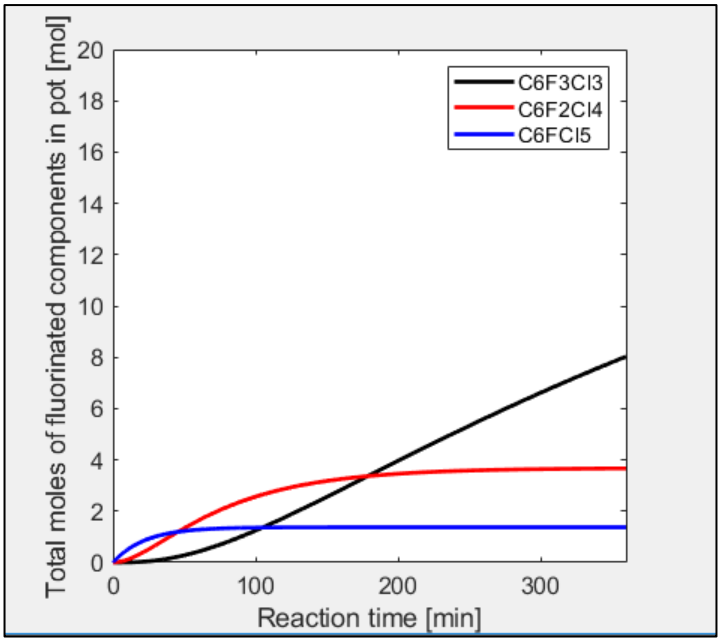


Figure 6.3: Total moles of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 in reaction still pot versus time using KF as the fluorinating agent

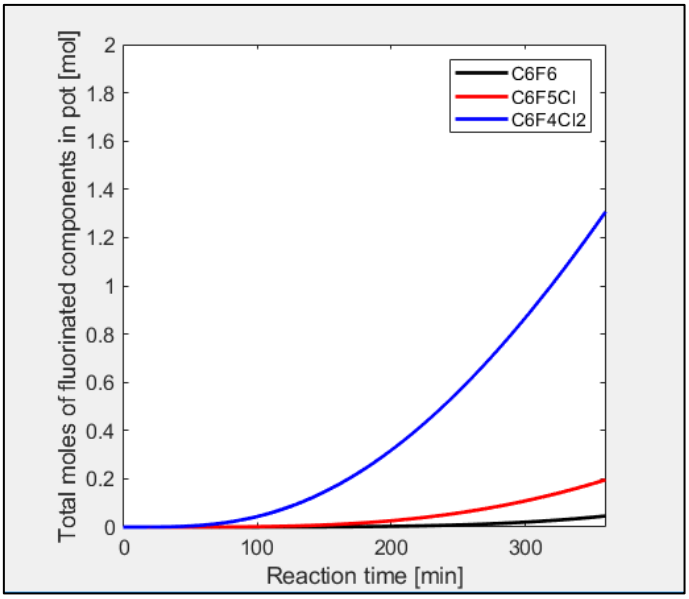


Figure 6.4: Total moles of C_6F_6, C_6F_5Cl and $C_6F_4Cl_2$ in reaction still pot versus time using KF as the fluorinating agent

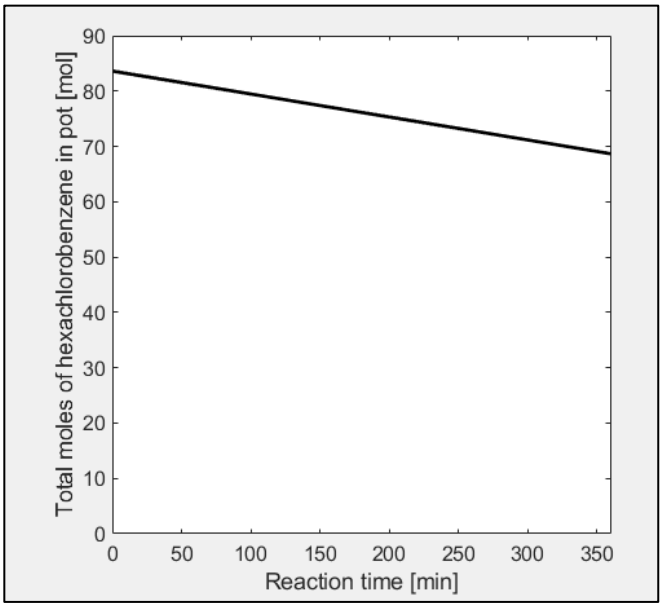


Figure 6.5: Total moles of hexachlorobenzene in reaction still pot versus time using CsF as the fluorinating

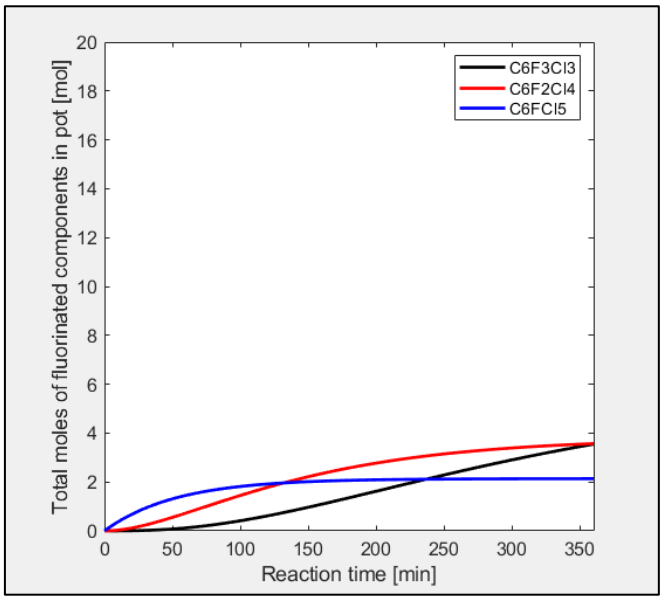


Figure 6.6: Total moles of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 in reaction still pot versus time using CsF as the fluorinating agent

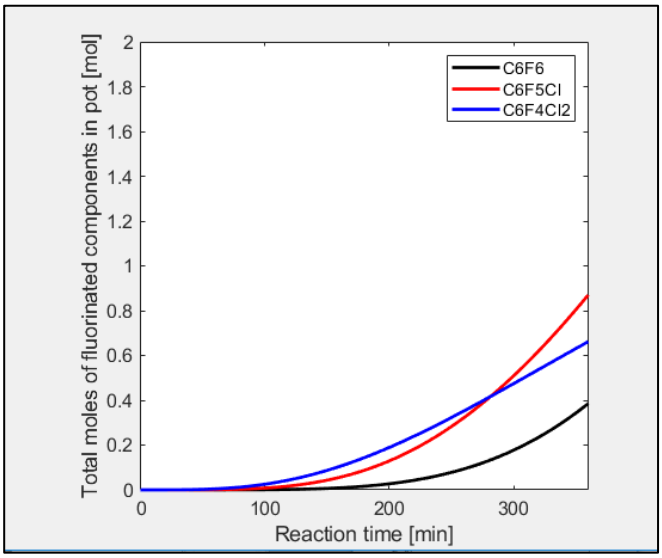


Figure 6.7: Total moles of C_6F_6, C_6F_5Cl and $C_6F_4Cl_2$ in reaction still pot versus time using CsF as the fluorinating agent

An American Company, Albermarle, produces several tons of hexafluorobenzene per year (Furin & Deev, 2006). Using 5 tons per year as a basis, this approximates to 0.57 kg·hour^{-1}. Using the model developed in Chapter 5, a production rate of 0.57 kg·hour^{-1} of hexafluorobenzene will require an unreasonably large quantity of hexachlorobenzene.

Conclusively, the presented experimental method alone will not be able to produce justifying yields of hexafluorobenzene. However, when scaled up, if paired with a suitable separation and recycle system, appreciable yields of hexafluorobenzene could be achieved.

7

CHAPTER SEVEN

7. CONCLUSIONS & RECOMMENDATIONS

7.1. CONCLUSIONS

This study was carried out under the patronage of the Fluorochemical Expansion Initiative which was established to improve the understanding of fluorochemical technology. The objective of this study was to research and develop a method for improving the yield of the perfluorinated aromatic compound, hexafluorobenzene (C_6F_6) which is a product within the fluorspar beneficiation value chain that has utility in the engineering and pharmaceutical field. The study additionally included the generation of performance data in order to develop a high level conceptual design of a commercial process. Part of the study included validating the experimental apparatus by conducting previously carried out experiments and ensuring replication of results..

7.1.1. VALIDATION EXPERIMENT: PRODUCTION OF BIODIESEL

Validation of the equipment was attained by carrying out the esterification reaction of methanol and oleic acid to produce methyl oleate (biodiesel) and then, comparing the percentage conversion of oleic acid results to those obtained by Nakkash and Al-Karkhi (2013). For all experiments carried out, the experimental runs followed the same trends as depicted by Nakkash and Al-Karkhi (2013). However, the conversion was slightly lower than that presented by Nakkash and Al-Karkhi (2013). This was due to the loss of heat during the reaction which was owed to the lack of insulation. This problem was alleviated by the use of insulation and heating tape and resulted in an increase in conversion of oleic acid. Therefore, it was concluded that the batch reactive distillation

unit operated adequately, within experimental error, and could therefore be used to conduct the experiments for the main hexafluorobenzene system.

7.1.2. MAIN EXPERIMENT: SYNTHESIS OF HEXAFLUOROBENZENE THROUGH BATCH REACTIVE DISTILLATION

Once the experimental apparatus was validated, the experiments for the hexafluorobenzene system were carried out. The experiments of Fuller (1971) and Furin (2007) were used as the basis for the experimental procedure conducted. Sulfolane and the alkali metal fluoride were dried before being introduced into a round bottom flask together with hexachlorobenzene. The mixture was then continuously stirred for a period of 8 hours. Samples were then analysed using gas chromatography. This investigation only considered the effects of temperature and the type and mass of alkali metal fluoride used. Reaction time was kept constant for all experiments. The effects of the aforementioned variables on the yield of hexafluorobenzene were determined.

The two alkali metal fluorides used in this study were potassium fluoride (KF) and caesium fluoride (CsF). It was found that the yield of hexafluorobenzene (C_6F_6) increased with an increase in KF:C_6Cl_6. The same trend was depicted when using CsF. This supports the hypothesis for a series reaction taking place; as a greater amount of alkali metal fluoride would favour further fluorination of intermediate products to hexafluorobenzene. When comparing KF and CsF as a fluorinating agent, it was noted that CsF more than doubled the molar yield of C_6F_6 from 0.27% to 0.59%. This was largely due to the higher activity and solubility of CsF. The more soluble the alkali metal fluoride, the easier the fluoride anion becomes unpaired with the cation and subsequently the reactivity of the fluoride ion increases thus producing a higher yield of products (Henson, 1975). The results also showed that the surface area of the alkali metal fluoride affects the product yield. The finely crushed CsF produced a higher yield of C_6F_6 as opposed to the larger clumps of KF. Ultimately, it was concluded that CsF was a better fluorinating agent than KF for the synthesis of hexafluorobenzene via batch reactive distillation.

In terms of temperature, it was found that the highest yield of C_6F_6 was produced at the highest temperature of 503.15 K. However, this increase in yield is very minimal. A plausible explanation for this occurrence could be due to the high activation energies

(favoured at higher temperatures) of the fluorination reactions which produce hexafluorobenzene. If higher temperatures were used, solvent degradation would occur.

