SAFETY AND TECHNO-ECONOMIC ANALYSIS OF SOLVENT SELECTION FOR SUPERCRITICAL FISCHER-TROPSCH SYNTHESIS REACTORS

A Thesis

by

NATALIE ASMA HAMAD

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Safety Engineering

SAFETY AND TECHNO-ECONOMIC ANALYSIS OF SOLVENT SELECTION FOR SUPERCRITICAL FISCHER-TROPSCH SYNTHESIS REACTORS

A Thesis

by

NATALIE ASMA HAMAD

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Co-Chairs of Committee, Mahmoud M. El-Halwagi
Nimir O. Elbashir
Committee Member, Hisham A. Nasr-El-Din
Head of Department, Charles J. Glover

December 2011

Major Subject: Safety Engineering

ABSTRACT

Safety and Techno-Economic Analysis of Solvent Selection for Supercritical
Fischer-Tropsch Synthesis Reactors. (December 2011)

Natalie Asma Hamad, B.S., Texas A&M University at Qatar
Co-Chairs of Advisory Committee: Dr. Mahmoud M. El-Halwagi
Dr. Nimir O. Elbashir

Fisher-Tropsch Synthesis is a primary pathway for gas-to-liquid technology. In order to overcome commercial problems associated with reaction and transport phenomena, the use of supercritical solvents has been proposed to increase chemical conversion and improve temperature control. One of the major challenges in designing the supercritical FTS systems is the solvent selection. Numerous alternatives exist and should be screened based on relevant criteria. The main aim of the thesis was to develop a safety metric that can be incorporated in the selection of an optimal supercritical solvent or a mixture of solvents. The objective was to minimize the cost while satisfying safety constraints or to establish tradeoffs between cost and safety. Hydrocarbons from C_3 to C_9 were identified as feasible solvents for FTS purposes. The choice of these solvents is dependent on their mixture critical temperature and pressure requirements that need to be satisfied upon entry into the FTS reactor. A safety metric system was developed in order to compare the risk issues associated with using the aforementioned solvents. In addition, an economic analysis of using the different solvents was performed. Finally, a case study was solved to illustrate the use of the proposed metrics and the selection of solvents based on safety and techno-economic criteria.

DEDICATION

To

My mother,

Nawal

ACKNOWLEDGEMENTS

I would like to acknowledge the scholarship provided by ExxonMobil Middle East and North Africa Scholars Program (MENA) through the Institute of International Education. I would like to express my sincere gratitude to my thesis advisor, Dr. Mahmoud M. El-Halwagi, and to my co-advisor, Dr. Nimir O. Elbashir. I would also like to acknowledge the assistance and advice I regularly received from Elfatih E. Elmalik and from Aswani Mogalicherla from the Texas A&M University at Qatar campus. I would also like to thank Dr. Sam M. Mannan from the Mark Kay O' Connor Process Safety Center at Texas A&M University for his valuable insight concerning the safety sections of this paper.

TABLE OF CONTENTS

Page

CHAPTER

LIST OF FIGURES

LIST OF TABLES

Page

CHAPTER I

INTRODUCTION

Fisher-Tropsch Synthesis (FTS) is a primary pathway for gas-to-liquid (GTL) technology. The two main commercial FTS reactors that are used today are the fixed-bed and slurry reactors. Both reactors do not work perfectly and have several disadvantages. A main disadvantage of the fixed-bed reactor, among other disadvantages, is that the reaction is very exothermic, which is a concern in terms of safety hazards and also in terms of cost of heat removal. With the slurry reactor, a problem is that in the liquid media, it is difficult to separate the catalyst from the slurry. Also, conversion drop issues arise when using the slurry reactor.[1]

An idea to resolve the imperfections of both reactors is to invent a novel reactor that combines the advantages of both of the reactors without having to incur the disadvantages. A method would be to use supercritical phase conditions, because then the properties of both the gas- like diffusion and the liquid heat transfer could be optimized, and the parameters in the supercritical phase can be tuned with slight changes in temperature and pressure. In the laboratory- scale, it has been shown that by using supercritical phase conditions, the FTS performance was improved.[1]

This thesis follows the style of the *AICHE Journal*.

The kinetic reactions in FTS can become very complex, and it is difficult to represent them in simulations such as ASPEN Plus. In order to provide a basis for future supercritical phase simulations, a simplified method was developed to input FTS kinetics into ASPEN Plus.

In dealing with supercritical phase conditions, solvent selection is a main challenge. Elmalik et al.[2] have indicated that light hydrocarbon pure solvents or solvent blends are the most appropriate solvents to be used for FTS. The aim of this paper is to analyze the list of recommended solvents, and to compare them based on two critical criteria: safety and cost. Basically, paper introduces an approach to the integration of safety with techno-economic analysis for the screening and selection of solvents in supercritical FTS.

In order to evaluate safety, a safety index was calculated by using methods related to the safety index developed by Pokoo-Aikins et al.[3]. The higher the value of the safety index, the higher the safety risk is. In the evaluation of a FTS facility however, there are several important locations where safety aspects should be considered, so several safety indices were calculated. A technique that can be used to determine the most effective balance between two parameters is the Pareto-curve optimization, which represents the tradeoff between different objectives Finally, the results from the Pareto curve were analyzed and recommendations about which solvents to select were generated. Chapter II includes a literature review of GTL and FTS processes, as well as a background into supercritical FTS processes and existing safety metrics. Chapter III includes an analysis of FTS product distributions and conversions using ASPEN Plus.

Chapter IV shows the method used to analyze safety and cost of supercritical FTS processes. Chapter V shows the results obtained from the safety and cost analysis, and Chapter VI shows the conclusions and recommendations obtained from the results.

CHAPTER II

LITERATURE REVIEW

Gas-to-Liquid (GTL) Technology

Natural gas is one of the cleanest and most readily obtainable forms of fossil fuels. In order for natural gas to be made available to different areas in the world, it can be transported by three different means which are mentioned as follows:

- Using pipelines under the ground to transport the gas,
- Changing its phase into liquefied natural gas (LNG) and transporting it through ships,
- Changing its chemical composition into long-chain hydrocarbons in the liquid phase through the use of the GTL.[4]

Interest in GTL technology emerged after the limitations of using pipelines were realized i.e., its dependence on strong relationships with other countries, the increase in environmental regulations, and after new technologies were developed that enabled GTL to be used.[5] From Wakamura[6], it can be stated that the importance of GTL is related to three important factors as follows:

- Energy security: There would be less dependence on potentially unstable oil resources since untapped fields which include carbon dioxide can become utilized in areas such as Australia and Southeast Asia. In addition, monopolies from countries who supply oil can be reduced and therefore costs would decrease.

- Ecology: The reduction of flaring gases in countries that produce oil and gas can be achieved. In addition, GTL produces one of the cleanest and environmentally friendly fuels today.
- Economy: This is related to the improvement of developments of gas fields in domestic facilities.

GTL is also a method to produce fuels and other products of hydrocarbons. The use of GTL is continually expanding, even though oil resources are decreasing. GTL is also environmentally friendly since the amount of sulfur is small and there are less NO_x and CO emissions.[7] The main steps in a GTL process plant are as follows:

1. Reforming: in order to obtain synthesis gas i.e., a mixture of hydrogen and carbon monoxide from reforming of natural gas (several technologies have been commercialized including steam reforming),[8]
2. Fischer-Tropsch Synthesis (FTS) technology: in order to obtain hydrocarbons and oxygenates,
3. Upgrading of hydrocarbons: by using methods such as hydrocracking and isomerization in order to obtain purified diesel, gasoline and other valued chemicals.[1]

Figure II.1 shows a typical GTL commercial process including the three main steps involved.

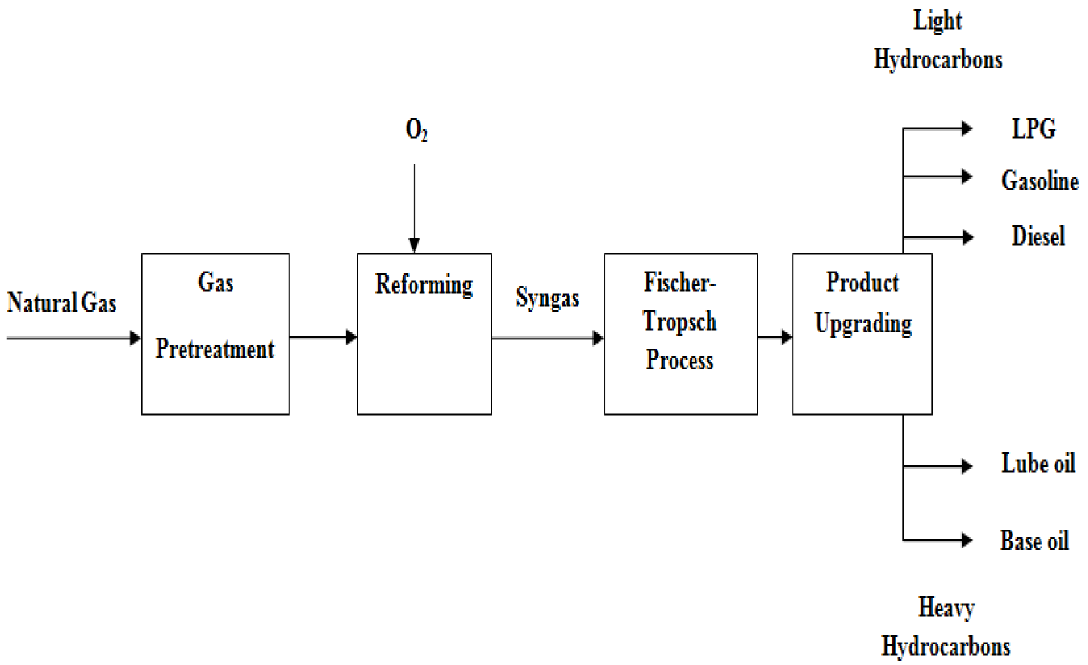


Figure II.1 Gas-to-Liquid Technology Representation[1]

Commercial FTS Processes

Elbashir et al.[1] state that one of the principal pathways for converting GTL is the Fisher-Tropsch Synthesis (FTS).There are other methods to produce syngas such as from coal and biomass, but the production of syngas from natural gas is the most common method to be used commercially.[8] FTS is named after Franz Fischer and Hans Tropsch; the German scientists who invented the technology, and was discovered late in the 1920s.[1] It is essentially a polymerization reaction where syngas reacts on a catalyst metal surface to produce oligomers of different carbon numbers. Desired products include higher molecular weight hydrocarbons, olefins, paraffins and oxygenates.[9] Other products include alcohols and acids at different lengths.[4] After the reaction takes place, the amount of carbon monoxide consumed decreases and carbon dioxide is produced as a side product.[9] The FTS reaction is an extremely exothermic process, which represents serious challenges to the efficiency of the overall system. The main reaction can be expressed as follows:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O \quad -\Delta H_{298}=-167 \text{ kJ/mol/CO} \qquad (1)$$

More detailed mechanisms have been reported in literature.[9] There are several steps that take place before the polymerization reaction is complete. In the first step, carbon monoxide and hydrogen are adsorbed onto a metal catalyst, which is usually made up of cobalt or iron metals. The typical ratio of hydrogen to carbon monoxide used for FTS is 2:1.[10] In the second step, oxygen on the surface is removed and water and carbon dioxide form as byproducts of the reaction. The third step includes hydrogenation of the carbon that is adsorbed and the production of oligomers. The fourth step includes the production of longer-chain hydrocarbons, and the final step includes the termination of methane.[11] These steps are shown as follows:

1. $H_2 + 2S \Leftrightarrow 2H.S$

   $CO+S \Leftrightarrow CO.S$

   $CO.S + S \Leftrightarrow C.S + O.S$

2. $O.S + H.S \Leftrightarrow OH.S + S$

   $OH.S + H.S \Rightarrow H_2O + 2S$

   $CO.S + O.S \Rightarrow CO_2 + 2S$

3. $C.S + H.S \Leftrightarrow CH.S + S$

   $CH.S + H.S \Leftrightarrow CH_2.S + S$

   $CH_2.S + H.S \Leftrightarrow CH_3.S + S$

4. $CH_3.S + H.S \Rightarrow CH_4 + 2S$

The Anderson-Schulz-Flory (ASF) distribution was derived from a series of assumptions about the product distribution resulting from the kinetics of the reaction. These include the assumption that the probability of product distribution is only either propagation or termination of the monomer, and that the temperature change does not affect the overall process. The ASF distribution is a plot of $\ln(W_n/n)$ versus n, where W_n is the weight fraction of hydrocarbons with n carbon, and n is the number of carbon molecules. The slope of the plot is called the chain growth probability of the molecules to continue reacting α, whose value is a number between zero and one.[4] The ASF plot is shown in Figure II.2 below.