Conclusively, for this experimental method, it can be noted that when hexachlorobenzene is reacted with CsF, both dissolved in sulfolane, better yields of C_6F_6 are produced as compared to when KF is used as the alkali metal fluoride. The temperature of the system does not heavily affect the yield of C_6F_6, however a temperature between 483.15 and 503.15 K is recommended as higher temperatures would result in solvent degradation whilst at lower temperatures, the reaction would take place at an exceedingly slow rate resulting in low yields of hexafluorobenzene (Maynard & Hundred, 1966) .

Additionally, it was observed that as molar ratio of KF: C_6Cl_6 increased the molar conversion percentage of C_6Cl_6 similarly increased. Once again, this increase is explained by the shift in equilibrium which was caused by the excess KF which favoured the forward reaction. On the other hand, the conversion of C_6Cl_6 decreased with an increasing molar ratio of CsF: C_6Cl_6 which suggested that a solubility limit of CsF in sulfolane had most likely been reached. Therefore, as the molar ratio of CsF: C_6Cl_6 increased, the amount of un-dissolved CsF also increased. This increased amount of un-dissolved CsF hindered adequate agitation resulting in a lower amount of CsF being able to take part in the reaction and hence causing a lower conversion of hexachlorobenzene.

When hexachlorobenzene was reacted with an alkali metal fluoride, both submersed in a solvent, six fluorinated aromatics were produced including C_6Cl_5F, $C_6Cl_4F_2$, $C_6Cl_3F_3$, $C_6Cl_2F_4$, C_6ClF_5 and C_6F_6. It was concluded that a change in amount of KF did not significantly affect the selectivity products as similar molar selectivity's of products were achieved for varied amounts of KF. The selectivity for the same products was determined for the varied amounts of CsF. The results illustrated that there was an increase in molar selectivity's of the higher fluorinated compounds as the molar amount of CsF increased.

The selectivity's of products with varying temperature using KF and CsF as the alkali-metal fluoride was additionally determined. It was conclude that the temperature had a larger impact on the selectivity's of the products as compared to varying the molar amount of alkali metal fluoride. When temperature was increased, it was noted that the higher fluorinated species increased in molar selectivity. The opposite was observed for

the low fluorinated species. These results indicate that for low molar selectivity's of the highly fluorinated products, the less fluorinated product molar selectivity's are better.

Literature presents limited data regarding the reaction rate constants and phase equilibrium data of the components involved in the reaction. Therefore, a simplified model of the system was developed to determine the kinetic parameters of the hexafluorobenzene system using either KF or CsF as the fluorinating agent. The KF model predicted superior results when compared to the CsF model and this is most likely due to the non-uniform temperature due to the low degree of mixing encountered with the CsF experiments. Using the regressed kinetic parameters, a simulation was modelled to determine the effect of time on the moles of products and hexachlorobenzene using either KF or CsF as the fluorinating agent. The results proved that using KF as the fluorinating agent increases the rate of consumption of hexachlorobenzene as opposed to using CsF. Additionally, the lower fluorinated products are produced at a higher rate when KF is used. Contrariwise, the higher fluorinated products are produced at higher rates when using CsF as the fluorinating agent.

Using the model developed, practical production rates of hexafluorobenzene will require an inordinate quantity of hexachlorobenzene. Conclusively, the presented experimental method alone will not be able to produce qualifying yields of hexafluorobenzene. However, if paired with an appropriate separation and recycle system, substantial yields of hexafluorobenzene could be achieved.

7.2. RECOMMENDATIONS

The heating system used in this study was a MRC MNS-500 Laboratory Heating Mantle whereby temperature was monitored via a PHTC1/G Thermocouple and manually controlled. To improve heating accuracy and control, it is recommended that a digital heating mantle be used, such as the Jisico GLHMD Laboratory Heating Mantle.

Pure samples of $C_6Cl_4F_2$, $C_6Cl_3F_3$, $C_6Cl_4F_2$ and C_6Cl_5F could not be obtained and therefore calibrations for the aforementioned compounds were carried out using the effective carbon number method. Calibration accuracies would be improved if pure samples were obtained and samples were calibrated using the internal standard method.

The experimental results and observations of this study support the hypothesis that a system of series reactions is taking place. Knowledge of kinetic data would improve the accuracy of modelling the reaction kinetics of the system and verifying the reaction mechanism taking place.

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APPENDICES

APPENDIX A: GAS CHROMATOGRAPHY CALIBRATION PLOTS

A Validation Experiment

Table A.3: Raw oleic acid (OA) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard.

Sample mass ratio $\left(\frac{M_{OA}}{M_{IS}}\right)$	Observed area ratios $\left(\frac{A_{OA}}{A_{IS}}\right)$				
	Run 1	Run 2	Run 3	Run 4	Run 5
0.031	0.028	0.017	0.019	0.016	0.032
0.061	0.047	0.047	0.035	0.048	0.045
0.092	0.070	0.086	0.084	0.080	0.081
0.123	0.027	0.122	0.090	0.098	0.062

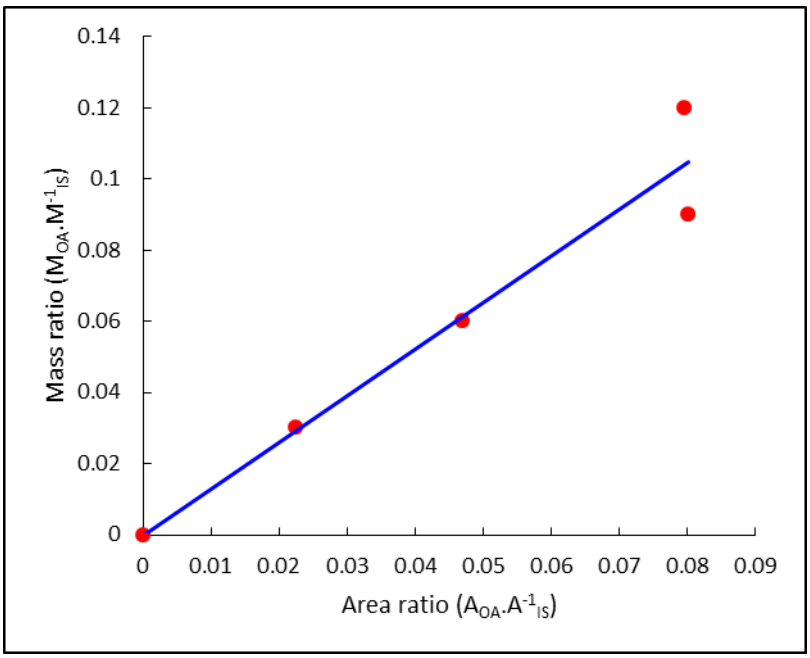

Figure A.2: Oleic acid gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = 1.3088x$

B Main Experiment

Table A.4: Raw hexafluorobenzene (C_6F_6) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard.

Sample mass ratio $\left(\frac{M_{C6f6}}{M_{IS}}\right)$	Observed area ratios $\left(\frac{A_{C6F6}}{A_{IS}}\right)$				
	Run 1	Run 2	Run 3	Run 3	Run 5
0.007	0.007	0.007	0.006	0.007	0.007
0.013	0.011	0.011	0.011	0.011	0.011
0.020	0.015	0.015	0.015	0.015	0.015
0.026	0.019	0.019	0.017	0.017	0.016
0.007	0.007	0.007	0.006	0.007	0.007

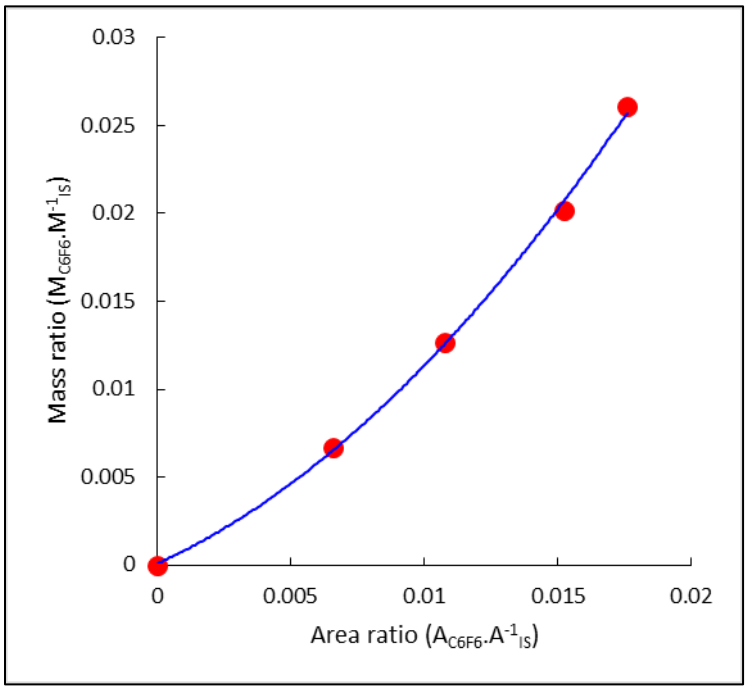

Figure A.2: Hexafluorobenzene gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = 43.41x^2 + 0.70x + 8 \times 10^{-5}$

Table A.3: Raw pentafluorochlorobenzene (C_6F_5Cl) gas chromatograph calibration data for the internal standard (IS) quantification method. *N*-Butanol was used as the internal standard.

Sample mass ratio $\left(\frac{M_{C6F5Cl}}{M_{IS}}\right)$	Observed area ratios $\left(\frac{A_{C6F5Cl}}{A_{IS}}\right)$				
	Run 1	Run 2	Run 3	Run 3	Run 5
0.007	0.007	0.007	0.006	0.007	0.007
0.013	0.011	0.011	0.011	0.011	0.011
0.020	0.015	0.015	0.015	0.015	0.015
0.026	0.019	0.019	0.017	0.017	0.016
0.007	0.007	0.007	0.006	0.007	0.007

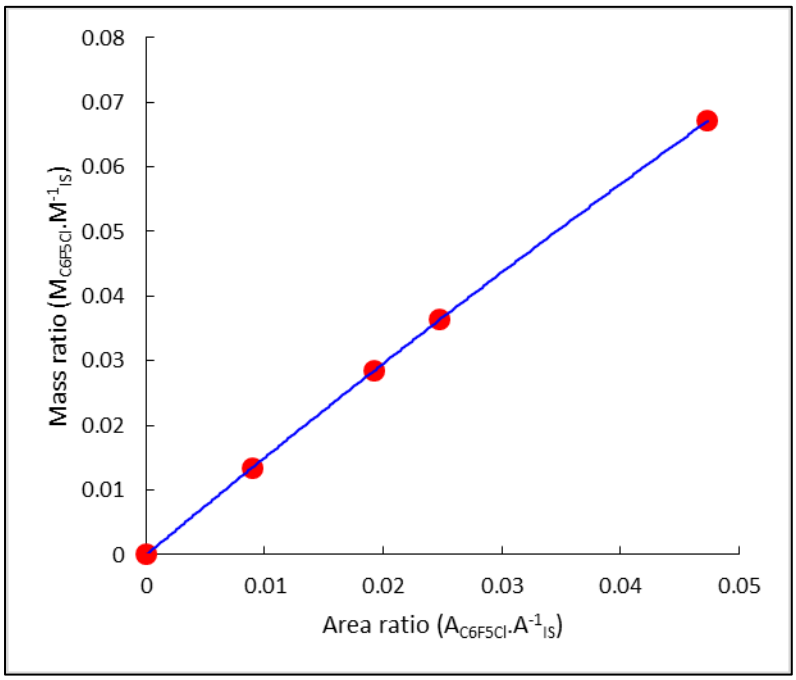

Figure A.3: Pentafluorochlorobenzene gas chromatograph calibration plot for the internal standard quantification (IS) method on a Shimadzu 2010 GC using a Restek® capillary column (30 m × 0.25 mm) coated with in a 0.25μm layer of polyethylene glycol with helium as the carrier gas. Calibration equation was $y = -2.31x^2 + 1.53x + 5 \times 10^{-5}$

As no pure samples could be obtained for $C_6F_4Cl_2$, $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5, the above mentioned calibration method could not be utilized to carry out the calibrations. Therefore the Effective Carbon Number method was used to quantify these products as outlined in Appendix C.

APPENDIX B: RAW DATA

A. Preliminary experiment

Table B.3: Gas-chromatograph raw data for the validation experiment on the production of biodiesel based on the conversion of oleic acid (OA).

Peak	Exp.	Butanol	Oleic Acid
Retention time (min)	1	5.28	20.103
Area		27428210.3	2042308.6
Retention time (min)	2	5.392	20.095
Area		48304494.7	1226769.2
Retention time (min)	3	5.266	20.875
Area		36743015.7	366942.1
Retention time (min)	4	5.298	20.083
Area		32987088.5	1652137
Retention time (min)	5	5.2	19.862
Area		35667033.4	1414793.6
Retention time (min)	6	5.153	20.309
Area		16624674.8	125914.4
Retention time (min)	1-Rerun	5.161	20.593
Area		28922376.9	202510.6

Table B.4: Extended results for the preliminary experiments on the production of biodiesel based on the conversion of oleic acid.

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	OA mass in sample(g)	OA mass fraction in sample	Total mass of flask product (g)	Mass OA in flask product (g)	Initial Mass of OA (g)	Conversion of OA (%)
1	0.425	0.582	0.057	0.134	119.041	15.952	41.325	61.573
2	0.261	0.801	0.027	0.103	109.666	11.296	41.325	72.971
3	0.193	0.657	0.009	0.047	128.417	6.036	41.325	86.183
4	0.423	0.795	0.052	0.123	103.621	12.745	41.325	69.087
5	0.391	0.933	0.048	0.123	84.871	10.439	41.325	74.543
6	0.202	0.631	0.006	0.030	109.666	3.290	41.325	91.773
1-Rerun	0.307	0.933	0.030	0.098	120.097	11.629	41.325	71.861

B. Main experiment

Table B.3: Gas-chromatograph raw data for the main experiment on the synthesis of hexafluorobenzene and other fluorinated products in the reboiler flask

Peak	Exp.	Butanol	C_6F_6	C_6F_5Cl	$C_6F_4Cl_2$	$C_6F_3Cl_3$	$C_6F_2Cl_4$	C_6FCl_5
Retention time (min)	1	9.184	1.96	3.591	9.335	13.481	19.312	22.717
Area		18680806.2	1653	12782.2	280699.5	1018024.5	297449.2	96164.2
Retention time (min)	2	9.123	1.945	3.625	9.246	13.169	19.266	22.66
Area		30307649.6	3459.4	21387.5	135448.1	620529.5	408214.1	20802.4
Retention time (min)	3	9.24	1.964	3.941	9.374	13.169	19.26	22.657
Area		28476470.6	6513.5	27248.6	408759.8	708126	397564.3	11357.5
Retention time (min)	4	9.292	1.906	3.560	9.412	13.495	19.308	22.723
Area		36560345.3	3324.2	15917	65346.9	952313.6	477753.9	26844.4
Retention time (min)	5	9.269	2.001	3.94	9.4	13.156	19.292	22.728
Area		32816057.7	1567.8	19350.6	6224.2	171112.9	685398.1	442115.8
Retention time (min)	6	9.284	2.285	3.947	10.407	13.158	19.276	22.727
Area		35347257.1	1043.1	16011.6	4594.8	173717.9	373092.7	393270.3
Retention time (min)	7	9.078	2.196	3.853	9.816	13.086	19.287	22.729
Area		40069029.7	3273.1	3304.1	1198.8	176176.8	7544.5	17660.8
Retention time (min)	8	9.232	1.832	4.058	9.37	13.158	19.311	22.744
Area		26012385.2	981.2	9073	1308.2	221623.5	935354.4	794468.1
Retention time (min)	9	8.878	1.922	3.991	10.082	13.028	19.277	22.732
Area		33899029.9	1000.8	6738.7	1432	207563.3	804792.4	545253.6
Retention time (min)	10	9.275	1.878	4.059	9.404	13.165	19.321	22.745
Area		33788971.7	454.5	7601.8	1597.9	232077	781213.9	552102.4
Retention time (min)	11	8.27	2.015	3.851	8.35	12.976	19.27	22.717
Area		32577400.4	1994.9	10596.1	1008.4	665750.4	429047.7	199546.4
Retention time (min)	12	8.071	1.880	3.806	8.168	12.943	19.244	22.715
Area		26015797.1	4073.4	9638.9	1970.4	436221.3	109529.6	12876.5
Retention time (min)	13	9.247	2.005	4.059	9.384	13.178	19.292	22.716
Area		27775047.4	2818.9	8500.7	1080.3	725782.6	465448.1	161601.2

Table B.4: Gas-chromatograph raw data for the main experiment on the synthesis of hexafluorobenzene and other fluorinated products in the distillate

Peak	Exp.	Butanol	C_6F_6	C_6F_5Cl	$C_6F_4Cl_2$	$C_6F_3Cl_3$	$C_6F_2Cl_4$	C_6FCl_5
Retention time (min)	1	8.086	2.127	3.730	8.182	13.177	19.26	22.713
Area		27646989.7	11305.9	10754.7	16984.1	825815.8	280595.2	68574.9
Retention time (min)	2	9.255	1.808	3.642	9.465	13.677	19.308	22.723
Area		28533492.1	680.4	80403.4	5815030.8	18127787.5	980703.5	21190.3
Retention time (min)	3	9.294	1.956	4.071	10.003	13.337	19.295	22.723
Area		34475627.5	10960	52942.2	3180.3	12693828.1	746465.1	21229.1
Retention time (min)	4	9.275	1.91	3.768	9.518	13.377	19.308	22.734
Area		30368124.3	115996.1	333319.1	7650644.6	9769048.4	477753.9	12319.8
Retention time (min)	5	8.325	1.911	4.034	9.256	13.06	19.373	22.742
Area		39319493.9	63703.6	34142.1	6332.7	4615117.5	2991087.7	642876.6
Retention time (min)	6	9.33	2.196	4.086	10.416	13.249	19.365	22.741
Area		43416670	21663.7	22567.9	814.3	4488797.2	2366484.1	685693.4
Retention time (min)	7	9.358	2.001	4.103	9.464	13.172	19.268	22.723
Area		45436075.2	167757.7	703932.2	1146338.5	539836.1	202868.3	13407.3

Table B.5: Extended results for the main experiments on the yield of hexafluorobenzene (C_6F_6) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	C_6F_6 mass in sample(g)	C_6F_6 mass fraction in sample	Total mass of flask product (g)	Mass C_6F_6 in flask product (g)
1	0.623	0.896	8.837×10^{-5}	9.863×10^{-5}	142.996	1.410×10^{-2}
2	0.721	0.806	1.054×10^{-4}	1.307×10^{-4}	156.886	2.051×10^{-2}
3	0.57	0.697	1.375×10^{-4}	1.973×10^{-4}	174.863	3.450×10^{-2}
4	0.624	0.752	1.090×10^{-4}	1.446×10^{-4}	178.965	2.588×10^{-2}
5	0.858	0.769	9.722×10^{-5}	1.264×10^{-4}	191.182	2.417×10^{-2}
6	0.868	0.698	8.727×10^{-5}	1.251×10^{-4}	275.060	3.441×10^{-2}
7	1.046	0.519	1.433×10^{-4}	2.764×10^{-4}	235.160	6.500×10^{-2}
8	0.648	1.262	6.880×10^{-5}	5.451×10^{-5}	151.069	8.234×10^{-3}
9	0.893	0.795	8.981×10^{-5}	1.130×10^{-4}	151.965	1.717×10^{-2}
10	0.969	0.776	8.659×10^{-5}	1.115×10^{-4}	152.652	1.702×10^{-2}
11	0.908	0.786	1.114×10^{-4}	1.418×10^{-4}	198.986	2.821×10^{-2}
12	0.768	0.865	1.458×10^{-4}	$1.686E\times10^{-4}$	199.011	3.355×10^{-2}
13	0.816	0.883	1.232×10^{-4}	1.394×10^{-4}	199.326	2.779×10^{-2}

Table B.6: Extended results for the main experiments on the yield of hexafluorobenzene (C_6F_6) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	C_6F_6 mass in sample(g)	C_6F_6 mass fraction in sample	Total mass of flask product (g)	Mass C_6F_6 in flask product (g)
1	0.611	0.618	2.27×10^{-4}	3.67×10^{-4}	9.032	3.318×10^{-3}
2	0.528	0.941	1.54×10^{-4}	1.64×10^{-4}	10.101	1.655×10^{-3}
3	0.730	0.668	2.23×10^{-4}	3.34×10^{-4}	7.122	2.377×10^{-3}
4	0.677	0.705	2.28×10^{-3}	3.24×10^{-3}	8.021	2.595×10^{-2}
5	0.500	0.555	6.60×10^{-4}	1.19×10^{-3}	7.590	9.027×10^{-3}
6	2.622	0.875	2.48×10^{-4}	2.84×10^{-4}	0.855	2.428×10^{-4}
7	1.086	0.255	3.52×10^{-3}	1.38×10^{-2}	1.924	2.652×10^{-2}

Table B.7: Extended results for the main experiments on the yield of chloropentafluorobenzene (C_6F_5Cl) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	C_6F_5Cl mass in sample(g)	C_6F_5Cl mass fraction in sample	Total mass of flask product (g)	Mass C_6F_5Cl in flask product (g)
1	0.623	0.896	6.192×10^{-4}	6.910×10^{-4}	142.996	0.099
2	0.721	0.806	6.075×10^{-4}	7.537×10^{-4}	156.886	0.118
3	0.57	0.697	8.032×10^{-4}	1.152×10^{-3}	174.863	0.202
4	0.624	0.752	5.820×10^{-4}	7.740×10^{-4}	178.965	0.139
5	0.858	0.769	7.290×10^{-4}	9.480×10^{-4}	191.182	0.181
6	0.868	0.698	5.566×10^{-4}	7.979×10^{-4}	275.060	0.221
7	1.046	0.519	7.939×10^{-5}	1.531×10^{-4}	235.160	0.036
8	0.648	1.262	3.116×10^{-4}	2.469×10^{-4}	151.069	0.037
9	0.893	0.795	2.264×10^{-4}	2.849×10^{-4}	151.965	0.043
10	0.969	0.776	2.844×10^{-4}	3.662×10^{-4}	152.652	0.056
11	0.908	0.786	3.090×10^{-4}	3.933×10^{-4}	198.986	0.078
12	0.768	0.865	3.959×10^{-4}	4.577×10^{-4}	199.011	0.091
13	0.816	0.883	3.402×10^{-4}	3.851×10^{-4}	199.326	0.077