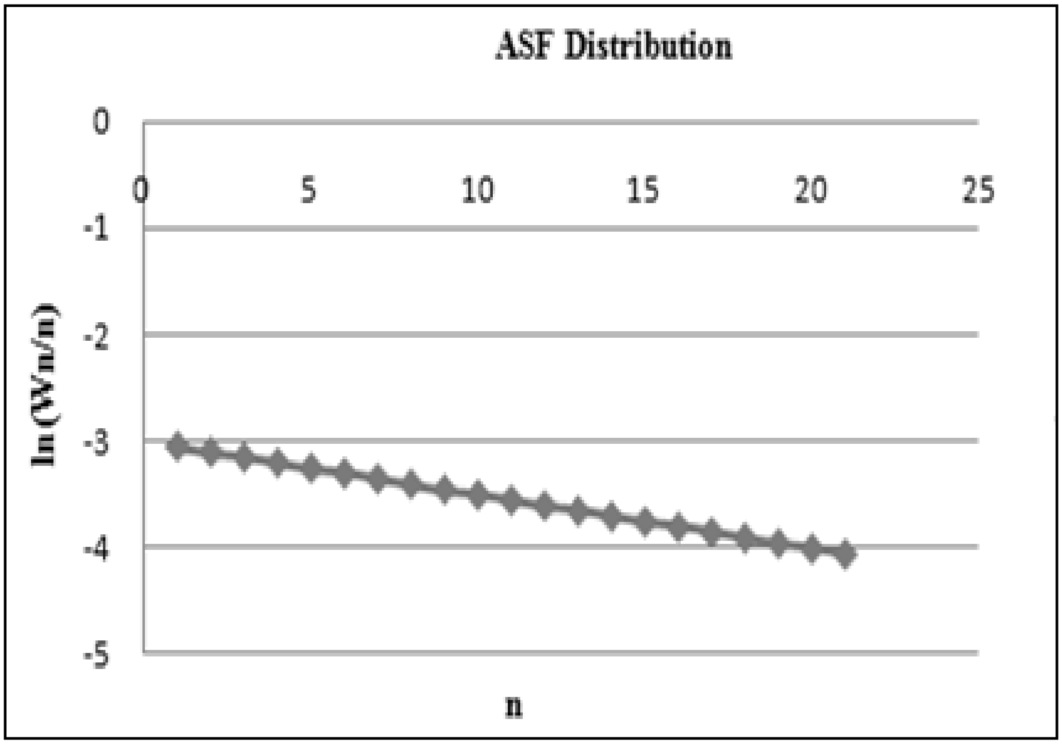
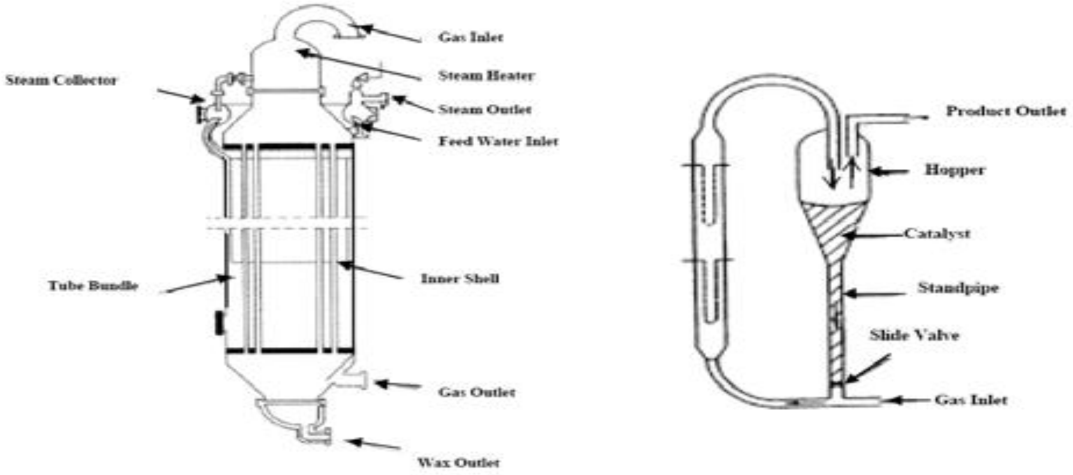


Figure II.2 Example of an ASF Distribution[4]

Elbashir et al.[12] state that the catalysts made from cobalt have been shown to have the best balance between pricing and performance for FTS. Cobalt catalysts have been shown to offer the greatest yields and to work for the longest periods of time. The majority of the commercial FTS systems that use cobalt catalysts employ the alumina or silica supported catalysts. In general, stability of catalysts is a major problem in FTS facilities. A large portion of the total cost of the process is the cost of the catalyst and its regeneration cost. Sometimes, regeneration of the catalyst is more expensive than buying a new one.

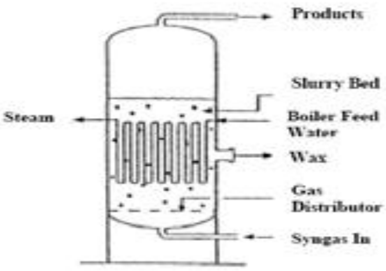
A major problem with FTS processes is the unwanted production of methane from the reaction. In gas-phase reaction technologies, the high temperature involved creates a large amount of surrounding heat, which can cause cracking of the longer-chain hydrocarbons into shorter-chains. The worst possible result would be for the cracking to result in methane formation, because the process was initiated with methane (which is the main composition of natural gas). To avoid this issue, heat needs to be removed from the catalyst pores in an effective manner.[8]

Elbashir et al.[1] summarized that the two main reactors to be used commercially for FTS purposes are the multitubular fixed-bed reactor and slurry reactor. The oldest reactor to be used for FTS is the fixed-bed reactor. The first design of a fixed bed reactor included internal cooling plates at high conversions to lower the amount of heat coming from the highly exothermic reaction. The next advancement was called the multi-tubular fixed bed reactor and it contained a gas recycle at moderate per pass conversion. The gas recycle greatly improved the quantity of heat removed, but the cost of installing a gas recycle was very large. Another technology is called the fluidized bed reactor, and this reactor runs in the bubbling system. The heat involved is taken away within the reactor bed through the use of cooling tubes. The newest FTS reactor is called the slurry reactor works when syngas is bubbled through heavier hydrocarbons in the liquid phase called slurries. The reaction heat is removed from the cooling coils within the reactor. Products present in the gaseous phase exit the slurry reactor from the top and are generally light hydrocarbons. At the middle of the reactor, the fuels present in the liquid phase exit. Other reactors were invented after that, but the commercialized ones so far are the fixed bed, fluidized bed, and the slurry reactors.[1] Figure II.3 shows the three types of currently used FTS commercialized reactors.



(a) Multitubular Fixed Bed

(b) Circulating Fluidized Bed



(c) Slurry Reactor

Figure II.3 The Three Commercialized FTS Reactors Today[13]

Commercial FTS facilities today include the Oryx GTL slurry-phase plant, Shell's fixed-bed GTL plant in Malaysia, and Shell's Pearl plant (Shell's newest multitubular fixed-bed GTL plant) in Qatar.[7] Additional companies are involved in the FTS technology such as ExxonMobil, Sasol ConocoPhillips and Syntroleum.[4,7]

The advantage of using a fixed-bed reactor is that it facilitates high diffusivity of the reactant to the catalyst pores which results in higher reaction rates and syngas conversions. A disadvantage, however, is that the reaction is highly exothermic and high cost efficient removal of the heat is required.[1] Another disadvantage is that since the catalyst particles have a large diameter of about 1mm, intra particle diffusion may become limited within the pores as heavy hydrocarbons (liquids) are formed.[14] A major advantage to the slurry reactor technology is that it overcomes the problem of the exothermic reaction by efficiently removing the exothermic heat in the liquid media of high heat capacity. Another advantage is that the reactants are well mixed resulting in an isothermal operation in a semi-continuous stirred tank reactor process. However, a disadvantage is that back mixing of the bubbling gas occurs, which causes a large conversion drop, in addition to other problems during the separation of the catalyst from the slurry.

It can be seen that both the fixed bed and slurry reactors have major disadvantages, and that if one reactor is used, it is not currently possible to overcome the disadvantages involved. Although both reactors have major disadvantages, alternatives to these reactors are still under development and are unavailable commercially. A resolution to this issue would be to create a reactor that combines the advantages of both of the technologies. In order to be able to do that, an idea would be to use supercritical conditions, since they are able to optimize both the properties of gas like diffusion and also of liquid heat transfer.[1] Therefore, densities could be tuned to be similar to those of liquids, and transport properties could be tuned to be similar to those of gases.[15] In this case, the advantages of both reactors can be used and the disadvantages would not be present.

Hao et al.[5] worked on modeling the complete GTL process in ASPEN Plus in order to be able to compare the product distribution result when using two different catalysts. The FTS reactor was modeled in ASPEN Plus in two different ways; using the plug flow reactor (PFR) and using the continuously-stirred tank reactor (CSTR). The PFR is considered to be the ASPEN Plus model of a fixed-bed reactor, and the CSTR is considered to be the ASPEN Plus model of a slurry reactor. ASPEN Plus simulations for the FTS reactor were conducted in this research project about a techno-economic analysis of different solvents supercritical FTS processes, in order to provide a basis for future supercritical phase simulations.

Supercritical FTS

Elbashir et al.[1] have shown that operating in the supercritical region improves the FTS performance compared to using non-supercritical media, and it also improves stability of the catalyst used. This has been attributed to the “in situ extraction of heavy hydrocarbons from the catalyst pores”, as the supercritical solvent media facilitates such processes. This greatly lowers the amount of coke that is formed within the pores of the catalyst, as well as offers an opportunity for selective control of hydrocarbon product distribution towards the most desired products. By tuning the pressure slightly in the supercritical phase, large changes in the solubility and in the density of the products can be achieved.[15] Another advantage to conducting FTS in supercritical media is that less unwanted methane is produced from the FTS reaction when compared to gas-phase media. A main reason for this is that there is better heat dissipation locally in supercritical phase FTS. In the supercritical phase, there is a much flatter temperature profile along the length of the reactor.[8] From Elbashir et al.[12] it was stated that by operating in the supercritical region for FTS purposes, the stability of the catalyst was improved as compared to the conventional two phases in FTS. Supercritical phase FTS is used at very high temperatures of approximately between 230 °C and 250 °C. The highest temperature that can be used for the FTS catalyst bed was found to be 300 °C for cobalt catalysts. An appropriate solvent to syngas ratio was found to be 3:1.[2]

In using supercritical FTS, solvent selection is a key challenge. From the work of Elmalik et al.[2], it has been decided that the mixing of a light hydrocarbon as a solvent with the syngas is advisable for FTS processes. This is supported by the fact that improved heat elimination is found for fixed-bed reactors, and that diffusivity is improved in relation to the wavy contents of the slurry reactor. In choosing a supercritical solvent for FTS purposes, it is important that the critical temperature of the mixture of the solvent with the syngas be lower by a small amount than the desired temperature of the FTS reactor catalyst bed, and the solvent is required to be stable under the conditions used, and the solvent should have a large affinity to non-aromatic hydrocarbons (to allow for enough extraction of wax from the FTS reactor). From these criteria, it was established that the supercritical solvents that can be used include hydrocarbons from C_3 until C_{10}, a combination of mixture of the hydrocarbons, or even fuel cuts that have already been made such as diesel and naphtha. The choice of these solvents is mainly dependent on their mixture critical temperature and pressure requirements that need to be satisfied upon entry into the FTS reactor. For example, carbon dioxide is a commonly used solvent in most supercritical applications such as in in the pharmaceutical, oil, food and biochemical fields.[15] Carbon dioxide is omitted as a possible choice for supercritical FTS purposes because its critical temperature and pressure are beyond the required range of conditions applicable for FTS. Another advantage of using these hydrocarbons is that they are products of the FTS reaction themselves. Since there is no foreign solvent added to the system, there would be no need for additional costly equipment to be added to the process in order to accommodate a foreign solvent.[2] The Elmalik et al.[2] paper identifies the different solvents, solvent blends and fuel cuts that are considered worthwhile for an analysis into supercritical FTS processes. The paper also incorporates a techno-economic analysis of select solvent blends.

Elmalik et al.[2] established that N-Propane, N-Butane, N-Nonane and N-Decane could not be used as solvents by themselves for FTS since their critical temperatures are beyond the acceptable range of conditions that is required for an FTS catalyst bed. The critical temperatures of N-Propane and N-Butane are too low to be used for FTS purposes, and the critical temperatures of N-Nonane and N-Decane are too high to be used (and are beyond the maximum temperature for FTS of 300 ^{o}C). When considering

N-Propane and N-Butane, the critical pressures were also found to be too high to be used for FTS purposes since at such elevated pressures, additional equipment would need to be purchased and would greatly increase the cost involved. It was established however that N-Pentane and N-Hexane are able to be used as sole solvents for supercritical FTS purposes due to their critical temperature and pressure conditions. N-Heptane and N-Octane were found to be difficult to upgrade and to purify for use as supercritical FTS solvents. Elmalik et al.[2] proposed a blend of N-Pentane and N-Hexane, which is called light naphtha. Raw naphtha is also thought be a possible supercritical FTS candidate because it is the cheapest blend when purchased raw and because it will not need additional new equipment to be incorporated into the FTS system. In the current research being conducted, solvents from C_3 until C_{10} were first analyzed, and the mixtures of different solvent blends were later investigated.

However, the scale-up of operating supercritical fluids in FTS reactor technology is still considered to be a challenge as it has not developed beyond the lab-scale. The reason behind this is that a thorough comprehension of the kinetics of the reactions as well as the phase behaviors involved is required in order to operate industrial scale reactors. In addition, FTS is a complex process and it has proven to be complicated to control the thermophysical characteristics of the reaction mixture.[1]

A study of the techno-economic aspects of solvent selection has been conducted by Elmalik et al.[2]. Notwithstanding the usefulness of the techno-economic aspects, it is important to include safety as a primary criterion in solvent selection. This is particularly important given the impact that solvent selection has on the operating temperature and pressure of the FTS reaction system as well as on downstream processing. This paper introduces an approach to the integration of safety with techno-economic analysis for the screening and selection of solvents in supercritical FTS.

Available Safety Metrics

There are different methods that have been presented in literature in order to evaluate the different safety concerns inside a chemical process. Before the 1990's, the methods to evaluate a process-safety concerns required exhaustive information about the process to be given.[16] The detailed information is usually available however later in the process stages and would not be available in the design phases of projects. Such methods include the Dow F&EI methods the Mond indices.[17] These approaches and other methods have been described and analyzed in literature by researchers such as Rahman et al.[16]. The Dow F&EI is used in many process facilities and it is able to rank hazards such as fire, explosion and exposure to different chemicals.[18] The Mond Index however is used in order to be able to define toxic hazards, fire hazards and explosion hazards.[19] The Dow Chemical Exposure Index is used in order to rank acute hazards from exposure to toxic chemicals and others.[20] Other methods that also require detailed information about the process to be known and are advanced in locating hazards include the Fault Tree Analysis (FTA), Event Tree Analysis (ETA), Hazard and Operability Analysis (HAZOP), Layers of Protection Analysis (LOPA), Failure Modes and Effects Analysis (FMEA), Human Reliability Analysis (HRA) and Cause and Consequence Analysis (CCA). Of interest in the current supercritical FTS solvent research is to analyze supercritical solvents within the design phase of a plant, since no FTS facility has been designed beforehand using supercritical conditions. Therefore, indices such as the Dow F&EI and others, although very useful for application during the process stages, would not prove to be helpful for design phase research activities such as the comparison of supercritical solvents in FTS processes. The same issue applies when attempting to utilize tools that these advanced methods mentioned above were built on. Some examples would be the "What-if" and Checklist methods. They are useful tools for identifying and listing hazards and potential incidents, but would not be tools that provide the most information for the comparison of supercritical FTS solvents.[18]

Since the 1990's, another method called the Prototype Inherent Safety Index (PIIS) has then been discovered in literature.[21] This method is found to be straight forward and easy to use, and its purpose is specified as for the analysis of process routes. After an analysis of this method, it was found that the PIIS was intended specifically for the comparison of different process routes, whereas the current research on comparing supercritical solvents for FTS is focused on one specific route and does not consider or compare any others. The supercritical solvents in FTS research project compares different solvents, but by using one specific route i.e. the entry to the FTS process. Therefore, although useful for comparing process routes, the PIIS method was not found to be applicable to the supercritical solvents in FTS research where only one route is considered. A graphical procedure was developed by Gupta and Edwards.[22] This method is a graphical approach to the PIIS method by Edwards and Lawrence.[21] The indices that correspond to hazards are graphed separately, and then are evaluated comparatively against each other. This method can be used as an alternative to the PIIS method, and is also used for the comparison of process routes.

An alternative method is called the Inherent Safety Index (ISI).[23,24] This method expands on the PIIS by taking into account the separation sections as well as the process routes involved. The main purpose of the ISI is also to account for the differences in process routes. The I-Safe index is also intended to compare process routes and it uses information from both the PIIS and ISI methods.[25,26] In addition, it includes NFPA ratings for the chemicals involved. All of these methods expand on the PIIS method and include additional useful information to evaluate different process routes. However, the aim of the supercritical solvents in FTS research is not to compare process routes, but to compare different supercritical solvents; therefore a way to incorporate the above indices into the current research project was not found.

Another method is called I2SI, and it considers the damage potential of a process after accounting for control measures and inherent safety of a process.[27] In the supercritical solvents for FTS purposes research project, the process controls in the FTS process are not considered. From Crowl and Louvar[28], control measures are considered to be add-on measures to help reduce the effects of a spill or leak in a process. What is considered in the supercritical solvents in FTS project is inherent safety instead of add-on controls, and the solvents are being considered based on their inherent properties in regards to safety. In the design phase of projects, inherent safety is considered first in order to design for systems not to leak, and after that is add-on controls incorporated in order to mitigate the consequences of a leak. Since this project is still in the design phase, the control measures have not been considered yet. Safety is addressed, but will focus on inherent safety instead of control measures. Therefore, the I2SI method was not used for the analysis of different supercritical solvents in FTS. A tool that was based on the original I2SI method was created by Tugnoli et al.[29]. The indices in the I2SI method were modified in order to include "attenuation, simplification and limitation of effects" into the planning of a chemical facility. The Domino Hazard Index (DHI) was also developed by Tugnoli et al.[29], which accounts for the "Domino Effect", where one part of a plant at risk can affect other parts of the plant. A method that accounts for inherent safety in the design phase was recently developed by Patel et al.[30]. This method is mainly used for solvent analysis, and it uses CAMD in order to select inherently safer solvents. This method seems to be a detailed and technical method to select solvents, but what is needed for the supercritical FTS solvents research is a simple and basic tool to incorporate safety into the solvent selection.

Additional methods to evaluate safety were invented in the years 2003 and 2004. The Safety Weighted Hazard Index (SWeHi) tool was created in order to have an index for assessing hazards in chemical facilities.[31] The Hazardous Waste Index (HWI) was created in order to assess hazards such as toxicity and flammability of waste substances.[27,31] The Transportation Risk Screening Model (ADLTRS®) is useful for identifying transportation risks from moving chemicals to different.[31] Also, the Fuzzy Logic-Based Inherent Safety Index (FLISI) is a method to measure inherent safety instead of relying of qualitative reasoning by using techniques such as "If-Then" rules.[32] All of these methods are very useful for the methods that they are intended for. Of interest to the research on comparing supercritical solvents in FTS however is a simple but effective tool that can evaluate different hazards for all of the solvents at hand and that can help to compare one solvent over another based on the results of the hazard analysis.

The EHS is a tool used to evaluate environmental, safety and health concerns.[33] It has been shows to be very useful in the application of batch processes and in using fine chemicals.[16] The INSET Toolkit is also a tool used to evaluate environmental, safety and health concerns and is also useful for identifying inherently safer methods within a facility.[34] Another tool is called the Environmental Risk Management Screening Tool (ERMST®) and is used for ranking purposes in order to analyze hazards to the environment such as pollution to the air and water.[19] These tools are very useful for the analyses they are intended for, but it was found that the above three methods were not able to give insight into identifying which supercritical solvents should be used for FTS.

Several methods have been published specifically to compare different solvents. A software called Pro-Computer-Aided Molecular Design (ProCAMD) in order to pick solvents that contain similar or improved properties as others that are of interest.[35,36] Folić et al.[37] were able to demonstrate that the Gani et al.[36] method can be effectively used for generating an initial list of solvents, as well as a secondary group of solvents (in order to give the user an opportunity to rationalize the usefulness of the solvents among the whole synthesis process). These methods are useful for looking at solvents in multi-stage synthesis processes. For the research on supercritical solvents for FTS, there is only one process stage that is being considered. In addition, since it is the first step of a safety metric analysis in the supercritical FTS field, a method which does not involve detailed programming would be preferred for the first stage of the process.

The safety metric that is chosen for the comparison of supercritical solvents for FTS purposes was developed by Pokoo-Aikins et al.[3]. It is a simplified matrix and uses a process specific and chemical specific factor in the same way as PIIS does. The chemical specific factor deals with the properties of the chemical itself and the process specific factor deals with the process conditions. Pokoo-Aikins et al.[3] use the lethal concentration dose for half a population (LC_{50}) and vapor density as chemical specific factors. They use a temperature factor and a pressure factor for the process specific factors, where the temperature factor can be calculated through a relationship between maximum operating temperature and boiling point, and the pressure factor can be calculated through a relationship between maximum operating pressure and vapor pressures. The resulting safety metric is a measure of both the chemical and the process specific factors and is called the safety index (SI). The higher the SI, the higher the safety risk is. The equation used to calculate the SI is as follows[3]:

$$SI= a_{i,1}* LC_{50\,i,k} + a_{i,2}* VD_{i,k} + a_{i,3}*T_{f\,i,k} + a_{i,4}*P_{f\,i,k} \tag{2}$$

where LC_{50} is the lethal concentration dose for half of the population, VD is the vapor density, T_f is the temperature factor, P_f is the pressure factor and $a_{i,j}$ is a weighting factor that is used for each parameter. In the weighting factor $a_{i,j}$, i is used for the different chemicals and k is used for the different steps in the process.

The purpose of a weighting factor is to highlight the parameters that have an important contribution to the solvent index. By using weighting factors, the parameters that have a larger effect will weigh more in the equation, and thus affect the process more than other parameters.[3]

CHAPTER III

MODELING FTS CONVERSION AND PRODUCT DISTRIBUTION

The complex kinetic reactions involved in an FTS reactor are difficult to be represented by process simulators such as ASPEN Plus. Different researchers have programmed the kinetics separately into Microsoft Excel or FORTRAN, and then linked the results into ASPEN Plus.[5] A method used for this research is derived from the ASF distribution, and provides a simpler way to input the kinetics directly into ASPEN Plus. The steps involved are represented as follows:

- The product distribution in FTS for successive monomer addition is described by the following equation:

  $$C_n/\sum C_n = X_n = (1-\alpha)\alpha^{n-1} \qquad (3)$$

  where X_n is the mole fraction of hydrocarbon product having n carbon atom, α is the chain growth probability function and C_n is moles of hydrocarbon with carbon number n.
- From the ASF model, it is known that $\sum C_n = (1-\alpha)$ for one mole of carbon monoxide consumed.
- The product distribution can then be represented in the following manner:

C_1= (1-α)* (1-α)

C_2: α * (1-α)* (1-α)

C_3: α^2 * (1-α)* (1-α)

-

-

C_n : α^{n-1} * (1-α)* (1-α)

- The stoichiometry for the FTS reaction can be represented as follows:

  $$CO + (2n+1)/n\ H_2 \rightarrow (1/n)\ C_nH_{2n+2} + H_2O \quad (4)$$

- From the above equations, one can deduce that n = $(1-\alpha)^{-1}$.Therefore, the stoichiometry that can be inputted into ASPEN Plus ® can be represented as follows:

  $$CO + (3-\alpha)\ H2 \rightarrow (1-\alpha)^2\ CH_4 + \alpha\ (1-\alpha)^2\ C_2H_6 + \alpha^2\ (1-\alpha)^2\ C_3H_8 + \ldots\ldots\ldots\ldots\ldots\ldots.. + \alpha^{39}\ (1-\alpha)^2\ C_{40}H_{82} + \ldots\ldots..+H_2O \quad (5)$$

Therefore, at an inputted α value of 0.9, the stoichiometry of FTS could be inputted into the simulation. In order to represent the product components with a higher carbon than 30, the following steps were taken:

1. An excel spreadsheet was created with one column including n from 1 till 100.
2. The second column included the stoichiometric coefficients at α=0.9. For example, for n=1, (1-0.9) ^2 is the inputted value in the second column of the first row.

3. The third column included the molecular weights of all the components from n=1 till 100. Each entry in the fourth column included the product of the molecular weight and the stoichiometric coefficient at each n.
4. The sum of the values in the fourth column were taken from n=31-100.
5. After that, the molecular weight for $C_{32}H_{66}$ was divided by the sum from 31-100. This value was represented by C_{32} H_{66} in the simulation, and it represented the carbon from 31-100.

The effect of changing the value of α on the product distribution was the main parametric study conducted for the ASPEN Plus simulation. The aim was to find a certain value of α that would yield the results closest to those from the Shell GTL plant opening in Qatar. However, as the α value changes in FTS, the temperature of the system also changes since α is highly dependent on temperature. Therefore, changing the value of α in the simulation by solely changing the stoichiometric coefficients does not reflect a realistic plug flow model. Therefore, an equation relating α to temperature was needed. The Levenberg–Marquardt algorithm was used to develop am empirical correlation for α. It is represented as follows:

$$\alpha = a * (t/200)^{b} * (p/45)^{c} * (U/2)^{d} \tag{6}$$

where a: 0.92± 0.03, b: -1 ± 0.2, c: 0.27 ± 0.1 and d: -0.112 ± 0.03.[38]

The value of a was taken to 0.92, b was taken to be -1, c was taken to be 0.27 and d was taken to be -0.112. U (syngas ratio) was constant at 2 and pressure was set to be constant at 45 bar. Pressure is dependent on α, but at a lesser extent than temperature, which is the reason why it was set to be constant. The temperature of the system was varied between 210 and 250℃, with ten degrees increments in value. Experimental results of α at different temperatures were obtained by Elbashir et al.[1]. The experimental results were compared with the results obtained from the Levenberg-Marquardt equation in order to determine the equation's validity. The results are shown in Table III.1.