Table B.8: Extended results for the main experiments on the yield of chloropentafluorobenzene (C_6F_5Cl) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	C_6F_5Cl mass in sample(g)	C_6F_5Cl mass fraction in sample	Total mass of flask product (g)	Mass C_6F_5Cl in flask product (g)
1	0.611	0.618	3.322×10^{-4}	5.375×10^{-4}	9.032	4.855×10^{-3}
2	0.528	0.941	2.236×10^{-3}	2.376×10^{-3}	10.101	2.400×10^{-2}
3	0.730	0.668	1.671×10^{-3}	2.502×10^{-3}	7.122	1.782×10^{-2}
4	0.677	0.705	1.113×10^{-2}	1.578×10^{-2}	8.021	1.266×10^{-1}
5	0.500	0.555	6.371×10^{-4}	1.148×10^{-3}	7.590	8.713×10^{-3}
6	2.622	0.875	1.221×10^{-3}	1.395×10^{-3}	0.855	1.193×10^{-3}
7	1.086	0.255	2.503×10^{-2}	9.815×10^{-2}	1.924	1.888×10^{-1}

Table B.9: Extended results for the main experiments on the yield of dichlorotetrafluorobenzene ($C_6F_4Cl_2$) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	$C_6F_4Cl_2$ mass in sample(g)	$C_6F_4Cl_2$ mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_4Cl_2$ in flask product (g)
1	0.623	0.896	4.844×10^{-3}	5.406×10^{-3}	142.996	7.730×10^{-1}
2	0.721	0.806	6.668×10^{-4}	8.273×10^{-4}	156.886	1.298×10^{-1}
3	0.570	0.697	4.233×10^{-3}	6.074×10^{-3}	174.863	1.062
4	0.624	0.752	1.404×10^{-3}	1.866×10^{-3}	178.965	3.340×10^{-1}
5	0.858	0.769	8.420×10^{-5}	1.095×10^{-4}	191.182	2.093×10^{-2}
6	0.868	0.698	5.837×10^{-5}	8.369×10^{-5}	277.000	2.318×10^{-2}
7	1.046	0.519	1.619×10^{-5}	3.122×10^{-5}	235.160	7.341×10^{-3}
8	0.648	1.262	1.682×10^{-5}	1.332×10^{-5}	151.069	2.013×10^{-3}
9	0.893	0.795	1.952×10^{-5}	2.456×10^{-5}	151.965	3.733×10^{-3}
10	0.969	0.776	2.371×10^{-5}	3.054×10^{-5}	151.965	4.641×10^{-3}
11	0.908	0.786	1.454×10^{-5}	1.850×10^{-5}	198.986	3.681×10^{-3}
12	0.768	0.865	3.010×10^{-5}	3.479×10^{-5}	199.011	6.924×10^{-3}
13	0.816	0.883	1.641×10^{-5}	1.858×10^{-5}	199.326	3.703×10^{-3}

Table B.10: Extended results for the main experiments on the yield of dichlorotetrafluorobenzene ($C_6F_4Cl_2$) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	$C_6F_4Cl_2$ mass in sample(g)	$C_6F_4Cl_2$mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_4Cl_2$ in flask product (g)
1	0.611	0.618	1.942×10^{-4}	3.143×10^{-4}	9.032	2.838×10^{-3}
2	0.528	0.941	5.568×10^{-2}	5.917×10^{-2}	10.101	5.976×10^{-1}
3	0.730	0.668	3.484×10^{-5}	5.216×10^{-5}	7.122	3.715×10^{-4}
4	0.677	0.705	8.825×10^{-2}	1.252E-01	8.021	1.004
5	0.500	0.555	4.167×10^{-5}	7.508×10^{-5}	7.590	5.698×10^{-4}
6	2.622	0.875	2.545×10^{-5}	2.908×10^{-5}	0.855	2.486×10^{-5}
7	1.086	0.255	1.417×10^{-2}	5.557×10^{-2}	1.924	1.069×10^{-1}

Table B.11: Extended results for the main experiments on the yield of trichlorotrifluorobenzene ($C_6F_3Cl_3$) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	$C_6F_3Cl_3$ mass in sample(g)	$C_6F_3Cl_3$ mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_3Cl_3$ in flask product (g)
1	0.623	0.896	1.532×10^{-2}	1.710×10^{-2}	142.996	2.445
2	0.721	0.806	5.522×10^{-3}	6.851×10^{-3}	156.886	1.075
3	0.570	0.697	6.396×10^{-3}	9.176×10^{-3}	174.863	1.605
4	0.624	0.752	1.085×10^{-2}	1.443×10^{-2}	178.965	2.582
5	0.858	0.769	2.019×10^{-3}	2.625×10^{-3}	191.182	0.502
6	0.868	0.698	1.925×10^{-3}	2.759×10^{-3}	277.000	0.764
7	1.046	0.519	2.075×10^{-3}	4.001×10^{-3}	235.160	0.941
8	0.648	1.262	2.484×10^{-3}	1.968×10^{-3}	151.069	0.297
9	0.893	0.795	2.467×10^{-3}	3.105×10^{-3}	151.965	0.472
10	0.969	0.776	3.003×10^{-3}	3.868×10^{-3}	151.965	0.588
11	0.908	0.786	8.369×10^{-3}	1.065×10^{-2}	198.986	2.119
12	0.768	0.865	5.811×10^{-3}	6.717×10^{-3}	199.011	1.337
13	0.816	0.883	9.617×10^{-3}	1.089×10^{-2}	199.326	2.170

Table B.12: Extended results for the main experiments on the yield of trichlorotrifluorobenzene ($C_6F_3Cl_3$) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	$C_6F_3Cl_3$ mass in sample(g)	$C_6F_3Cl_3$ mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_3Cl_3$ in flask product (g)
1	0.611	0.618	0.008	0.013	9.032	0.120
2	0.528	0.941	0.151	0.161	10.101	1.625
3	0.730	0.668	0.121	0.182	7.122	1.293
4	0.677	0.705	0.098	0.139	8.021	1.118
5	0.500	0.555	0.026	0.048	7.590	0.362
6	2.622	0.875	0.122	0.140	0.855	0.120
7	1.086	0.255	0.006	0.023	1.924	0.044

Table B.13: Extended results for the main experiments on the yield of tetrachlorodifluorobenzene ($C_6F_2Cl_4$) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	$C_6F_2Cl_4$ mass in sample(g)	$C_6F_2Cl_4$ mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_2Cl_4$ in flask product (g)
1	0.623	0.896	3.905×10^{-3}	4.359×10^{-3}	142.996	0.623
2	0.721	0.806	3.169×10^{-3}	3.932×10^{-3}	156.886	0.617
3	0.570	0.697	3.133×10^{-3}	4.495×10^{-3}	174.863	0.786
4	0.624	0.752	4.750×10^{-3}	6.316×10^{-3}	178.965	1.130
5	0.858	0.769	7.055×10^{-3}	9.174×10^{-3}	191.182	1.754
6	0.868	0.698	3.606×10^{-3}	5.171×10^{-3}	277.000	1.432
7	1.046	0.519	7.752×10^{-5}	1.495×10^{-4}	235.160	0.035
8	0.648	1.262	9.148×10^{-3}	7.248×10^{-3}	151.069	1.095
9	0.893	0.795	8.347×10^{-3}	1.050×10^{-2}	151.965	1.596
10	0.969	0.776	8.820×10^{-3}	1.136×10^{-2}	151.965	1.726
11	0.908	0.786	4.706×10^{-3}	5.989×10^{-3}	198.986	1.192
12	0.768	0.865	1.273×10^{-3}	1.472×10^{-3}	199.011	0.293
13	0.816	0.883	5.381×10^{-3}	6.091×10^{-3}	199.326	1.214

Table B.14: Extended results for the main experiments on the yield of tetrachlorodifluorobenzene ($C_6F_2Cl_4$) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	$C_6F_2Cl_4$ mass in sample(g)	$C_6F_2Cl_4$ mass fraction in sample	Total mass of flask product (g)	Mass $C_6F_2Cl_4$ in flask product (g)
1	0.611	0.618	2.44×10^{-3}	3.95×10^{-3}	9.032	0.035
2	0.528	0.941	7.14×10^{-3}	7.59×10^{-3}	10.101	0.077
3	0.73	0.668	6.22×10^{-3}	9.32×10^{-3}	7.122	0.066
4	0.677	0.705	3.94×10^{-3}	5.58×10^{-3}	8.021	0.045
5	0.5	0.555	1.50×10^{-2}	2.70×10^{-2}	7.59	0.204
6	2.622	0.875	5.63×10^{-2}	6.43×10^{-2}	0.855	0.055
7	1.086	0.255	1.91×10^{-3}	7.48×10^{-3}	1.924	0.014

Table B.15: Extended results for the main experiments on the yield of pentachlorofluorobenzene (C_6FCl_5) in the reboiler flask

Exp. No.	IS mass in sample (g)	Product mass in sample (g)	C_6FCl_5 mass in sample(g)	C_6FCl_5 mass fraction in sample	Total mass of flask product (g)	Mass C_6FCl_5 in flask product (g)
1	0.623	0.896	1.101×10^{-3}	1.228×10^{-3}	142.996	0.176
2	0.721	0.806	1.408×10^{-4}	1.747×10^{-4}	156.886	0.027
3	0.570	0.697	7.802×10^{-5}	1.119×10^{-4}	174.863	0.020
4	0.624	0.752	2.327×10^{-4}	3.094×10^{-4}	178.965	0.055
5	0.858	0.769	3.967×10^{-3}	5.159×10^{-3}	191.182	0.986
6	0.868	0.698	3.314×10^{-3}	4.751×10^{-3}	277.000	1.316
7	1.046	0.519	1.582×10^{-4}	3.050×10^{-4}	235.160	0.072
8	0.648	1.262	6.774×10^{-3}	5.366×10^{-3}	151.069	0.811
9	0.893	0.795	4.930×10^{-3}	6.204×10^{-3}	151.965	0.943
10	0.969	0.776	5.434×10^{-3}	6.999×10^{-3}	151.965	1.064
11	0.908	0.786	1.908×10^{-3}	2.428×10^{-3}	198.986	0.483
12	0.768	0.865	1.305×10^{-4}	1.508×10^{-4}	199.011	0.030
13	0.816	0.883	1.629×10^{-3}	1.844×10^{-3}	199.326	0.367

Table B.16: Extended results for the main experiments on the yield of pentachlorofluorobenzene (C_6FCl_5) in the distillate

Exp. No.	Product mass in sample (g)	IS mass in sample (g)	C_6FCl_5 mass in sample(g)	C_6FCl_5 mass fraction in sample	Total mass of flask product (g)	Mass C_6FCl_5 in flask product (g)
1	0.611	0.618	5.201×10^{-4}	8.416×10^{-4}	9.032	0.008
2	0.528	0.941	1.346×10^{-4}	1.430×10^{-4}	10.101	0.001
3	0.730	0.668	1.543×10^{-4}	2.309×10^{-4}	7.122	0.002
4	0.677	0.705	9.426×10^{-5}	1.337×10^{-4}	8.021	0.001
5	0.500	0.555	2.806×10^{-3}	5.055×10^{-3}	7.590	0.038
6	2.622	0.875	1.421×10^{-2}	1.624×10^{-2}	0.855	0.014
7	1.086	0.255	1.099×10^{-4}	4.311×10^{-4}	1.924	0.001