Table III.1 Comparison between Experimental and Levenberg-Marquardt Results[38]

Temperature (^oC)	Pressure	Experimental α	Levenberg-Marquardt α	Percent Difference
210	45	0.86	0.876	1.826484018
220	45	0.85	0.836	1.674641148
240	45	0.77	0.767	0.391134289
250	45	0.71	0.736	3.532608696

The percentage difference between the experimental values and the equation values was relatively small, and the results were compatible. Therefore, the Levenberg-Marquardt equation was used to vary the value of α and the temperature simultaneously. Five different simulations were run using ASPEN Plus as follows:

- T=210 ℃ and α=0.876
- T=220℃ and α=0.836
- T=230℃ and α=0.800
- T=240℃ and α=0.767
- T=250℃ and α=0.736

At each temperature that the simulation was run at, the product distribution and the percentage of CO converted into product differed. Figure III.1 shows a graph of the percentage CO conversion versus temperature of the system.

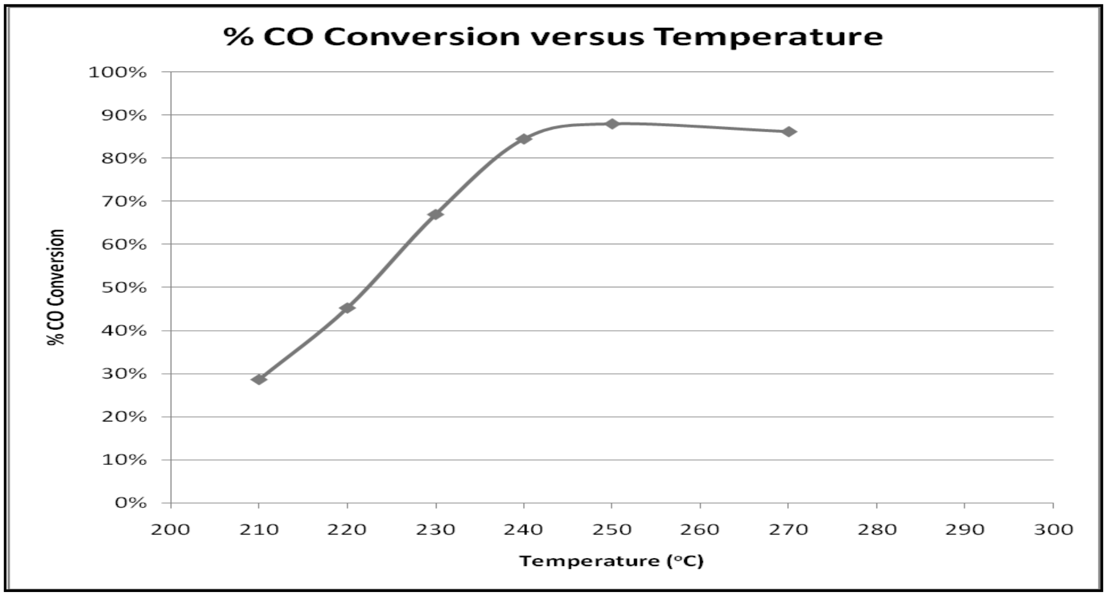


Figure III.1 Graph of % CO Conversion versus Temperature

Figure III.1 shows that as temperature increases, the percentage of CO converted into product increases. A sixth simulation run was conducted at T=270 °C, which gives an α value of 0.681. This run was performed in order to determine if there is a maximum point on the curve. The results show that after 250 °C, the percentage of CO converted into product decreases, which explains the fact that CO is being used up in the process. Figure III.2 shows the ASF distribution of the five simulation runs.

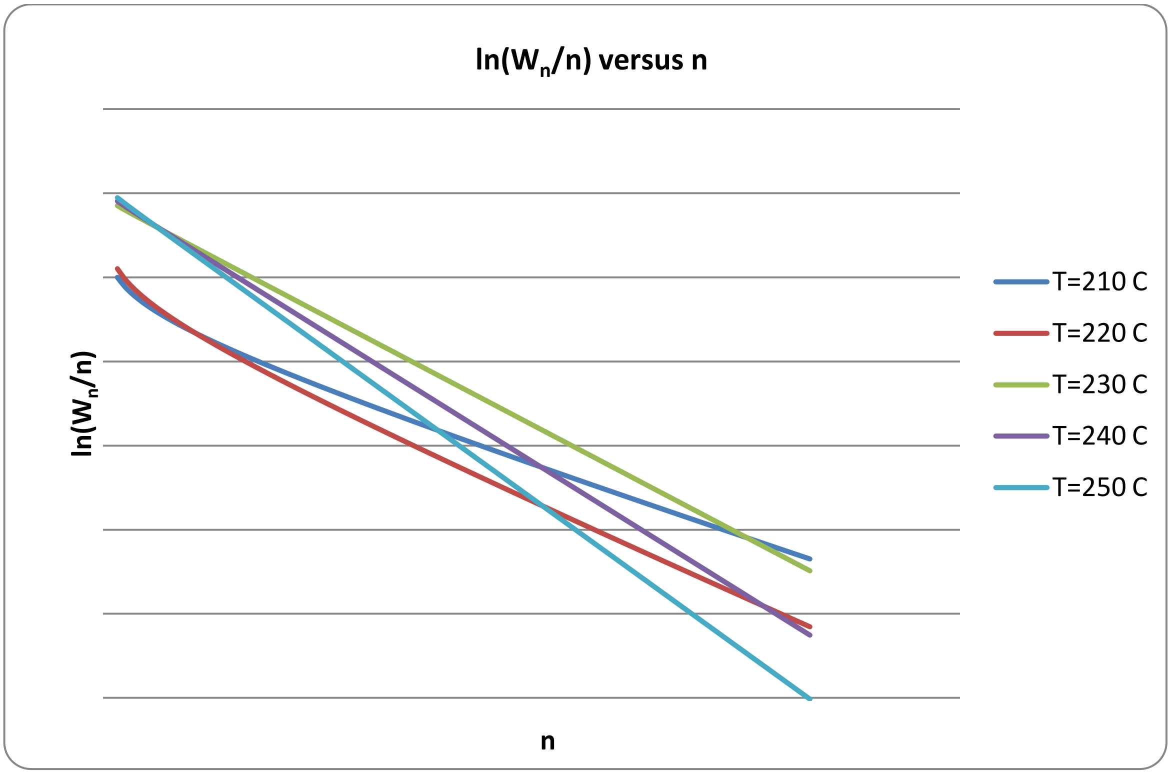


Figure III.2 Graph of ASF Distribution

The results from Figure III.2 show that as temperature increases (and consequently as α decreases), the slope of the line becomes less steep. This result conveys the same trend as expected from literature because the slope of the line is ln(α). As α decreases, ln(α) increases and the slope becomes more steep.

The selectivity of the products was determined by first summing up all of the molar flow rates of the hydrocarbons, and then dividing each hydrocarbon flow rate by the sum of all the flow rates. The hydrocarbons were represented in groups in order to make the results easier to visualize. This is shown in Figure III.3.

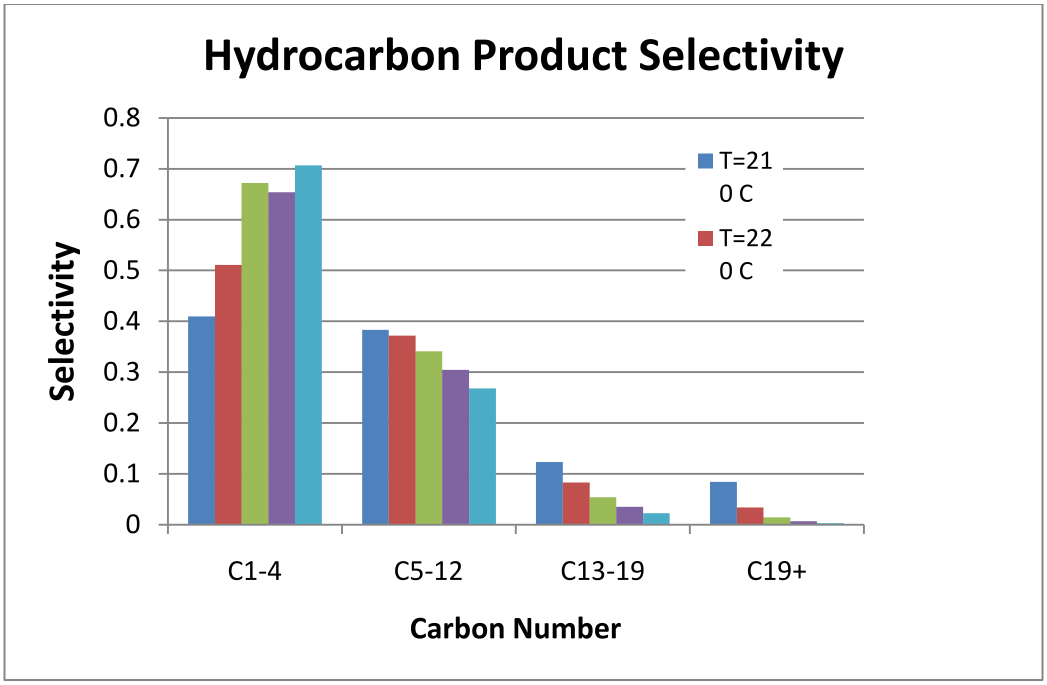


Figure III.3 Graph of Hydrocarbon Product Selectivity

The results obtained from the ASPEN Plus simulations are the foundations needed to begin incorporating supercritical phase conditions into ASPEN Plus. The next step would be to input supercritical phase conductions into the already setup PFR model. The research project also yielded valuable information about α values, CO conversion, temperature and selectivity. These parameters can be manipulated in order to obtain similar product distributions from the ASPEN Plus simulation as is obtained from the Shell GTL Pearl project in Qatar.

CHAPTER IV

SAFETY AND COST ANALYSIS

Safety Metric Analysis

After an analysis of the Pokoo-Aikins et al.[3] metric, it was discovered that several factors may differ from one case study to another. The chemical and process specific factors can vary, as well as the chosen weighting factors. In deciding on a solvent or solvent blend to use for FTS purposes, the chemicals are different from Pokoo-Aikins et al.[3], causing the chemical specific factors to change. The process specific factors can also vary. Therefore, a separate analysis was conducted for the supercritical solvents at hand in order to determine the chemical and process specific factors needed. The following is a list of chemical-specific indicators as well as the reasons behind the choice of these indicators:

1. <u>Flammability (LFL was chosen):</u> For the safety analysis of different supercritical solvents, flammability is a clear concern at such supercritical temperatures and pressures. In order to evaluate flammability, there are different parameters that can be used. From Crowl and Louvar[28], the lower flammability limit of a component (LFL) and the upper flammability limit of a component (UFL) are the main methods of identifying the limits at which a mixture is flammable. A mixture will not ignite unless it is within the LFL and the UFL of the mixture. Since the LFL and the UFL are dependent on temperature, and the UFL is also

dependent on pressure, flammability would be a major concern at supercritical temperature and pressure conditions. Another possible parameter to use is the difference of the two (UFL-LFL). It was decided that UFL-LFL shows the range of conditions at which a mixture will be flammable, but does not reflect the first point of concern at a chemical facility. LFL was decided to be used as a flammability parameter since below that limit there are no flammability concerns, and this limit identifies the first point at which flammable hazards are present. Other measures of flammability such as autoignition temperature (AIT; "the temperature at which vapor ignites spontaneously") occur at a much higher temperature than the LFL. It is important to verify whether the mixture reaches an autoignition temperature, but the first point of interest would be the lowest flammability value, which is the LFL.[28]

When calculating the LFL of different solvents, it is important to consider the fact that LFL changes with temperature. An equation from Crowl and Louvar[28] to account for elevated temperatures is given below:

$$\mathrm{LFL_T} = \mathrm{LFL_{25}} - \frac{0.75}{\Delta \mathrm{H_c}}(\mathrm{T} - 25) \tag{7}$$

where $\Delta \mathrm{H_c}$ is the net heat of combustion in kcal/mole and T is the temperature in ^{o}C.[28] The temperature to be used would depend on the section within the plant that is being considered. As will be discussed later, different sections in the FTS process will be analyzed. If a mixture stream is being analyzed, then the temperature of the mixture i.e. solvent and syngas, should be used. If however only the pure solvent stream is being analyzed, then the temperature of the pure solvent should be used.

2. Toxicity (TLV-TWA was chosen): A second concern would be toxicity when using the different solvents. From Crowl and Louvar[28] a toxic hazard is defined as the possibility of harm resulting from an exposure of a chemical to a living organism. Pokoo-Aikins et al.[3] used LC_{50} as an indicator of toxicity for the solvents she was interested in. For hydrocarbon solvents, it was found that the threshold limit value with a time-weighted average (TLV-TWA) had the most information for representing hydrocarbon solvents. This parameter represents the time-weighted average in which most workers can be exposed to a chemical every day in a regular eight hour workday without suffering from any effects. Not much information was available for solvents when using LC_{50} or other measures of toxicity.[28]
3. Reactivity (no reactivity concerns): An idea obtained from the I-Safe method was to use reactivity as a chemical specific factor.[16] All of the hydrocarbon solvents were investigated for any reactivity issues, but they are all found to be non-reactive in air. Reactivity concerns of the hydrocarbon solvents with the syngas i.e. with carbon monoxide or hydrogen were also investigated. However, the Material Safety Data Sheets of the hydrocarbons showed that no reactivity concerns when in contact with the materials in syngas is available.[2]
4. Vapor pressure: Of importance is also to account for adverse effects if the solvents leak from the piping systems into the atmosphere. When in contact with

air, the solvents with higher vapor pressures will be able to form vapors quicker and there will be a greater potential for dangerous vapor clouds to ignite. Therefore, the vapor pressures of all of the solvents were calculated. Vapor pressure is dependent on temperature. The temperature at which the vapor pressures are calculated is at ambient temperature i.e. 25 °C, since any release of material in the system will be to the atmosphere.[28]

In order to calculate vapor pressures, the Antoine Equation may be used (e.g., Reid et al.[39]). The Antoine Equation is represented as follows:

$$\ln(P^{sat}) = A - \frac{B}{T+C} \tag{8}$$

where T is the given temperature in K, P^{sat} is the vapor pressure at saturation in mm Hg, and A, B and C are constants that were published by Reid et al.[39]. The listed process specific indicators as well as the reasons behind the choices are shown below:

1. <u>Temperature:</u> This includes two distinct temperature readings. The first is the critical temperature of the mixture of solvent with syngas. The second is the critical temperature of the pure solvent. From Table IV.1, it can be seen that the values for these two temperatures are slightly different. Depending on the section in the FTS plant being considered, the critical mixture temperature or the pure critical temperature should be utilized.
2. <u>Pressure:</u> This also includes two distinct pressure readings. The first is the critical pressure of the mixture of solvent with syngas. The second is the critical

pressure of the pure solvent. From Table IV.1, it can be seen that the values for these two pressures can vary drastically. Again, depending on the section of the FTS plant being considered, the critical mixture pressure or the pure critical pressure should be utilized.