Table B.17: Extended results for the main experiments on the total yield of all fluorinated products

Exp. No.	C_6F_6 molar yield (%)	C_6F_5Cl molar yield (%)	$C_6F_4Cl_2$ molar yield (%)	$C_6F_3Cl_3$ molar yield (%)	$C_6F_2Cl_4$ molar yield (%)	C_6FCl_5 molar yield (%)
1	0.112	0.612	4.238	13.034	3.129	0.817
2	0.143	0.840	3.974	13.716	3.294	0.129
3	0.237	1.295	5.804	14.723	4.048	0.095
4	0.272	1.279	5.972	15.362	4.560	0.206
5	0.214	1.122	0.118	4.392	9.306	4.570
6	0.223	1.313	0.127	4.491	7.063	5.929
7	0.588	1.328	0.624	5.003	0.235	0.323
8	0.053	0.220	0.011	1.511	5.200	3.614
9	0.110	0.256	0.020	2.397	7.580	4.203
10	0.109	0.329	0.025	2.987	8.198	4.741
11	0.181	0.462	0.020	10.768	5.659	2.154
12	0.216	0.538	0.538	6.792	1.391	0.134
13	0.179	0.453	0.020	11.025	5.766	1.638

APPENDIX C: SAMPLE CALCULATIONS

A. Yield computation

The internal standard quantification technique was used to determine the mass of oleic acid (preliminary experiment), hexafluorobenzene and chloropentafluorobenzene (main experiment) in the reaction product. The mass of the unknown product is solved for using the relevant calibration equation as outlined in Appendix A. As an example, the mass of hexafluorobenzene (M_{C6F6}) in Experiment 1 in the reboiler is calculated:

Table C.1: Data for the yield computation of hexafluorobenzene

Product mass in sample (g) M_{Sample}	IS mass in sample (g) M_{IS}	Area ratio$\left(\frac{A_{C6F6}}{A_{IS}}\right)$	Total mass of flask product (g) M_{Total}
0.896	0.623	8.849×10^{-5}	142.996

$$M_{C6F6} = M_{IS}\left(43.41\left(\frac{A_{C6F6}}{A_{IS}}\right)^2 + 0.70\left(\frac{A_{C6F6}}{A_{IS}}\right) + 8\times10^{-5}\right) \quad \text{C.1}$$

$$= (0.623)(43.41(8.849\times10^{-5})^2 + 0.70(8.849\times10^{-5}) + 8\times10^{-5})$$

$$= 8.864\times10^{-5}$$

The mass fraction of the C_6F_6 (x_{C6F6}) in the product sample is subsequently:

$$X_{C6F6} = \frac{M_{C6F6}}{M_{Sample}} = \frac{8.864\times10^{-5}}{0.896} = 9.893\times10^{-5} \quad \text{C.2}$$

Therefore the mass of C_6F_6 in the reboiler flask is:

$$M_{C6F6,Total} = X_{C6F6}\cdot M_{Total} \quad \text{C.3}$$

$$= (9.893\times10^{-5})\cdot(142.996)$$

$$= 0.014\ \text{g}$$

Number of moles of C_6F_6 produced in the reboiler:

$$\mathrm{N}_{\mathrm{C6F6}} = \frac{\mathrm{M}_{\mathrm{C6F6}}}{\mathrm{MM}_{\mathrm{C6F6}}} = \frac{0.014}{186.055} = 7.603 \times 10^{-5}\ \mathrm{Mol} \quad \text{C.4}$$

The number of moles of C_6F_6 produced in the distillate was similarly calculated to be 1.783×10^{-5} Mol

The number of moles of C_6Cl_6 introduced into the reboiler flask:

$$\mathrm{N}_{\mathrm{C6Cl6}} = \frac{\mathrm{M}_{\mathrm{C6Cl6}}}{\mathrm{MM}_{\mathrm{C6Cl6}}} = \frac{23.81}{284.8} = 0.0836\ \mathrm{mol} \quad \text{C.5}$$

Therefore, the total molar yield percentage of C_6F_6:

$$\%\ \mathrm{Yield} = \frac{\left(7.603\times10^{-5}+1.783\times10^{-5}\right)}{0.0836} \times 100 = 0.112\ \% \quad \text{C.6}$$

B. Conversion computation

The conversion of oleic acid was calculated based on the initial (OA_{in}) and final mass (OA_f) of oleic acid. Experiment 1 is used as an example:

$$\%\ \mathrm{Conversion} = 1 - \frac{OA_f}{OA_{in}} \times 100 = 1 - \frac{15.952}{41.325} \times 100 = 61.573\% \quad \text{C.7}$$

The conversion of C_6Cl_6 was calculated by implementing a carbon balance across the system. Experiment 1 is used as an example:

$$Carbon\ input = 6 \times n_{C6Cl6} = 6 \times 0.084 = 0.51\ moles \quad \text{C.8}$$

$$Carbon\ output = (6 \times n_{C6F6}) + (6 \times n_{C6F5Cl}) + (6 \times n_{C6F4Cl2}) + (6 \times n_{C6F3Cl3}) + (6 \times n_{C6F2Cl4}) + (6 \times n_{C6FCl5}) = 0.11\ moles \quad \text{C.9}$$

$$\%Molar\ conversion = 1 - \frac{C6Cl6_f}{C6Cl6_{in}} \times 100 = 1 - \frac{0.11}{0.51} \times 100 = 21.94\% \quad \text{C.10}$$

C. Selectivity

The selectivity of products was calculated as follows:

$$\%\ Selectivity_i = \frac{n_i}{total\ moles} \times 100 \qquad \text{C.11}$$

As an example, the molar selectivity of C_6F_6 for experiment 1 is used as an example:

$$\%\ Selectivity_{C6F6} = \frac{n_{C6F6}}{total\ moles} \times 100 = \frac{9.36\times10^{-5}}{0.018} \times 100 = 0.51\% \qquad \text{C.12}$$

D. Effective Carbon Number (ECN)

As pure samples of $C_6F_4Cl_2$, $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 could not be obtained, the effective carbon number method was used to calculate the yields of the above mentioned products.

The general relationship between the relative response factor (RRF), molar masses (*MM*) and ECN of the component of interest (*i*) and the internal standard (*is*) is defined as:

$$RRF_{i/is} = \frac{ECN_{is}}{ECN_i} \times \frac{MM_i}{MM_{is}} \qquad \text{C.13}$$

The relative response factor for C_6F_6 was determined from the respective calibration plot:

$$RRF_{C6F6/butanol} = 1.46$$

Literature states that the ECN of butanol is 3.4 (Brebbia & Popov, 2009). Using this information, the above can be substituted into Equation C.8 to determine the ECN of C_6F_6.

$$ECN_{C6F6} = \frac{3.4}{1.46} \times \frac{186.05}{74.122} = 5.84 \qquad \text{C.14}$$

It is known that the ECN of benzene is 6. Using this information and the results from Equation C.9, the contribution of a single fluorine atom (F_F) can be calculated:

$$ECN_{C6F6} = 6 - 6F_F \quad \text{C.15}$$

Solving for F:

$$F_F = \frac{6-5.84}{6} = 0.027 \quad \text{C.16}$$

Szulejko and Kim (2014) found that the contribution of a single chlorine atom is -0.35. Using this information and the results from Equation C.11, the ECN for $C_6F_4Cl_2$, $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 were calculated (Szulejko & Kim, 2014) .

As an example, the ECN of $C_6F_4Cl_2$ is shown below:

$$ECN_{C6F4Cl2} = 6 - (4 \times 0.027) - (2 \times -0.35) = 5.20 \quad \text{C.17}$$

The results were then substituted into Equation C.8 to solve for the relative response factors.

$$RRF_{C6F4Cl2/is} = \frac{ECN_{is}}{ECN_{C6F4Cl2}} \times \frac{MM_{C6F4Cl2}}{MM_{is}} = \frac{3.4}{5.20} \times \frac{218.964}{74.122} = 1.932 \quad \text{C.18}$$

Using the following equation and the area ratios, the mass of $C_6F_4Cl_2$ in the sample product was determined.

$$RRF_{i/is} = \frac{M_i}{M_{is}} \times \frac{A_{is}}{A_i} \quad \text{C.19}$$

As an example, the mass of $C_6F_4Cl_2$ for Experiment 1 is calculated below:

Table C.2: Data for the mass computation of tetrafluorodichlorobenzene

Product mass in sample (g) M_{Sample}	IS mass in sample (g) M_{IS}	Area ratio $\left(\frac{A_{C6F6}}{A_{IS}}\right)$	Total mass of flask product (g) M_{Total}
0.896	0.623	0.015	142.996

$$M_{C6F4Cl2} = (RRF_{C6F4Cl2/is} \times M_{is}) \times \frac{A_i}{A_{is}} = (1.932 \times 0.623) \times 0.015 = 0.005$$

The yield was then calculated following the same procedure outlined in Section A of this Appendix. The same method was used to calculate the yields of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5.

E. Uncertainty

In this study, the uncertainty on yield and conversion was calculated using the Division Error Propagation Technique outlined in the Harvard University, Physical Sciences 2 module (Fall 2007) which states the following (University, 2007) :

If

$$Q = \frac{ab\ldots c}{xy\ldots z} \qquad \text{C.20}$$

Then the uncertainty on Q is defined as:

$$\delta Q = |Q|\sqrt{\left(\frac{\delta a}{a}\right)^2 + \left(\frac{\delta b}{b}\right)^2 + \left(\frac{\delta c}{c}\right)^2 \ldots + \left(\frac{\delta z}{z}\right)^2} \qquad \text{C.21}$$

Equation C.16 suggests that the fractional uncertainties add in quadrature.

The yield of C_6F_6 was calculated as follows:

$$Yield_{C6F6} = \frac{M_{C6F6(final)}}{M_{C6Cl6(initial)}} = \frac{\mathrm{X_{C6F6}} m_{Total}}{M} = \frac{\frac{\mathrm{M_{C6F6}}}{\mathrm{M_{Sample}}} M_{Total}}{M_{C6Cl6(initial)}}$$

$$= \frac{\frac{M_{IS}\left(43.41\left(\frac{\mathrm{A_{C6F6}}}{\mathrm{A_{IS}}}\right)^2 + 0.70\left(\frac{\mathrm{A_{C6F6}}}{\mathrm{A_{IS}}}\right) + 8\times10^{-5}\right)}{\mathrm{M_{Sample}}} M_{Total}}{M_{C6Cl6(initial)}} \qquad \text{C.22}$$

Let $43.41\left(\frac{\mathrm{A_{C6F6}}}{\mathrm{A_{IS}}}\right)^2 + 0.70\left(\frac{\mathrm{A_{C6F6}}}{\mathrm{A_{IS}}}\right) + 8 \times 10^{-5} = J$ C.23

Therefore using Equation C.16, the uncertainty on the yield of C_6F_6 was calculated as follows:

$$\delta Yield_{C6F6} =$$

$$|Yield_{C6F6}|\sqrt{\left(\frac{\delta J}{J}\right)^2+\left(\frac{\delta M_{IS}}{M_{IS}}\right)^2+\left(\frac{\delta M_{Total}}{M_{Total}}\right)^2+\left(\frac{\delta M_{sample}}{M_{sample}}\right)^2+\left(\frac{\delta M_{C6Cl6(initial)}}{M_{C6Cl6(initial)}}\right)^2} \quad \text{C.24}$$

The calibration Equation C.1 was rearranged to solve for the calculated area ratio for each calibration point. The average value was then taken for all points:

$$Average\left|\frac{Actual\ Area\ Ratio-Calculated\ Area\ Ratio}{Calculated\ Area\ Ratio}\right| = \frac{\delta J}{J} \quad \text{C.25}$$

The initial mass of C_6Cl_6, mass of the sample and total mass of the product were all measured using a mass balance scale. Due to the precision of the scale, the uncertainty on the scale was neglected as $\delta M_{C6F6(final)} \gg \delta M_{C6Cl6(initial)}$, δM_{sample}, δM_{Total} and δM_{IS}. Therefore Equation C.19 reduces to:

$$\delta Yield_{C6F6} = |Yield_{C6F6}|\sqrt{\left(\frac{\delta J}{J}\right)^2} = |Yield_{C6F6}|\left(\frac{\delta J}{J}\right) \quad \text{C.26}$$

The uncertainty on the %yield of C_6F_6 for Experiment 1 is shown below as an example.