By including the chemical and process specific factor values, the solvent safety index (SSI) equation can be represented as follows:

$$SSI = I_{\text{flammability}} \times WF_{\text{flammability}} + I_{\text{toxicity}} \times WF_{\text{toxicity}} + I_{\text{vapor pressure}} \times WF_{\text{vapor pressure}} + I_{\text{temperature}} \times WF_{\text{temperature}} + I_{\text{pressure}} \times WF_{\text{pressure}} \quad (9)$$

where "I" is the index for each safety category and "WF" is the weighting factor for respective safety category.

For the SSI to be calculated, the different units of the indicators cannot simply be added. For example, units of flammability cannot be added to the units of toxicity and so forth in a single equation. Therefore, normalization of units within the equation is needed. In order for the properties of all the different safety factors to be multiplied together, they need to be represented as dimensionless quantities (since all the factors have different units i.e. bar, ppm, etc.). A basis needs to be determined so that all the different dimensions can be divided by the basis in order to create a dimensionless quantity. A typical safety table at hand will include all the solvent mixtures in different rows in one column, and all the indicators (flammability, toxicity, etc.) in subsequent columns.

N-Hexane was identified to be the basis of all of the other solvents, since it has been found to be the most feasible solvent to be used for supercritical FTS purposes in terms of applicability and practicality, and most supercritical FTS laboratory experiments are conducted with N-Hexane as a solvent. In addition it has been found to be very successful as a single supercritical solvent for FTS purposes.[2] Therefore, after of the chemical and process specific factors are determined, all of the values will be divided by those of N-Hexane (so, the critical temperature of N-Propane mixture will be divided by that of N-Hexane; the flammability of the N-Propane mixture will be divided by that of N-Hexane, and so forth) so that all the properties become dimensionless.[2] This way, the values to be inputted into the SSI will be dimensionless and can be added together after multiplying each property by its weighting factor.[3]

The weighting factor values can in general be evaluated based on the specific application and the relative importance to the user.[3] For example, an individual reading this paper who is trying to conduct a safety analysis on a chemical plant that has recently been involved in a large fire, would be able to raise the flammability factor in the SSI for their analysis. Therefore, the weighting factors are relative and can be changed depending on the aims and focus of different audiences. In order to develop a case study for this research however, weighting factor values were assumed based on the chemical and process specific factor values, as will be discussed later.

In order to assess the solvent involvement in the process, it is important to understand the method of entry of solvent into the reactor. The solvent is first mixed with the syngas in a static mixer, and then heating occurs within the static mixture to ensure the formation of a single phase as the feed to the reactor. After that, the exit stream of the static mixer gets compressed to an elevated pressure before entering the catalyst bed. It is important to have proper mixing prior compression to avoid the complication of compressing multiphase mixtures.[2]

Therefore, there should be a differentiation between the pure solvent(s) stream and the solvent with syngas stream entering the catalyst bed i.e. the mixed stream. The pure solvent stream is the solvent feed prior to being mixed with syngas. The mixed stream is the stream that contains both solvent and syngas. Both streams are considered for different purposes that will be explained later. The critical properties of the solvent and the reaction mixture may differ as indicated in previous studies.[4] As shown in Table IV.1 below, the values for the critical temperatures and pressures of the pure and of the mixed streams significantly differ.

Table IV.1 Critical Properties of Pure and Mixed Solvents by using a 3:1 Molar Ratio of Solvent: Syngas[2]

Solvent	Pure T_c (°C)	Mix T_c (°C)	Pure P_c (bar)	Mix P_c (bar)	Pure ρ_c (kg/m^3)	Mix ρ_c (kg/m^3)
Propane	96.75	89.2	42.5	99.6	224.81	207.7
n-Butane	151.84	145.6	38.0	90.3	227.78	214.2
n-Pentane	196.6	192.0	33.6	82.0	232.27	213.7
n-Hexane	234.5	230.7	30.2	73.9	233.49	212.3
n-Heptane	266.85	264.2	27.4	67.6	235.44	211.2
n-Octane	295.75	293.4	24.9	61.5	232.31	208.6
n-Nonane	321.85	319.6	23.0	56.7	230.83	205.5
n-Decane	344.65	342.9	21.1	52.0	227.63	202.9

Next, attention is given to the evaluation of the safety index for the complete FTS system. Pokoo-Aikins et al.[3] developed a safety metric based on a single location in a facility. In the evaluation of a FTS facility however, there are several important locations where safety aspects should be considered. These identified can be seen in Figure IV.1 and are listed below:

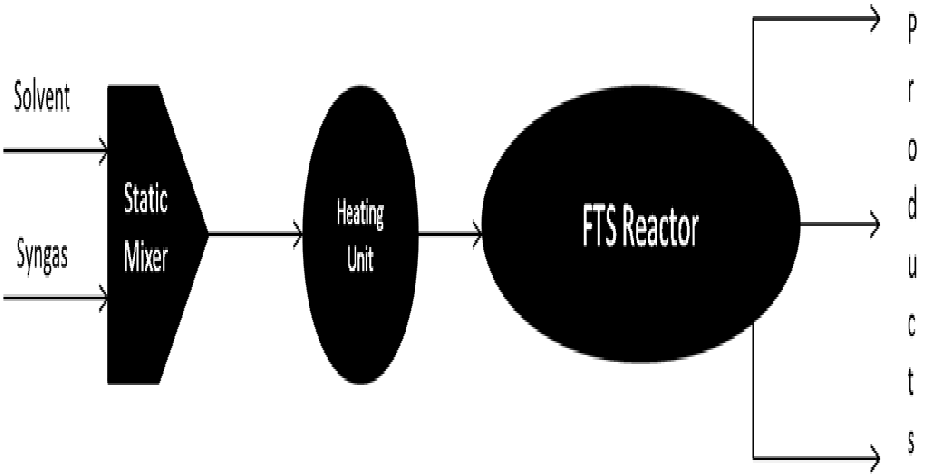


Figure IV.1 Entry Points to the FTS System

1. Pure solvent stream:

   The pure supercritical solvent streams in themselves have safety concerns since they are at elevated temperatures and pressures. The supercritical solvents are first fed separately into a stream and are then later mixed with the syngas in a static mixer. It is important to consider the effect of the leakage of the pure hydrocarbons into the environment. Although he probability that the pure solvents into an external system is low, the consequence could be very high. Therefore, an SSI needs to be evaluated for the pure solvent stream before it is mixed with the syngas.

   In order to calculate SSI_1 (for pure solvent stream), the process specific factors (temperature and pressure) should include the critical temperatures and pressures of the pure solvent. For the chemical specific factors, the calculation of the LFL at elevated temperatures will include the value of the critical temperature of pure solvent, the TLV will remain constant, and the vapor pressure will include ambient temperature conditions.

2. Exit stream from the static mixer:

   A second point of interest is at the exit of the static mixer. Within the static mixer, the pure solvent and the syngas are mixed together and temperature in the static mixer increases. Therefore, at the exit of the static mixer, a mixture of solvent and syngas exists and presents a separate safety hazard. An SSI needs to be conducted at the outlet point of the static mixer.

   In order to calculate SSI_2 (for exit stream from the static mixer), the process specific factors (temperature and pressure) should include the critical temperatures and pressures of the mixture of solvent with syngas. For the chemical specific factors, the calculation of the LFL at elevated temperatures will include the critical temperature of the mixture, the TLV will remain constant, and the vapor pressure will include ambient temperature conditions.

3. Input stream to the FTS reactor:

   The FTS catalyst bed has a specific range of operating temperatures and pressures that it can withstand. Therefore, after the static mixer, the system undergoes heating and compression in order to reach the desired temperature and pressure parameters to satisfy the FTS catalyst bed. The entry point to the FTS reactor would be a third point of analysis since it would have a different temperature and pressure than at the outlet of the static mixer. It is recognized that the performance of the different solvents may slightly change since the solvent to syngas ratio is set at a fixed ratio. The conversion and selectivity values may vary slightly, but this variation is considered to be within an acceptable margin of error. The solvent to syngas ratio, as well as the temperature and pressure for the FTS reactor are set to be fixed in order to be able to change different parameters and in order to compare the behavior of the different solvents.[2]

In order to calculate SSI_3 (for input stream into the FTS reactor), the process specific factors (temperature and pressure) include an average desired temperature and pressure value of the catalyst bed (taken to be 250 ^{o}C and 65 bar).[1] For the chemical specific factors, the calculation of the LFL at elevated temperatures will include the 250 ^{o}C, the TLV will remain constant, and the vapor pressure will include ambient temperature conditions.

4. Within the FTS reactor:

Within the FTS reactor, heating takes place. Temperature increases within the reactor until a peak point, and then decreases until it reaches the outlet of the reactor. The most hazardous place within the FTS reactor would be the peak point at the highest temperature; therefore, a fourth SSI will be calculated at the peak temperature point within the reactor.

In order to calculate SSI_4 (for within the FTS reactor), a shortcut method for establishing the steady state criteria for a reactor to be stable is used.[40] The shortcut method can be expressed as follows:

$$\Theta = \frac{T_{max} - T_{wall}}{\Delta T_c} \qquad (10)$$

where $\Theta < 1$ implies that the reactor is stable and $\Theta > 1$ implies that the reactor will never reach steady state. The equation used to calculate ΔT_c is as follows:

$$\Delta T_c = \frac{R x T^2}{E} \qquad (11)$$

where R is the universal gas constant, E is the activation energy, T_{max} is the maximum temperature that is reached within the reactor, T is the reactor temperature, T_{wall} is the reactor temperature at the wall and ΔT_c is the critical temperature difference.

Using a supercritical fluid FTS activation energy of 103.9 kJ/mol, a250 ^{o}C temperature at the entrance of the reactor and a pressure of 65 bar, ΔT_c can be calculated from Equation 11 to be 21.9 ^{o}C. Therefore, T_{max} can be calculated to be 271.9 ^{o}C.[40] For the chemical specific factors, the calculation of the LFL at elevated temperatures will include the 271.9 °C, the TLV will remain constant, and the vapor pressure will include ambient temperature conditions.

An SSI value will be calculated for each of the four systems at hand. After that, the total SSI will be calculated as the sum of the individual SSI's of the different systems. In this case, it is thought that al the SSI's are equally weighted. For example, the safety concerns within the FTS reactor are considered to be as important as the safety concerns from the exit of the static mixer. The reason behind this choice is that no information about the process is available yet in order to state that one SSI is more important than another, since the supercritical FTS process is still in its design phase. The equation to calculate the overall SSI is shown as follows:

$$SSI_{Total}=SSI_1+ SSI_2+ SSI_3+ SSI_4 \tag{12}$$

Trading Off Objectives

In order to decide on the best solvent blend to be used, both cost and safety need to be evaluated. A technique that can be used to determine the most effective balance between two parameters is the Pareto-curve optimization which represents the tradeoff between different objectives. An example of using the Pareto-curve was obtained from Al-Mutairi et al.[41], who were attempting to find a balance between profit and safety metric. In their case, the safety metric that was used is the Dow F&EI index. It was stated that the Pareto-curve was beneficial in clarifying the process being investigated, especially when the process is still in the design phase. In the case of analyzing supercritical solvents for FTS purposes, the goal is to show the tradeoff between the safety and economic criteria for solvent selection. The graph of SSI versus cost can help to decide if it is convenient to pay a little more money in order to improve safety.[2]

There are many factors that affect the cost of process safety such as the cost of fire and explosion protection, alarms and controls, cost of equipment, maintenance of equipment and others.[42] What is considered however for the analysis of supercritical solvents for FTS is the cost of the raw material i.e. the solvent. Add-on measures such as alarms and controls are generally accounted for in later stages of the process. The cost of heating is assumed to be constant, since all the solvents are assumed to enter the reactor at an average desired temperature and pressure of the catalyst bed i.e. 250 ^{o}C and 65 bar. Therefore, the cost of heating is not included in the cost analysis.

CHAPTER V

RESULTS

Safety Metric Results

The steps to calculate the overall safety metric below will only illustrate the calculations for SSI_2 i.e. for the exit stream of the static mixer. In order to calculate SSI_1, SSI_3 and SSI_4, similar steps will be taken and are illustrated in Appendix I. Table V.1 shows the solvents in one column and all of the process specific factors in subsequent columns. The mixture temperatures obtained from the paper by Elmalik et al.[2] were listed in units of °C and were then converted to absolute units i.e. in K. The mixture pressures were obtained from Elmalik et al.[2] and are presented in units of bars.

Table V.1 Process Specific Factors for the Supercritical Solvents for SSI_2

Solvent	Mixture Tc (°C)	Mixture Tc (K)	Mixture Pc (bar)
Propane	89.20	362.35	99.60
n-Butane	145.60	418.75	90.30
n-Pentane	192	465.15	82
n-Hexane (Basis)	230.70	503.85	73.90
n-Heptane	264.20	537.35	67.60
n-Octane	293.40	566.55	61.50
n-Nonane	319.60	592.75	56.70
n-Decane	342.90	616.05	52

Table V.2 shows the supercritical solvents in one column, and the chemical specific factors in subsequent columns. The LFL of the different solvents at 25 °C were obtained from Material Safety Data Sheets for each chemical. In order to calculate the LFL at elevated temperatures, the ΔH_c values were found for each solvent from Crowl and Louvar[28] in units of kJ/mol, and were converted into kCal/mol for consistency of units into the "LFL at elevated temperatures" equation. The LFL values were then calculated at the critical mixture temperatures of the solvents mixed with syngas. The TLV values were obtained from Material Safety Data Sheets. The vapor pressures were obtained from Antoine Equations from Reid et al.[39] and were evaluated at ambient temperatures.

Table V.2 Chemical Specific Factors for the Supercritical Solvents for SSI_2

Solvent	LFL at 25 °C (%)	ΔHc (KJ/mol)	ΔHc (kCal/mol)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	2.20	2219.90	530.57	2.11	800	7093.41
n-Butane	1.90	2877.50	687.74	1.71	1000	1821.37
n-Pentane	1.50	3536.60	845.27	1.35	600	512.89
n-Hexane (Basis)	1.20	4194.50	1002.51	1.05	50	151.28
n-Heptane	1.20	4780.60	1142.59	1.04	400	45.86
n-Octane	1	5511.60	1317.30	0.84	300	13.98
n-Nonane	0.80	0	0.00	0.80	200	4.29
n-Decane	0.80	6737	1610.18	0.65	0	1.30

The solvent fractions were then calculated in Table V.3 i.e. the values of the factors (both process and chemical specific) divided by the basis value of N-Hexane (for both the process and chemical specific factors) in order to obtain dimensionless quantities to be used in the SSI equations.

Table V.3 Solvent Fractions for the Process and Chemical Specific Factors for SSI_2

Solvent Fractions	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	0.72	1.35	2.02	16	46.89
n-Butane	0.83	1.22	1.69	20	12.04
n-Pentane	0.92	1.11	1.29	12	3.39
n-Hexane	1	1	1	1	1
n-Heptane	1.07	0.91	0.99	8	0.30
n-Octane	1.12	0.83	0.81	6	0.09
n-Nonane	1.18	0.77	0.76	4	0.03
n-Decane	1.22	0.70	0.62	0	0.009

The next step was to assign priority indices for each range of values within a process or chemical specific factor. In order to do this, the list of mixture temperatures for example was analyzed and divided into sections from 1 until 5 (with 1 including the least hazardous conditions and 5 including the most hazardous conditions). The remaining factors i.e. mixture pressure, LFL, etc. were also divided into sections of five. Table V.4 shows the priority indices for the process and chemical specific factors of the solvents.

Table V.4 Priority Indices for the Process and Chemical Specific Factors for SSI_2

Priority Index	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
1	340-400	50-60	0.65-0.95	0-200	<5
2	400-460	60-70	0.95-1.25	200-400	<50
3	460-520	70-80	1.25-1.55	400-600	<500
4	520-580	80-90	1.55-1.85	600-800	<5000
5	580-640	90-100	1.85-2.15	800-1000	<50000

From the priority indices, weighting factors can be assigned. For example, starting with N-Propane and continuing to the other solvents, the mixture temperatures were ranked by using weighting factors. Therefore, since the mixture critical temperature of N-Propane was 362. 35 K, it was ranked with a weighting factor of 1 (since it is between 340 and 400 K). The same is applied for all the solvents and for all of the factors. Table V.5 shows the weighting factor results for the different solvents.

Table V.5 Weighting Factor Results for the Supercritical FTS Solvents for SSI_2

Solvent	WF for Mixture Tc (K)	WF for Mixture Pc (bar)	WF for LFL at Mixture Tc (%)	WF for TLV (ppm)	WF for Vapor P (mm Hg)
Propane	1	5	5	5	5
n-Butane	2	5	4	5	4
n-Pentane	3	4	3	4	4
n-Hexane	3	3	2	1	3
n-Heptane	4	2	2	3	2
n-Octane	4	2	1	2	2
n-Nonane	5	1	1	1	1
n-Decane	5	1	2	1	1

Since the solvent fractions and the weighting factors of all the solvents and for all the factors were available, SSI 2 could then be calculated. The SSI is then calculated using Equation 9 and the values are shown in Table V.6.

Table V.6 SSI_2 Values for the Different Solvents

Solvent	SSI_2
Propane	331.98
n-Butane	174.73
n-Pentane	72.65
n-Hexane	10
n-Heptane	33
n-Octane	19.16
n-Nonane	11.44
n-Decane	8.07

Similar steps are conducted in order to calculate SSI_1, SSI_3 and SSI_4. When the values of SSI_1, SSI_2, SSI_3 and SSI_4 are added together, the final result of the safety metric (the overall SSI) is achieved. The overall SSI value for each supercritical solvent is shown in Table V.7.

Table V.7 Overall SSI Values for the Supercritical FTS Solvents

Solvent	SSI Total
Propane	1315.38
n-Butane	673.59
n-Pentane	277.59
n-Hexane	34
n-Heptane	122.58
n-Octane	67.52
n-Nonane	36.48
n-Decane	22.88

The safety metric results show that the lowest SSI is for N-Decane, and the highest SSI is for N-Propane. Even before conducting a cost analysis, it is considered unlikely that solvents such as Propane and N-Butane will be used as supercritical FTS solvents since they have the highest SSI values.

Trading Off Objectives Results and Discussion

The cost of the analyzed hydrocarbons especially the higher molecular weight hydrocarbons, are difficult to come across in the open literature. What is needed for the research on supercritical solvents for FTS purposes is simply an estimate of the cost of the hydrocarbons in order to get a feel for the tradeoff between cost and safety. N-Propane and N-Butane were available from a Chemical Week[43], n-Pentane and n-

Hexane were obtained from the paper by Elmalik et al.[2]. n-Heptane was available from the ICIS pricing[44] and n-Octane was obtained from Chemical Market Reporter[45]. These were the latest dates that were found to be published in literature about these hydrocarbon solvents. For n-Nonane and N-Decane, no information was found in the open literature. This may be due to the fact that these hydrocarbons are not commonly used as single solvents in industry. Therefore, an assumption was made about the heat of combustion of these chemicals in order to estimate and update their prices. It is assumed that there is a linear relationship between the cost of the basis solvent (n-Hexane) and its heat of combustion. Therefore, using this relationship and using the heat of combustion of n-Nonane, the cost of n-Nonane can be calculated. The same can be done for the cost of n-Decane. Basic unit conversions were applied to the cost values in order for all of them to be presented in the units of \$/gallon. Table V.8 shows the cost of each hydrocarbon solvent that was analyzed for supercritical FTS purposes, as well as the SSI_{Total} value for each solvent.

Table V.8 Cost and SSI Value of Pure Supercritical Solvents for FTS Purposes

Solvent	Cost ($/gallon)	SSI
n-Propane	1.13	1315.38
n-Butane	1.33	673.59
n-Pentane	2.67	277.56
n-Hexane	2.65	34
n-Heptane	1.43	122.58
n-Octane	6.62	67.52
n-Nonane	6.36	36.48
n-Decane	7.94	22.88

From Elmalik et al.[2], it was clearly specified that Propane, N-Butane, n-Nonane and N-Decane could not be used as sole solvents for supercritical FTS purposes. Therefore, a cost analysis for single solvents was conducted for C_5 until C_8 (since the other solvents cannot be applied in FTS reactors). Figure V.1 shows the Pareto curve in which the overall SSI for the solvents from C_5 until C_8 are plotted on the vertical axis, and the overall cost of each solvent is plotted on the horizontal axis.

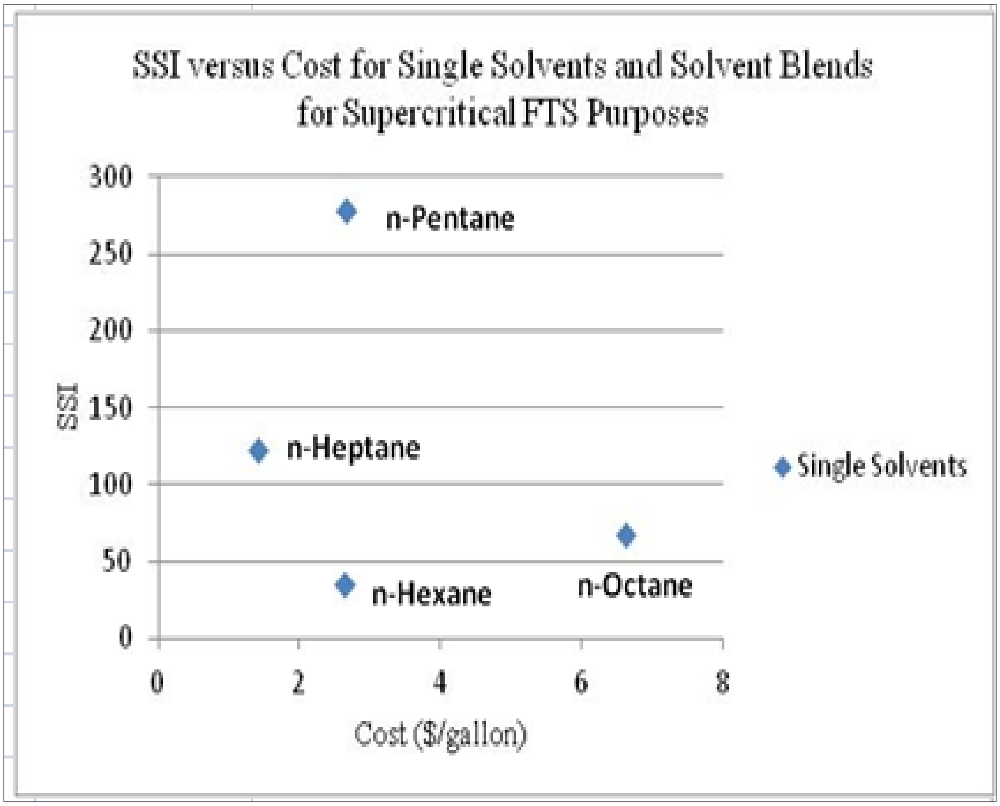


Figure V.1 Pareto Curve of Single Supercritical Solvents for FTS Purposes

From Figure V.1, the following results can be deduced:

- N-Pentane has the highest SSI value (much higher than any of the other solvents) and does not have the lowest cost. This is an important finding since researchers such as Elmalik et al.[2] have indicated that n-Pentane is favorable as a solvent for technical and cost reasons. However, Figure V.1 shows that n-Pentane can be eliminated from the choice of possible single supercritical FTS solvents because of its very high SSI value compared to the other solvents.

- N-Octane has the highest cost compared to the other supercritical solvents (much higher than any other cost in Figure V.1), but has the second to lowest SSI value. Since Elmalik et al.[2] have suggested that n-Octane is difficult to purify, it can most eliminated from the possible choice of single FTS solvents.
- The main tradeoff is between n-Hexane and n-Heptane. N-Hexane has the lowest SSI value, but n-Heptane has the lowest cost. Therefore, a possibility of a solvent blend between n-Hexane and n-Heptane is investigated.

Even though it may be relatively cheap as shown by the Pareto-curve in Figure V.1 to use single solvents for supercritical FTS purposes, it is generally preferred to use solvent blends on the commercial scale. The list of preferred solvents were chosen partly because they are products of the FTS reaction themselves, so additional equipment would not need to be purchased to accommodate the solvents. Also, if pure hydrocarbon solvents are chosen, it would be difficult technically and well as in terms of cost to separate and then recycle the hydrocarbon from the mixtures coming out of the FTS reaction. Therefore, solvent blends as well as predefined fuel cuts are preferred to pure solvents for supercritical FTS purposes.[2]

Different supercritical solvent blends were investigated for FTS purposes. As mentioned earlier, the calculated cost is assumed to be a weighted average of the cost of all of the solvents, and the SSI is assumed to be a weighted average of the SSI of all of the solvents. The first blend was decided upon based on the results from Figure V.1. Blends 2 and 3 were investigated based on results Linghu et al.[46]. Blend 4 was investigated based on results from Jacobs et al.[47]. Blend 5 is considered to be a predefined fuel cut of light naphtha. Researchers such as Elmalik et al.[2] included chemicals such as 2,2-Dimethylbutane, 2,3-Dimethylbutane and 3-Methylpentane in their composition of light naphtha. Such chemicals are not products of the FTS reaction, so a suggestion would be to include chemicals that are mainly products of the FTS reaction into the light naphtha composition. The composition in all light naphtha blends include mostly n-Hexane, as well as other middle-distillate hydrocarbons such as n-Pentane, n-Heptane and n-Octane. Therefore, the compositions of different mixtures of light naphtha were assumed. These blends are shown as follows:

- Blend 1: 50 % n-Hexane and 50% n-Heptane by volume
- Blend 2: 90% n-Hexane, 2% n-Pentane, 2% n-Heptane, 2% n-Octane, 2% n-Nonane and 2% n-Decane[46]
- Blend 3: 75% n-Hexane and 25% n-Decane[46]
- Blend 4: 55 % n-Hexane and 45 % n-Pentane[47]
- Blend 5: 70 % n-Hexane, 10 % n-Pentane, 10 % n-Heptane and 10 % n-Octane[2]

Table V.9 shows the weighted average of the cost and of the SSI of the identified solvent blends.