The calibration equation for C_6F_6 as shown in Appendix A is:

$$y = 43.41x^2 + 0.70x + 8 \times 10^{-5} \quad \text{C.27}$$

Where y: Mass ratio

X (measured): Area ratio

$X_{calculated}$ was determined by solving Equation C.22:

Table C.3: Data for the calculation of $X_{calculated}$:

Mass ratio (y)	Area Ratio ($x_{measured}$)	Area ratio ($x_{calculated}$)
0.007	6.556×10^{-3}	6.940×10^{-3}
0.013	1.077×10^{-2}	1.100×10^{-2}
0.020	1.521×10^{-2}	1.500×10^{-2}
0.026	1.758×10^{-2}	1.800×10^{-2}

Then,

$$\frac{\delta J}{J} = Average \left| \frac{Actual\ Area\ Ratio - Calculated\ Area\ Ratio}{Calculated\ Area\ Ratio} \right| = 0.028 \qquad \text{C.28}$$

Therefore,

$$\delta Yield_{C6F6} = \pm |Yield_{C6F6}|(0.028) \qquad \text{C.29}$$

As mentioned, the calibration plot and relative response factor of C_6F_6 was used as a basis to consequently calculate the yields of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5. Therefore the uncertainty on the yield of C_6F_6 was carried through and applied to the yields of $C_6F_3Cl_3$, $C_6F_2Cl_4$ and C_6FCl_5 to determine the uncertainty on these yields.

APPENDIX D: CHEMICAL DATA TABLE

Table D.1: Chemical Data Table

IUPAC name	CAS number	Supplier	Supplier specified purity (%)
Methanol	67-56-1	Merck (Pty) Ltd	99.5
Oleic Acid	112-80-1	Merck (Pty) Ltd	90
Sulphuric Acid	7664-93-9	Merck (Pty) Ltd	95-99
Butanol	71-36-3	Merck (Pty) Ltd	99
Hexachlorobenzene	118-74-1	Synquest Laboratories	99
Potassium Fluoride	7789-23-3	Merck (Pty) Ltd	99
Caesium Fluoride	13400-13-0	Capital Lab Supplies CC	99.9
Sulfolane	126-33-0	Merck (Pty) Ltd	99
Chloropentafluorobenzene	344-07-0	Capital Lab Supplies CC	99
Hexafluorobenzene	392-56-3	Merck (Pty) Ltd	98

APPENDIX E: HEXACHLOROBENZENE SAFETY AND HANDLING

E. 1.1 Product Identity

The following information was gathered from the following documents:

- Hexachlorobenzene Health and Safety Guide (World Health Organization, 1998) ;
- Toxguide for Hexachlorobenzene (2013); and
- IARC Monographs on the Evaluation of Carcinogenic Risks to Humans (2001)

CAS/IUPAC Name: Hexachlorobenzene

Chemical Formula: C_6Cl_6

Chemical Structure:

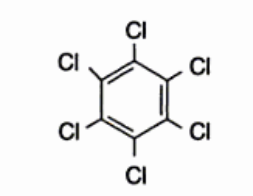

Figure E.1: Chemical Structure of Hexachlorobenzene

Common synonyms: perchlorobenzene, pentachlorophenyl chloride, phenyl perchloryl

CAS number: 118-74-1

E. 1.2 Physical and Chemical Properties

- Phase at room temperature: white crystalline solid.
- Solubility in water: insoluble.
- Soluble in: ether, benzene, chloroform and hot ethanol.

Table E.1: Physical and Chemical Properties of C_6Cl_6

Property	Value
Relative Molecular Mass	284.79
Melting Point (K)	505.15
Boiling Point (K)	595.15 (sublimes)
Vapour Pressure (Pa at 298.15K)	0.0023
Water Solubility ($mg \cdot litre^{-1}$ at 298.15K)	0.005
Flash Point (K)	515.15

E. 2. Human health hazards, prevention and protection

- C_6Cl_6 is dangerous by dust inhalation or if ingested.
- C_6Cl_6 may cause minor irritation to the eyes, skin and mucous membrane. The consequence of inhalation is the irritation of respiratory tract.
- Central nervous system toxicity is little. Ingestion of great amounts may result in headaches, dizziness, nausea, vomiting, numbness of hands and arms, apprehension, partial paralysis of extremities, coma and seizures.
- Prolonged periods of ingestion may result in porphyria cutanea tarda. Mortality rate can be as high as 10%.
- C_6Cl_6 is carcinogenic in animals.
- No cancer was reported in two follow-up studies of affected humans.

E. 3.1. Decontamination

In case of exposure after inhalation:

- The victim must be moved to fresh air;
- Assisted ventilation and administration of humidified oxygen may be necessary;
- When C_6Cl_6 is heated to decomposition, the poisonous gasses produced may result in pulmonary oedema;
- Contaminated clothing and shoes must be removed and isolated;
- Eyes or skin should be flushed with running water for 15min; and
- Skin, hair and nails should be vigorously washed.

E. 3.2. Prevention of absorption after oral exposure

- Emesis is not recommended.
- Activated charcoal should be administered.
- An oral saline cathartic is known to reduce absorption.
- Oils should not be orally administered

E. 3.3. Explosion and Fire Hazards

- There is a small fire potential when C_6Cl_6 is exposed to heat/flame.
- It must be noted that the C_6Cl_6-induced fire may produce irritating/poisonous gases.

E. 3.4. Fire extinguishing agents

- Fires involving C_6Cl_6 may be extinguished with dry chemical, CO_2, Halon, water spray or standard foam.

E. 4. Storage

- C_6Cl_6 must be stored separately from food.
- C_6Cl_6 must be stored in a cool, dry place.
- All formulations must be transported or stored in visibly labelled, firm and leak-proof containers.

E. 5. Spillage

- Small spillages may be taken up with sand or other non-combustible materials.
- Large spillages should first be dyked, and transferred to suitable containers.
- A suitable respirator with suitable eye protection must be worn for the above tasks

Table E.2: Prevention and Protection

Hazards	Prevention and Protection	First Aid
Skin Exposure:	Chemical resistant protective gloves (PVC) and clothing	Contaminated clothing must be removed; and Skin must be rinsed and washed with water and soap.
Eye Exposure:	Face shield/impact resistant eye protection	Eyes must be washed with water for 15min.
Inhalation	Where the potential exists for exposure over 0.002 mg/m^3, use a MSHA/NIOSH approved/supplied air respirator with a full face-piece must be used.	Victim must be removed to fresh air; Assisted ventilation and administration of humidified oxygen may be necessary; and Refer for medical attention.
Ingestion	Food or drink must not be consumed during work.	Mouth must be rinsed; and If the victim is unconscious, gastric lavage may be indicated if it can be executed shortly after ingestion.

E. 6.1. Occupational Exposure

Table E.3: Occupational Exposures

Country	Exposure Limit Value[a] ($mg \cdot m^{-3}$)	Effective date[b]
Czech Republic	1 (TWA)	1991^R
Commonwealth of Independent States (former USSR)	0.9 (STEL)	1991^R
USA (ACGIH)	0.002	1994

[A] TWA = time-weighted average (8 or 10 hour shift);

STEL = short-term exposure limit (15min) not to be exceeded at any time during a shift.

[B] 1991^R = effective date of ILO publication

E. 6.2. Toxicological Information

Hexachlorobenzene is listed as "extremely hazardous" by the World Health Organization (WHO). The LD50 values (the lethal dose-in milligrams of substance per kilogram of body weight that kills 50% of the test animals in a standard assay) are as follows (Gilbert, 2014):

- < 5 (for solids-oral exposure);
- < 20 (for liquid-oral exposure);
- < 10 (for solids-dermal exposure) and
- < 40 (for liquids-dermal exposure).

E. 7. Engineering Controls

- Operations are to be enclosed; and
- Provide local exhaust ventilation at the site of a chemical release.

E. 8. Waste Disposal

- Disposal methods are incineration, deep-well injection and landfill as required by local and national regulations.
- Incineration is most effective at 1573.15 K for 0.25 seconds.
- The vessel must either be incinerated or crushed and buried below the topsoil. The vessels or containers should not be reused and any material which has come into contact with hexachlorobenzene should not be reused and should be similarly disposed.

APPENDIX F: MATLAB SCRIPTS

F.1 Hexafluorobenzene system using KF as the fluorinating agent

F.1.1. Kinetic Parameters Regression

A) Main File

Excel input file (initial and final moles of compounds in the reaction pot and distillate):