Table V.9 Cost and SSI Value of Supercritical Solvent Blends for FTS Purposes

Solvent Blend	Cost ($/gallon)	SSI
50 % C6, 50 % C7	2.04	78.29
90 % C6, 2% C5, 2 % C7, 2% C8, 2 % C9, 2% C10	2.89	41.14
75 % C6, 25 % C10	3.97	31.22
55 % C6, 45 % C5	2.66	143.62
70 % C6, 10 % C5, 10 % C7, 10 % C8	2.93	70.57

Figure V.2 incorporates the results of Figure V.1, as well as the results of the investigated solvent blends.

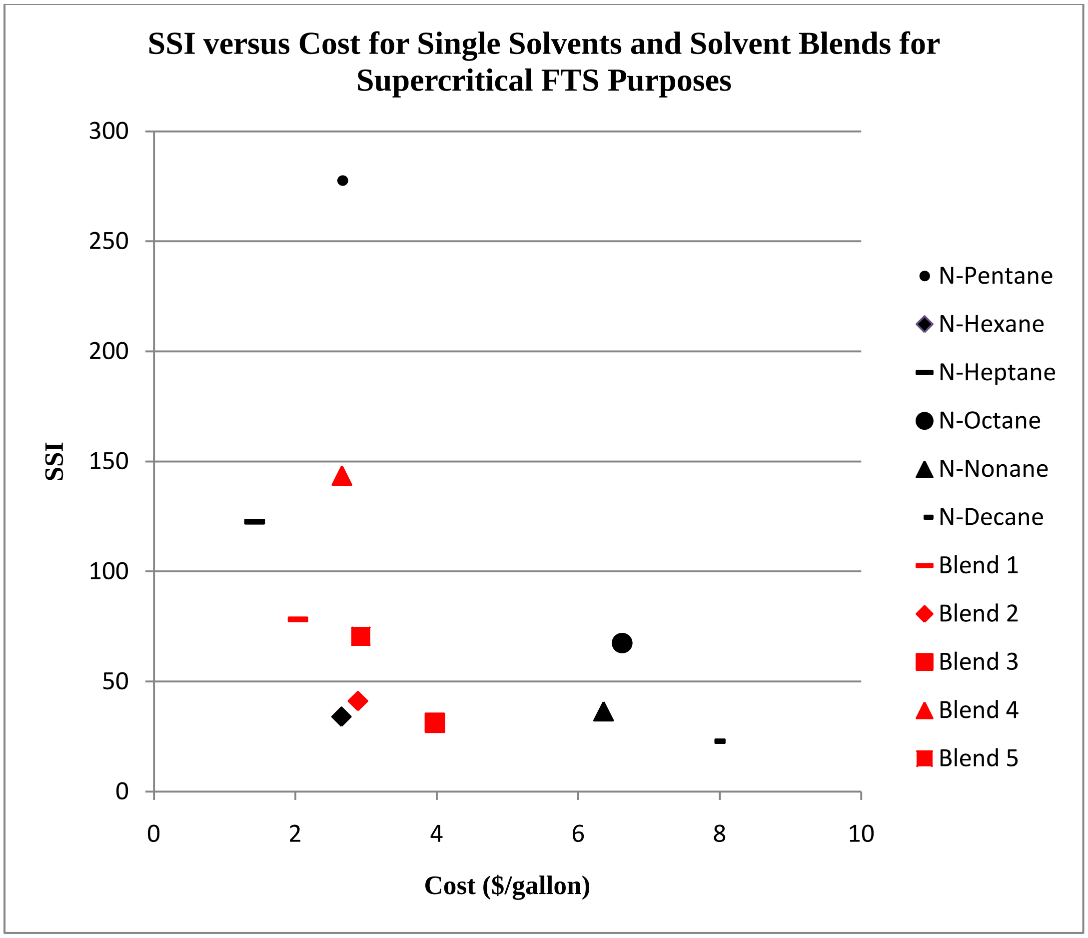


Figure V.2 Pareto Curve of Single Supercritical Solvents as well as Solvent Blends for FTS Purposes

The results obtained from the solvent blends can be described as follows:

- Blend 1 seems to solve the tradeoff issue between using either n-Hexane or n-Heptane for supercritical FTS purposes. It is at a lower cost than n-Hexane and at a lower SSI than n-Heptane. Blend 1 can be further investigated by using different mixture compositions. If a decision maker reading this paper would like a different SSI value for the given blend for example, then he will be able to use a different blend of n-Heptane and n-Hexane compositions.

- Blend 2 also seems to be an effective blend since it has a relatively low cost, as well as a relatively low SSI compared to the other solvents. However, Elmalik et al.[2] mention that it may be impractical to mix a large number of solvents together in terms of design of the commercial FTS unit.
- Blend 3 also seems to be an effective blend since it has the lowest SSI out of all the single solvents and solvent blends. It also has a relatively low cost. This blend can be further investigated to determine the practicality of using it in commercial FTS processes. It may be possible that this blend is difficult to be achieved commercially in terms of separation of the solvent blend from the FTS products.
- Blend 4 is not recommended for use because many other solvents have lower SSI and cost values than Blend 4.
- Blend 5 also seems to be a plausible blend to use since it has a relatively low cost as well as relatively low SSI. Light naphtha is also a predefined fuel cut and would be technically viable to use as a supercritical FTS solvent.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A systematic approach has been adopted for the incorporation of safety aspects in the conceptual design and solvent selection of supercritical FTS. A safety index comprising key design and operational factors has been constructed and integrated with techno-economic analysis. A Pareto-approach for simultaneously considering the various technical, economic, and safety objectives has been developed. In some cases, certain solvent blends can address the desired objectives for safety, cost, and performance. In other cases, the Pareto representation is used to trade off these objectives.[41]

The recommended single solvents include n-Hexane and possibly n-Heptane, even though it is more technically plausible to use solvent blends instead of pure solvents. The possible solvent blends for supercritical FTS purposes include the “ 50% n-Hexane and 50 % n-Heptane” blend, the “90% n-Hexane, 2% n-Pentane, 2% n-Heptane, 2% n-Octane, 2% n-Nonane and 2% n-Decane” blend, the “75% n-Hexane and 25% n-Decane” blend and the light naphtha blend.[46] All of these blends need to further investigated in terms of technical and commercial applicability.

Chemical processing companies are continuing to invest money into operating FTS plants and hopefully in the future, they will begin exploring the utilization of non-conventional operations, such as designing a reactor that facilitates conducting the reaction in the supercritical phase. The following recommendations are made for future work:

- Development of process-wide simulation model while incorporating detailed kinetic models
- Development of an optimization formulation that includes the developed safety metrics along with techno-economic models. The optimization formulation can be coded using computer-aided optimization software to automate the decision-making process for solvent selection and for establishing tradeoffs between safety and economics
- Experimental verification of the theoretical results obtained in this work

LITERATURE CITED

1. Elbashir NO, Bukur DB, Durham E, Roberts CB. Advancement in Fischer-Tropsch Synthesis via Utilization of Supercritical Fluids as Reaction Media. *AIChE Journal*, 2010;56:997--1015.
2. Elmalik E, Tora E, El-Halwagi MM, Elbashir NO. Solvent Selection for Commercial Supercritical Fischer-Tropsch Synthesis Process. *Fuel Processing Technology*, 2011;92:1525--1530.
3. Pokoo-Aikins G, Heath A, Mentzer RA, Mannan MS, Rogers WJ, El- Halwagi MM. A Multi-criteria Approach to Screening Alternatives for Converting Sewage Sludge to Biodiesel. *J. Loss Prevention in the Process Industries*, 2010; 23:412--420.
4. Bao B, El-Halwagi MM, Elbashir NO. Simulation, Integration, and Economic Analysis of Gas-to-Liquid Processes. *Fuel Processing Technology*, 2010a;91: 703--713.
5. Hao X, Djatmiko M, Xu Y, Wang Y, Chang J, Li Y. Simulation Analysis of a Gas-To-Liquid Process Using Aspen Plus. *Chem. Eng. Technology*, 2008;31:188--196.
6. Wakamura O. Development of GTL (Gas to Liquid) Technology. *Nippon Steel Technical Report*, 2005;382:2--7.
7. Bao B, El-Halwagi MM, Elbashir NO. Techno-Economic Analysis of a Gas-To-Liquid process. *Proceedings of the 2nd Annual Gas Processing Symposium*. The Netherlands, 2010b;2:287--296.
8. Huang X, Roberts CB. Selective Fischer-Tropsch synthesis over an A_{l2O3} supported cobalt catalyst in supercritical hexane. *Fuel Processing Technology*, 2003;283:81--99.
9. Uner DO. A Sensible Mechanism of Alkali Promotion in Fischer-Tropsch Synthesis: Adsorbate Mobilities. *Ind. Eng. Chem. Res., 1998;37:*2239--2245.

10. FOX III JM. Fischer-Tropsch Reactor Selection. *Catalysis Letters*, 1990;7:281--292.
11. Elbashir NO, Roberts C. Reaction pathway and kinetic modeling of Fischer-Tropsch synthesis over an alumina supported cobalt catalyst in supercritical-hexane. *Petroleum Chemistry Division Preprints*, 2004;49:157--160.
12. Elbashir NO, Dutta P, Manivannan A, Seehra MS, Roberts CB. Impact of cobalt-based catalyst characteristics on the performance of conventional gas-phase and supercritical-phase Fischer-Tropsch synthesis. *Applied Catalysis A*, 2005;285: 169--180.
13. Elbashir NO, Buping B, El-Halwagi MM. An approach to the design of advanced Fischer-Tropsch reactor for operation in near-critical and supercritical phase media. *Proceedings of the 1st Annual Gas Processing* Symposium. The Netherlands, 2009;1:423--433.
14. Sie S, Krishna R. Fundamentals and selection of advanced Fischer-Tropsch reactors. *Applied Catalysis A*, 1999;186: 55--70.
15. Abbaslou RM, Mohammadzadeh JS, Dalai AK. Review on Fischer- Tropsch synthesis in supercritical media. *Fuel Processing Technology*, 2009;90:849--856.
16. Rahman A, Heikkila¨ A, Hurme M. Comparison of inherent safety indices in process concept evaluation. *Journal of Loss Prevention in the Process Industries*, 2005;18:327--334.
17. Kletz TA. *Plant design for safety: A user-friendly approach.* New York, 1991.
18. Suardin J, Mannan MS, El-Halwagi MM. The integration of Dow’s fire and explosion index (F&EI) into process design and optimization to achieve inherently safer design. *Journal of Loss Prevention in the Process Industries*, 2007;20:79--90.
19. Hendershot D. Inherently safer chemical process design. *Journal of Loss Prevention in the Process Industries*, 1999; 10: 151--157.
20. Dow Chemical Company. *Fire & explosion index hazard classification guide, 7th ed.,* American Institute of Chemical Engineers. New York, 2003.

21. Edwards DW, Lawrence D. Assessing the inherent safety of chemical process routes: Is there a relation between plant costs and inherent safety? *Chemical Engineering Research & Design*, 1993;71(part B): 252--258.
22. Gupta JP, Edwards DW. A simple graphical method for measuring inherent safety. *Journal of Hazardous Materials*, 2003;104:15--30.
23. Heikkila¨ AM. Inherent safety in process plant design. *VTT Publications 384*: Finland, 1999.
24. Heikkila¨ AM, Hurme M, Ja¨rvela¨inen M. Safety considerations in process synthesis. *Computers and Chemical Engineering*, 1996;20:S115--S120.
25. Palaniappan C. Expert system for design of inherently safer chemical processes. *MEng Thesis, National University of Singapore*. Singapore, 2002.
26. Palaniappan C, Srinivasan R, Tan R. Selection of inherently safer process routes: A case study. *Chemical Engineering and Processing*, 2004;43,647--653.
27. Khan FI, Amyotte PR. Integrated inherent safety index (I2SI): A tool for inherent safety evaluation. *Process Safety Progress*, 2004;23:136--148.
28. Crowl D, Louvar J. C*hemical Process Safety. Fundamentals with Applications, Second Edition*. Pearson Education Canada: Canada, 2002.
29. Tugnoli A, Khan F, Amyotte P, Cozzani V. Safety assessment in plant layout design using indexing approach: Implementing inherent safety perspective. Part 1- Guideword applicability and method description. *Journal of Hazardous Materials*, 2008;160:100--109.
30. Patel SJ, Ng D, Mannan MS. Inherently safer design of solvent processed at the conceptual stage: Practical application for substitution. *Journal of Loss Prevention in the Process Industries*, 2010;23:483--491.
31. Khan FI, Sadiq R, Amyotte PR. Evaluation of Available Indices for Inherently Safer Design Options. *Process Safety Progress*, 2003;22:83--98.
32. Gentile M, Rogers WJ, Mannan MS. Development of a Fuzzy Logic-Based Inherent Safety Index. *Institution of Chemical Engineers*, 2003;81:444--456.

33. Koller G, Fischer U, Hungerbu¨hler K. Assessing safety, health, and environmental impact early during process development. *Industrial Engineering Chemistry Research*, 2000;39:960--972.
34. The INSET toolkit. Available at: http://www.aeat-safety-andrisk.com/html/inside.html. Updated March 14, 2002. Accessed September 12, 2011.
35. Gani R, Jiménez-Gonzáles C, Constable D. Method for Selection of solvents for promotion of organic reactions. *Computers and Chemical Engineering*, 2005;29:1661--1676.
36. Gani R, Gómez P, Folić M, Jiménez-Gonzáles C, Constable D. Solvents in organic synthesis: Replacement and multi-step reaction systems. *Computers and Chemical Engineering*, 2008;32:2420--2444.
37. Folić M, Gani R, Jiménez-Gonzáles C, Constable D. Systematic Selection of Green Solvents for Organic Reacting Systems. *Chinese Journal of Chemical Engineering*, 2008;16:376--383.
38. Rahimpour MR, Elekaei H. Optimization of a novel combination of fixed and fluidized-bed hydrogen-permselective membrane reactors for Fischer-Tropsch synthesis in GTL technology. *Chemical Engineering Journal*, 2009;152:543--555.
39. Reid RC, Prausnitz JM, Sherwood TK. *The Properties of Gases and Liquids, Third Edition*. New York, 1977.
40. Harriot P, Dekker M. *Chemical Reactor Design, 1st Edition*, CRC Press: New York, 2003.
41. Al-Mutairi EM, Suardin JA, Mannan MS, El-Halwagi MM. An optimization approach to the integration of inherently safer design and process scheduling. *Journal of Loss Prevention in the Process Industries*, 2008;21:543--549.
42. Gupta JP, Hendershot DC, Mannan MS. The Real Cost of Process Safety- A Clear Case for Inherent Safety. *Institution of Chemical Engineers*, 2003;81:406--413.

43. CW Price Report. Available at: http://www.chemweek.com/. Updated August 23, 2006. Accessed September 12, 2011.
44. ICIS Sample Price Report. Available at: http://www.icis.com/. Updated April 26, 2003. Accessed August 28, 2011.
45. *Price Reports*: *Chemical Market Reporter*. 1993.
46. Linghu WS, Li XH, Fujumoto K. Supercritical and near-critical Fischer-Tropsch synthesis: effects of solvents. *Journal of Fuel Chemistry and Technology*, 2007;35:51--55.
47. Jacobs G, Chaudhari K, Sparks D, Zhang Y, Shi B, Spicer R, Das TK, Li J, Davis BH. Fischer-Tropsch synthesis: supercritical conversion using a Co/Al2O3 catalyst in a fixed bed reactor. *Fuel*, 2003;82:1251--1260.

APPENDIX A

Table A.1 Process Specific Factors for the Supercritical Solvents for SSI1

Solvent	Mixture Tc (^oC)	Mixture Tc (K)	Mixture Pc (bar)
Propane	96.75	369.90	42.50
n-Butane	151.84	424.99	38
n-Pentane	196.60	469.75	33.60
n-Hexane (Basis)	234.50	507.65	30.20
n-Heptane	266.85	540	27.40
n-Octane	295.75	568.90	24.90
n-Nonane	321.85	595	23
n-Decane	344.65	617.80	21.10

Table A.2 Chemical Specific Factors for the Supercritical Solvents for SSI_1

Solvent	LFL at 25 °C (%)	ΔHc (KJ/mol)	ΔHc (Kcal/mol)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	2.20	2219.90	530.57	2.10	800	7093.41
n-Butane	1.90	2877.50	687.74	1.76	1000	1821.37
n-Pentane	1.50	3536.60	845.27	1.35	600	512.89
n-Hexane (Basis)	1.20	4194.50	1002.51	1.04	50	151.28
n-Heptane	1.20	4780.60	1142.59	1.04	400	45.86
n-Octane	1	5511.60	1317.30	0.85	300	13.98
n-Nonane	0.80	0	0	0.8	200	4.29
n-Decane	0.80	6737	1610.18	0.65	0	1.30

Table A.3 Solvent Fractions for the Process and Chemical Specific Factors for SSI_1

Solvent Fractions	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	0.73	1.41	2.01	16	46.89
n-Butane	0.84	1.26	1.69	20	12.04
n-Pentane	0.93	1.11	1.29	12	3.394
n-Hexane	1	1	1	1	1
n-Heptane	1.06	0.91	0.998	8	0.304
n-Octane	1.12	0.827	0.81	6	0.09448
n-Nonane	1.17	0.76	0.77	4	0.03
n-Decane	1.22	0.70	0.62	0	0.008

Table A.4 Priority Indices for the Process and Chemical Specific Factors for SSI_1

Priority Index	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
1	340-400	20-25	0.60-0.90	0-200	<5
2	400-460	25-30	0.90-1.20	200-400	<50
3	460-520	30-35	1.20-1.50	400-600	<500
4	520-580	35-40	1.50-1.80	600-800	<5000
5	580-640	40-45	1.80-2.10	800-1000	<50000

Table A.5 Weighting Factor Results for the Supercritical FTS Solvents for SSI_1

Solvent	WF for Mixture Tc (K)	WF for Mixture Pc (bar)	WF for LFL at Mixture Tc (%)	WF for TLV (ppm)	WF for Vapor P (mm Hg)
Propane	1	5	5	5	5
n-Butane	2	4	4	5	4
n-Pentane	3	3	2	4	4
n-Hexane	3	3	2	1	3
n-Heptane	4	2	1	3	2
n-Octane	4	1	1	2	2
n-Nonane	5	1	1	1	1
n-Decane	5	3	2	1	1

Table A.6 SSI $_1$ Values for the Different Solvents

Solvent	SSI_1
Propane	332.27
n-Butane	161.62
n-Pentane	70.26
n-Hexane	12
n-Heptane	31.67
n-Octane	18.30
n-Nonane	11.42
n-Decane	9.44

Table A.7 Process Specific Factors for the Supercritical Solvents for SSI_3

Solvent	Mixture Tc (°C)	Mixture Tc (K)	Mixture Pc (bar)
Propane	250	523.15	65
n-Butane	250	523.15	65
n-Pentane	250	523.15	65
n-Hexane (Basis)	250	523.15	65
n-Heptane	250	523.15	65
n-Octane	250	523.15	65
n-Nonane	250	523.15	65
n-Decane	250	523.15	65

Table A.8 Chemical Specific Factors for the Supercritical Solvents for SSI_3

Solvent	LFL at 25 °C (%)	ΔHc (KJ/mol)	ΔHc (Kcal/mol)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	2.20	2219.90	530.57	1.88	800	7093.41
n-Butane	1.90	2877.50	687.74	1.65	1000	1821.37
n-Pentane	1.50	3536.60	845.28	1.30	600	512.89
n-Hexane (Basis)	1.20	4194.50	1002.51	1.03	50	151.28
n-Heptane	1.20	4780.60	1142.59	1.05	400	45.86
n-Octane	1	5511.60	1317.30	0.87	300	13.98
n-Nonane	0.80	0	0	0.80	200	4.29
n-Decane	0.80	6737	1610.18	0.70	0	1.30

Table A.9 Solvent Fractions for the Process and Chemical Specific Factors for SSI_3

Solvent Fractions	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	1	1	1.82	16	46.89
n-Butane	1	1	1.60	20	12.04
n-Pentane	1	1	1.26	12	3.394
n-Hexane	1	1	1	1	1
n-Heptane	1	1	1.02	8	0.304
n-Octane	1	1	0.85	6	0.09
n-Nonane	1	1	0.78	4	0.03
n-Decane	1	1	0.67	0	0.009

Table A.10 Priority Indices for the Process and Chemical Specific Factors for SSI_3

Priority Index	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
1	1	1	0.65-0.95	0-200	<5
2	1	1	0.95-1.25	200-400	<50
3	1	1	1.25-1.55	400-600	<500
4	1	1	1.55-1.85	600-800	<5000
5	1	1	1.85-2.15	800-1000	<50000

Table A.11 Weighting Factor Results for the Supercritical FTS Solvents for SSI_3

Solvent	WF for Mixture Tc (K)	WF for Mixture Pc (bar)	WF for LFL at Mixture Tc (%)	WF for TLV (ppm)	WF for Vapor P (mm Hg)
Propane	1	1	5	5	5
n-Butane	1	1	4	5	4
n-Pentane	1	1	3	4	4
n-Hexane	1	1	2	1	3
n-Heptane	1	1	2	3	2
n-Octane	1	1	1	2	2
n-Nonane	1	1	1	1	1
n-Decane	1	1	1	1	1

Table A.12 SSI $_3$ Values for the Different Solvents

Solvent	SSI_3
Propane	325.57
n-Butane	168.61
n-Pentane	67.34
n-Hexane	6
n-Heptane	28.94
n-Octane	15.03
n-Nonane	6.80
n-Decane	2.68

Table A.13 Process Specific Factors for the Supercritical Solvents for SSI_4

Solvent	Mixture Tc (^{o}C)	Mixture Tc (K)	Mixture Pc (bar)
Propane	271.90	545.05	65
n-Butane	271.90	545.05	65
n-Pentane	271.90	545.05	65
n-Hexane (Basis)	271.90	545.05	65
n-Heptane	271.90	545.05	65
n-Octane	271.90	545.05	65
n-Nonane	271.90	545.05	65
n-Decane	271.90	545.05	65

Table A.14 Chemical Specific Factors for the Supercritical Solvents for SSI_4

Solvent	LFL at 25 °C (%)	ΔHc (KJ/mol)	ΔHc (Kcal/mol)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	2.20	2219.90	530.57	1.85	800	7093.40
n-Butane	1.90	2877.50	687.74	1.63	1000	1821.36
n-Pentane	1.50	3536.60	845.27	1.28	600	512.89
n-Hexane (Basis)	1.20	4194.50	1002.50	1.02	50	151.28
n-Heptane	1.20	4780.60	1142.59	1.04	400	45.86
n-Octane	1	5511.60	1317.30	0.86	300	13.98
n-Nonane	0.80	0	0	0.8	200	4.29
n-Decane	0.80	6737	1610.18	0.68	0	1.30

Table A.15 Solvent Fractions for the Process and Chemical Specific Factors for SSI_4

Solvent Fractions	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
Propane	1	1	1.82	16	46.89
n-Butane	1	1	1.61	20	12.04
n-Pentane	1	1	1.26	12	3.39
n-Hexane	1	1	1	1	1
n-Heptane	1	1	1.02	8	0.30
n-Octane	1	1	0.85	6	0.09
n-Nonane	1	1	0.79	4	0.03
n-Decane	1	1	0.67	0	0.009

Table A.16 Priority Indices for the Process and Chemical Specific Factors for SSI_4

Priority Index	Mixture Tc (K)	Mixture Pc (bar)	LFL at Mixture Tc (%)	TLV (ppm)	Vapor P (mm Hg)
1	1	1	0.60-0.86	0-200	<5
2	1	1	0.86-1.12	200-400	<50
3	1	1	1.12-1.38	400-600	<500
4	1	1	1.38-1.64	600-800	<5000
5	1	1	1.64-1.9	800-1000	<50000

Table A.17 Weighting Factor Results for the Supercritical FTS Solvents for SSI_4

Solvent	WF for Mixture Tc (K)	WF for Mixture Pc (bar)	WF for LFL at Mixture Tc (%)	WF for TLV (ppm)	WF for Vapor P (mm Hg)
Propane	1	1	5	5	5
n-Butane	1	1	4	5	4
n-Pentane	1	1	3	4	4
n-Hexane	1	1	2	1	3
n-Heptane	1	1	2	3	2
n-Octane	1	1	1	2	2
n-Nonane	1	1	1	1	1
n-Decane	1	1	1	1	1

Table A.18 SSI $_4$ Values for the Different Solvents

Solvent	SSI_4
Propane	325.56
n-Butane	168.62
n-Pentane	67.35
n-Hexane	6
n-Heptane	28.95
n-Octane	15.03
n-Nonane	6.82
n-Decane	2.68

VITA

Natalie Asma Hamad
Mary Kay O'Connor Process Safety Center
Texas A&M University
Jack E. Brown Engineering Building
College Station, TX, 77843-3122

Natalie Hamad is originally from Lebanon but was raised in Qatar. She received her B.S. degree in May 2010 from the branch campus of Texas A&M University at Qatar with a major in Chemical Engineering and a minor in Chemistry. She then received her M.S. degree in Safety Engineering at the main campus of Texas A&M University, after being awarded the ExxonMobil MENA Scholarship; a scholarship for scholars from the Middle East and North Africa.