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2												
3	Exp No		1	2	3	4	8	9	10			
4	Temp		503.15	503.15	503.15	503.15	463.15	483.15	483.15			
5	C6Cl6 initial		83.60253	83.60253	83.60253	83.60253	83.60253	83.60253	83.60253			
6	C6Cl6		65.25804	65.13048	61.69764	55.3095	74.73362	71.42437	69.90036			
7	C6F6 Pot		0.075803	0.110249	0.185436	0.139117	0.044258	0.092304	0.091502			
8	C6F5Cl Pot		0.487945	0.583898	0.995064	0.683974	0.184182	0.213764	0.274833			
9	C6F4Cl2 Pot		3.530336	0.592741	4.850518	1.525483	0.009191	0.017048	0.021194			
10	C6F3Cl3 Pot		10.38526	4.565489	6.815773	10.96951	1.263006	2.004262	2.496834			
11	C6F2Cl4 Pot		2.474507	2.449231	3.120533	4.487747	4.346929	6.337305	6.854005			
12	C6FCl5 Pot		0.654646	0.102135	0.072949	0.206346	3.021345	3.513475	3.963799			
13												
14	C6F6 distillate		0.235229	0.080678	0.068887	1.002504	0	0	0			0.346824
15	C6F5Cl distillate		0.049133	0.202987	0.088434	0.913874	0	0	0			0.313607
16	C6F4Cl2 distillate		0.003672	4.604756	0.00035	3.005847	0	0	0			1.903656
17	C6F3Cl3 distillate		0.049227	1.511687	0.805869	0.432938	0	0	0			0.69993
18	C6F2Cl4 distillate		0.057246	0.124317	0.084408	0.039627	0	0	0			0.0764
19	C6FCl5 distillate		0.043275	0.052711	0.084029	0.019369	0	0	0			0.049846

```
%Main file for regression of kinetic parameters (KF System)

close all
clear all
clc

global Tcent Npot c1 T NHCB_in Fdist

%------------Read in experimental data

T=xlsread('Datafitting','Sheet1','C4:I4');              % temperatures for all data points (Kelvin)
NHCB_in=xlsread('Datafitting','Sheet1','C5:I5');        % Initial moles of HCB (mmol)
Npot=xlsread('Datafitting','Sheet1','C6:I12');          % Final moles of component i in pot (mmol)
Fdist=xlsread('Datafitting','Sheet1','C14:I19');        % distillate/pot molar ratio for component i(mmol/min)


%------------count number of data points

c1=length(T);

lb=[0 0 0 0 0 0 0 0 0 0 0 0];                                   % lower bounds for parameter estimates
ub=[inf inf inf inf inf inf inf inf inf inf inf inf];           % upper bounds for parameter estimates
A0=[1e2 1e2 1e2 1e2 1e2 1e2];                                   % initial guess of pre-exponential factor
Ea=[50000 50000 45000 40000 80000 85000];                       % initial guess of activation energy (from
Arrhenius plots)

Tcent=498;

A_prime=A0.*exp(-Ea./(8.314*Tcent));



k0=[A_prime Ea];
```

```
options=optimset('Display','iter','MaxIter',200,'MaxFunEvals',5000,'TolFun',1e-20,'TolX',1e-
20,'LargeScale','on');

[k,resnorm,residual,exitflag,output,lambda,jacobian]=lsqnonlin(@objectivefun,k0,lb,ub,options);


%--------Post processing and regression evaluation



Nfinal_pred=zeros(7,c1);


for c4=1:c1

    T_p=T(c4);                          % reaction temperature for one data point
    NHCB_in_p=NHCB_in(c4);              % Initial moles of HCB for one data point
    Npot_p=Npot(:,c4);                  % Final moles of component i in pot for one data point
    Fdist_p=Fdist(:,c4);                % distillate rate for component i for one data point


    N0=[NHCB_in_p 0 0 0 0 0 0];     % initial number of moles of component i in the pot

   %------relative and absolute tolerance for ode solver

    reltol=1e-11;
    abstol=1e-11;


    %-----integrate differential equations


    options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);

    [t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);
```

```
    c5=length(N);

    Nfinal_pred(:,c4)=N(c5,:);              % final moles in pot of all components predicted by the model

end


%plotting results

figure(1)
plot(Npot(1,:),Nfinal_pred(1,:),'o','Marker','o','MarkerEdgeColor','b','MarkerFaceColor','b','MarkerSize',6);


hold on


FFDx=linspace(0,100,50);
FFDy=linspace(0,100,50);
ylim([0 100])
xlim([0 100])
plot(FFDx,FFDy,'k-','LineWidth',1)

axis square

xlabel('Measured moles of hexachlorobenzene in the pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
ylabel('Predicted moles of hexachlorobenzene in the pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)


hold off
```

```
figure(3)



plot(Npot,Nfinal_pred,'o','Marker','o','MarkerEdgeColor','b','MarkerFaceColor','b','MarkerSize',6);


hold on

FFDx=linspace(0,20,50);
FFDy=linspace(0,20,50);
ylim([0 20])
xlim([0 20])
plot(FFDx,FFDy,'k-','LineWidth',1)

axis square

xlabel('Measured moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
ylabel('Predicted moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)
hold off

Activation_energy=k(7:12)

Preexponential=k(1:6)./(exp(-k(7:12)./(8.314*Tcent)))

param=[Preexponential Activation_energy]

xlswrite('outputfile.xls',param,'Sheet1')
```

B) Rate File

```
function dN=ratefile(t,N,k,T_p,Fdist_p)

global Tcent Npot c1 T NHCB_in Fdist

dN=zeros(7,1);
C=zeros(7,1);

k1=k(1)*exp((-k(7)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for first reaction
k2=k(2)*exp((-k(8)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for second reaction
k3=k(3)*exp((-k(9)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for third reaction
k4=k(4)*exp((-k(10)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for fourth reaction
k5=k(5)*exp((-k(11)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for fifth reaction
k6=k(6)*exp((-k(12)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for sixth reaction
V=90;                                                            % reaction volume (sulfolane) 90 cm^3


C(1)=N(1)/V;                    % concentrations of components in pot (based on a sulfolane volume of 90 cm^3)
C(2)=N(2)/V;
C(3)=N(3)/V;
C(4)=N(4)/V;
C(5)=N(5)/V;
C(6)=N(6)/V;
C(7)=N(7)/V;


r1=k1;
r2=k2*C(7);
r3=k3*C(6);
r4=k4*C(5);
r5=k5*C(4);
r6=k6*C(3);


dN(1)=-r1*V;
```

```
dN(2)=+(1/(Fdist_p(1)+1))*(r6*V);
dN(3)=+(1/(Fdist_p(2)+1))*(r5*V-r6*V);
dN(4)=+(1/(Fdist_p(3)+1))*(r4*V-r5*V);
dN(5)=+(1/(Fdist_p(4)+1))*(r3*V-r4*V);
dN(6)=+(1/(Fdist_p(5)+1))*(r2*V-r3*V);
dN(7)=+(1/(Fdist_p(6)+1))*(r1*V-r2*V);
```

C) Objective Function File

```
function Fob=objectivefun(k)

global Tcent Npot c1 T NHCB_in Fdist

Fob=zeros(6,c1);
Nfinal_pred=zeros(c1,7);

for c2=1:c1;                          % cycle through data points

    T_p=T(c2);                        % reaction temperature for one data point
    NHCB_in_p=NHCB_in(c2);            % Initial moles of HCB for one data point
    Npot_p=Npot(:,c2);                % Final moles of component i in pot for one data point
    Fdist_p=Fdist(:,c2);              % distillate rate for component i for one data point


    N0=[NHCB_in_p 0 0 0 0 0 0];     % initial number of moles of component i in the pot

   %------relative and absolute tolerance for ode solver

    reltol=1e-11;
    abstol=1e-11;


    %-----integrate differential equations
```

```
    options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);

    [t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);

    c3=length(N);


    Nfinal_pred(:,c2)=N(c3,:);                    % final moles of all species predicted by the model. Rows
are data points, columns are species

end

NFINALPRED=Nfinal_pred(2:7,:);
NPOT=Npot(2:7,:);


Fob=((-NFINALPRED+NPOT).^2);


Fob=reshape(Fob,1,[]);
Fob=Fob';
```

F.2 Hexafluorobenzene system using CsF as the fluorinating agent

F.2.1. Kinetic Parameters Regression

A) Main File

Excel input file (initial and final moles of compounds in the reaction pot and distillate):

	A	B	C	D	E	F	G	H	I	J	K
1											
2											
3	Exp No		5	6	7	11	12	13			
4	Temp		503.15	503.15	503.15	463.15	483.15	483.15			
5	C6Cl6 initial		83.60253	83.60253	83.60253	83.60253	83.60253	83.60253			
6	C6Cl6		67.1224	68.91352	76.99193	67.51376	75.98757	67.65053			
7	C6F6 Pot		0.129905	0.158136	0.408645	0.151603	0.180346	0.149349			
8	C6F5Cl Pot		0.894993	0.926589	0.207919	0.38641	0.449766	0.379091			
9	C6F4Cl2 Pot		0.095603	0.089881	0.039215	0.016811	0.031623	0.016914			
10	C6F3Cl3 Pot		2.131842	2.756313	4.67449	9.002243	5.678618	9.21693			
11	C6F2Cl4 Pot		6.963571	4.827447	0.163242	4.731096	1.162744	4.820231			
12	C6FCl5 Pot		3.675722	4.163988	0.312702	1.800601	0.111858	1.369489			
13											
14	C6F6 distillate		0.373498	0.018568	0.155034	0	0	0			0.182367
15	C6F5Cl distillate		0.048075	0.014303	1.993006	0	0	0			0.685128
16	C6F4Cl2 distillate		0.02722	0.002843	5.533327	0	0	0			1.854464
17	C6F3Cl3 distillate		0.721588	0.414517	0.017731	0	0	0			0.384612
18	C6F2Cl4 distillate		0.116755	0.101752	0.155598	0	0	0			0.124702
19	C6FCl5 distillate		0.038903	0.02797	0.004393	0	0	0			0.023755

```
%Main file for regression of kinetic parameters (CsF System)

close all
clear all
clc

global Tcent Npot c1 T NHCB_in Fdist

%------------Read in experimental data

T=xlsread('Datafitting','Sheet1','C4:H4');              % temperatures for all data points (Kelvin)
NHCB_in=xlsread('Datafitting','Sheet1','C5:H5');        % Initial moles of HCB (mmol)
Npot=xlsread('Datafitting','Sheet1','C6:H12');          % Final moles of component i in pot (mmol)
Fdist=xlsread('Datafitting','Sheet1','C14:H19');        % distillate/pot molar ratio for component i(mmol/min)


%------------count number of data points

c1=length(T);

lb=[0 0 0 0 0 0 0 0 0 0 0 0];                                       % lower bounds for parameter estimates
ub=[inf inf inf inf inf inf inf inf inf inf inf inf];               % upper bounds for parameter estimates
A0=[1e2 1e2 1e2 1e2 1e2 1e2];                                       % initial guess of pre-exponential factor
Ea=[80000 80000 80000 80000 90000 90000];                            % initial guess of activation energy (from
Arrhenius plots

Tcent=498;

A_prime=A0.*exp(-Ea./(8.314*Tcent));



k0=[A_prime Ea];


options=optimset('Display','iter','MaxIter',300,'MaxFunEvals',5000,'TolFun',1e-20,'TolX',1e-
20,'LargeScale','on');
```

```
[k,resnorm,residual,exitflag,output,lambda,jacobian]=lsqnonlin(@objectivefun,k0,lb,ub,options);


%--------Post processing and regression evaluation



Nfinal_pred=zeros(7,c1);


for c4=1:c1

    T_p=T(c4);                          % reaction temperature for one data point
    NHCB_in_p=NHCB_in(c4);              % Initial moles of HCB for one data point
    Npot_p=Npot(:,c4);                  % Final moles of component i in pot for one data point
    Fdist_p=Fdist(:,c4);                % distillate rate for component i for one data point


    N0=[NHCB_in_p 0 0 0 0 0 0];     % initial number of moles of component i in the pot

   %------relative and absolute tolerance for ode solver

    reltol=1e-11;
    abstol=1e-11;


    %-----integrate differential equations


    options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);

    [t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);

    c5=length(N);
```

```
    Nfinal_pred(:,c4)=N(c5,:);              % final moles in pot of all components predicted by the model

end


%plotting results

figure(1)
plot(Npot(1,:),Nfinal_pred(1,:),'o','Marker','o','MarkerEdgeColor','b','MarkerFaceColor','b','MarkerSize',6);


hold on


FFDx=linspace(0,100,50);
FFDy=linspace(0,100,50);
ylim([0 100])
xlim([0 100])
plot(FFDx,FFDy,'k-','LineWidth',1)

axis square

xlabel('Measured moles of hexachlorobenzene in the pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
ylabel('Predicted moles of hexachlorobenzene in the pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)


hold off


figure(3)
```

```
plot(Npot,Nfinal_pred,'o','Marker','o','MarkerEdgeColor','b','MarkerFaceColor','b','MarkerSize',6);


hold on

FFDx=linspace(0,20,50);
FFDy=linspace(0,20,50);
ylim([0 20])
xlim([0 20])
plot(FFDx,FFDy,'k-','LineWidth',1)

axis square

xlabel('Measured moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
ylabel('Predicted moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)
hold off

Activation_energy=k(7:12)

Preexponential=k(1:6)./(exp(-k(7:12)./(8.314*Tcent)))

param=[Preexponential Activation_energy]

xlswrite('outputfile.xls',param,'Sheet1')
```

B) Rate File

```
function dN=ratefile(t,N,k,T_p,Fdist_p)
```

```
global Tcent Npot c1 T NHCB_in Fdist

dN=zeros(7,1);
C=zeros(7,1);

k1=k(1)*exp((-k(7)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for first reaction
k2=k(2)*exp((-k(8)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for second reaction
k3=k(3)*exp((-k(9)/8.314)*(1/T_p - 1/Tcent));                    % rate constant for third reaction
k4=k(4)*exp((-k(10)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for fourth reaction
k5=k(5)*exp((-k(11)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for fifth reaction
k6=k(6)*exp((-k(12)/8.314)*(1/T_p - 1/Tcent));                   % rate constant for sixth reaction
V=90;                                                            % reaction volume (sulfolane) 90 cm^3


C(1)=N(1)/V;                    % concentrations of components in pot (based on a sulfolane volume of 90 cm^3)
C(2)=N(2)/V;
C(3)=N(3)/V;
C(4)=N(4)/V;
C(5)=N(5)/V;
C(6)=N(6)/V;
C(7)=N(7)/V;


r1=k1;
r2=k2*C(7);
r3=k3*C(6);
r4=k4*C(5);
r5=k5*C(4);
r6=k6*C(3);

dN(1)=-r1*V;
dN(2)=+(1/(Fdist_p(1)+1))*(r6*V);
dN(3)=+(1/(Fdist_p(2)+1))*(r5*V-r6*V);
dN(4)=+(1/(Fdist_p(3)+1))*(r4*V-r5*V);
dN(5)=+(1/(Fdist_p(4)+1))*(r3*V-r4*V);
dN(6)=+(1/(Fdist_p(5)+1))*(r2*V-r3*V);
dN(7)=+(1/(Fdist_p(6)+1))*(r1*V-r2*V);
```

C) Objective Function

```
function Fob=objectivefun(k)

global Tcent Npot c1 T NHCB_in Fdist

Fob=zeros(6,c1);


for c2=1:c1;                          % cycle through data points

    T_p=T(c2);                        % reaction temperature for one data point
    NHCB_in_p=NHCB_in(c2);            % Initial moles of HCB for one data point
    Npot_p=Npot(:,c2);                % Final moles of component i in pot for one data point
    Fdist_p=Fdist(:,c2);              % distillate rate for component i for one data point


    N0=[NHCB_in_p 0 0 0 0 0 0];     % initial number of moles of component i in the pot

   %------relative and absolute tolerance for ode solver

    reltol=1e-11;
    abstol=1e-11;


    %-----integrate differential equations



    options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);
```

```
    [t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);

    c3=length(N);

    Nfinal_pred(:,c2)=N(c3,:);                    % final moles of all species predicted by the model. Rows
are data points, columns are species

end

NFINALPRED=Nfinal_pred(2:7,:);
NPOT=Npot(2:7,:);


Fob=((-NFINALPRED+NPOT).^2);

Fob=reshape(Fob,1,[]);
Fob=Fob';
```

F.3 Single simulation using regressed kinetic parameters using KF as the fluorinating agent

Determining the rate of consumption of C_6Cl_6 and rate production of fluorochlorobenzenes using KF as the fluorinating agent

A) Main File

```
close all
clear all
clc


k=[296.7113 5.69E+11    5.83E+17    0.6398  0.0023  3.27E+60    5.41E+04    1.26E+05    1.88E+05    2.21E+04
5.03E-08    6.06E+05];


T_p=503;                % reaction temperature for one data point
NHCB_in_p=83.6;         % Initial moles of HCB for one data point
Fdist_p=[0.346824444
0.313607192
1.903656215
0.699930429
0.076399507
0.049845997];           % average distillate/pot ratio for component i for one data point



N0=[NHCB_in_p 0 0 0 0 0 0];    % initial number of moles of component i in the pot

%------ relative and absolute tolerance for ode solver

reltol=1e-11;
abstol=1e-11;
```

```
%-----integrate differential equations


options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);

[t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);


%plotting results


figure(1)

plot(t,N(:,1),'k-','LineWidth',2);
hold on

axis square
ylim([0 90])
xlim([0 360])
ylabel('Total moles of hexachlorobenzene in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)
hold off


figure(2) % Fluorinated products C6F4Cl2, C6F5Cl and C6F6

plot(t,N(:,2),'k-','LineWidth',2);

hold on

axis square
ylim([0 2])
xlim([0 360])
```

```
plot(t,N(:,3),'r-','LineWidth',2);

plot(t,N(:,4),'b-','LineWidth',2);

ylabel('Total moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)

legend('C6F6','C6F5Cl','C6F4Cl2')

hold off


figure(3) % Fluorinated products C6F3Cl3, C6F2Cl4 and C6FCl5

plot(t,N(:,5),'k-','LineWidth',2);

hold on

axis square
ylim([0 20])
xlim([0 360])


plot(t,N(:,6),'r-','LineWidth',2);

plot(t,N(:,7),'b-','LineWidth',2);

ylabel('Total moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)

legend('C6F3Cl3','C6F2Cl4','C6FCl5')
```

```
hold off
```

B) Rate File

```
function dN=ratefile(t,N,k,T_p,Fdist_p)


dN=zeros(7,1);
C=zeros(7,1);

k1=k(1)*exp((-k(7)/(8.314*T_p)));                    % rate constant for first reaction
k2=k(2)*exp((-k(8)/(8.314*T_p)));                    % rate constant for reactions
k3=k(3)*exp((-k(9)/(8.314*T_p)));                    % rate constant for reactions
k4=k(4)*exp((-k(10)/(8.314*T_p)));                   % rate constant for reactions
k5=k(5)*exp((-k(11)/(8.314*T_p)));                   % rate constant for reactions
k6=k(6)*exp((-k(12)/(8.314*T_p)));                   % rate constant for reactions
V=90;                                                % reaction volume (sulfolane) 90 cm^3


C(1)=N(1)/V;                  % concentrations of components in pot (based on a sulfolane volume of 90 cm^3)
C(2)=N(2)/V;
C(3)=N(3)/V;
C(4)=N(4)/V;
C(5)=N(5)/V;
C(6)=N(6)/V;
C(7)=N(7)/V;


r1=k1;
r2=k2*C(7);
r3=k3*C(6);
r4=k4*C(5);
r5=k5*C(4);
```

```
r6=k6*C(3);


dN(1)=-r1*V;
dN(2)=+(1/(Fdist_p(1)+1))*(r6*V);
dN(3)=+(1/(Fdist_p(2)+1))*(r5*V-r6*V);
dN(4)=+(1/(Fdist_p(3)+1))*(r4*V-r5*V);
dN(5)=+(1/(Fdist_p(4)+1))*(r3*V-r4*V);
dN(6)=+(1/(Fdist_p(5)+1))*(r2*V-r3*V);
dN(7)=+(1/(Fdist_p(6)+1))*(r1*V-r2*V);
```

F.4 Single simulation using regressed kinetic parameters using CsF as the fluorinating agent

Determining the rate of consumption of C_6Cl_6 and rate production of fluorochlorobenzenes using CsF as the fluorinating agent

A) Main File

```
close all
clear all
clc


k = [0.0018 0.0194  0.0109  2.39E+17    0.0253  0.7901  5.70E+03    8.18E-09    7.49E-09    1.88E+05
36.425  2.04E+04];


T_p=503;                        % reaction temperature for one data point
NHCB_in_p=83.6;          % Initial moles of HCB for one data point
Fdist_p=[0.182366892
0.685128157
1.854463561
0.384611922
0.124701705
```

```
0.023755298];            % average distillate/pot ratio for component i for one data point



N0=[NHCB_in_p 0 0 0 0 0 0];    % initial number of moles of component i in the pot

%------relative and absolute tolerance for ode solver

reltol=1e-11;
abstol=1e-11;


%-----integrate differential equations


options=odeset('RelTol',reltol,'AbsTol',abstol,'NonNegative',[1 2 3 4 5 6 7]);

[t,N]=ode15s(@(t,N) ratefile(t,N,k,T_p,Fdist_p),[0 360],N0,options);


%plotting results


figure(1)

plot(t,N(:,1),'k-','LineWidth',2);
hold on

axis square
ylim([0 90])
xlim([0 360])
ylabel('Total moles of hexachlorobenzene in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)
```

```
hold off


figure(2) % Fluorinated products C6F4Cl2, C6F5Cl and C6F6

plot(t,N(:,2),'k-','LineWidth',2);

hold on

axis square
ylim([0 2])
xlim([0 360])


plot(t,N(:,3),'r-','LineWidth',2);

plot(t,N(:,4),'b-','LineWidth',2);

ylabel('Total moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)

legend('C6F6','C6F5Cl','C6F4Cl2')

hold off


figure(3) %  Fluorinated products C6F3Cl3, C6F2Cl4 and C6FCl5

plot(t,N(:,5),'k-','LineWidth',2);

hold on

axis square
ylim([0 20])
```

```
xlim([0 360])


plot(t,N(:,6),'r-','LineWidth',2);

plot(t,N(:,7),'b-','LineWidth',2);

ylabel('Total moles of fluorinated components in pot
[mol]','FontName','Arial','FontSize',14,'FontWeight','normal')
xlabel('Reaction time [min]','FontName','Arial','FontSize',14,'FontWeight','normal')
set(gca,'FontName','Arial','FontSize',12)

legend('C6F3Cl3','C6F2Cl4','C6FCl5')

hold off
```

B) Rate File

```
function dN=ratefile(t,N,k,T_p,Fdist_p)


dN=zeros(7,1);
C=zeros(7,1);

k1=k(1)*exp((-k(7)/(8.314*T_p)));                    % rate constant for first reaction
k2=k(2)*exp((-k(8)/(8.314*T_p)));                    % rate constant for reactions
k3=k(3)*exp((-k(9)/(8.314*T_p)));                    % rate constant for reactions
k4=k(4)*exp((-k(10)/(8.314*T_p)));                   % rate constant for reactions
k5=k(5)*exp((-k(11)/(8.314*T_p)));                   % rate constant for reactions
k6=k(6)*exp((-k(12)/(8.314*T_p)));                   % rate constant for reactions
V=90;                                                % reaction volume (sulfolane) 90 cm^3


C(1)=N(1)/V;                  % concentrations of components in pot (based on a sulfolane volume of 90 cm^3)
```

```
C(2)=N(2)/V;
C(3)=N(3)/V;
C(4)=N(4)/V;
C(5)=N(5)/V;
C(6)=N(6)/V;
C(7)=N(7)/V;


r1=k1;
r2=k2*C(7);
r3=k3*C(6);
r4=k4*C(5);
r5=k5*C(4);
r6=k6*C(3);


dN(1)=-r1*V;
dN(2)=+(1/(Fdist_p(1)+1))*(r6*V);
dN(3)=+(1/(Fdist_p(2)+1))*(r5*V-r6*V);
dN(4)=+(1/(Fdist_p(3)+1))*(r4*V-r5*V);
dN(5)=+(1/(Fdist_p(4)+1))*(r3*V-r4*V);
dN(6)=+(1/(Fdist_p(5)+1))*(r2*V-r3*V);
dN(7)=+(1/(Fdist_p(6)+1))*(r1*V-r2*V);
```

Appendix F may also be found on the CD submitted with the dissertation