

**INVESTIGATION OF HIGH-OLEIC SOYBEAN OIL AS AN
EXTRACTION SOLVENT TO REMOVE HYDROGEN SULFIDE FROM
NATURAL GAS**

by

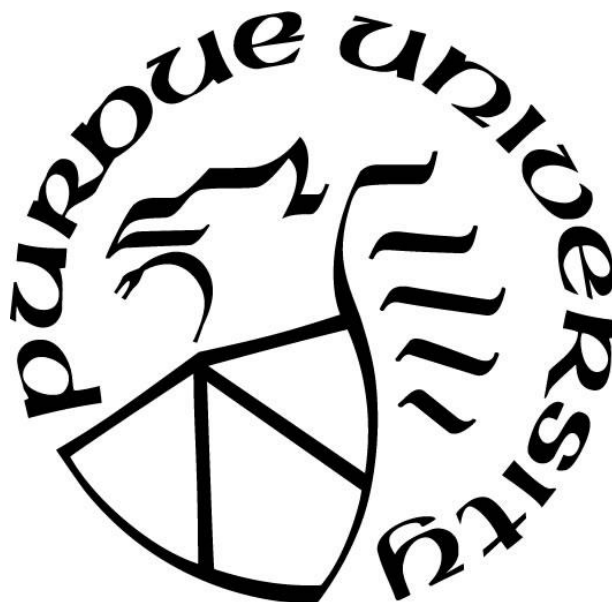
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*To Cathy, who encouraged and enabled my love of reading and learning;
to Antonio, who is my sunshine;
to all the strong women in my life who inspire and persist: thank you.*

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LIST OF ABBREVIATIONS

CH ₄	Methane
CO ₂	Carbon dioxide
COSMO-RS	COnductor-like Screening MOdel for Real Solvents
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
H ₂ S	Hydrogen Sulfide
HOSBO	High-oleic Soybean Oil
ppm	Parts per million
SBO	Soybean Oil

ABSTRACT

Conventional soybean oil and high-oleic soybean oil offer opportunities as bio-solvents for sweetening sour natural gas, adding value to the soybean oil industry and the natural gas industry. The rise of fracking in the United States and changing economics in the energy industry have increased use of natural gas, which is often rendered sour by high concentrations of hydrogen sulfide (H_2S), a toxic and corrosive impurity. The present work evaluates the viability of both conventional and high-oleic soybean oil to act as bio-solvents for removing gaseous H_2S . Predictive *in silico* methods, experimental validation, and economic feasibility analysis are included to draw conclusions regarding the overall capability and feasibility of using soybean oils as bio-solvents for gas sweetening.

In silico predictive methods for sweetening were implemented to assess the relationship between fatty acid composition in the soybean oils and the ability to effectively partition H_2S from methane or nitrogen gases. The Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict the partition coefficient (K) of H_2S in a bi-phasic liquid-vapor system made up of fatty acids in the liquid phase and methane or nitrogen gas in the vapor phase. The fatty acid mass fractions represented those found in soybean or high-oleic soybean oil. Methane represented gas and nitrogen was considered in order to compare to experimental conditions. This proof of concept work predicted K values for H_2S below 0.0005 at temperatures from 10 to 100 °C at atmospheric pressure; K values near zero indicate near-complete removal of H_2S from the gas phase.

Experimental validation included equilibrium extraction experiments as well as data collection for isotherm model development. Experimental equilibrium studies were carried out at residence times ranging from 0 – 60 minutes with mixing at ambient conditions. Experiments resulted in K values below 0.1 for H_2S in soybean oil and high-oleic soybean oil at 25 °C with residence times less than 15 minutes and a 2:1 gas to oil ratio. More than 90% of the H_2S was removed from the gas phase within 15 minutes. Isotherm models demonstrated the saturation limits of the soybean oils and compared them to saturation limits in water and heptane.

Economic feasibility experiments used graphical and algebraic methods to determine the number of equilibrium stages needed to remove 99.9% of H_2S from feed gas with H_2S concentrations ranging from 40 – 400 ppm. A gas flow rate equivalent to industrial levels was used to design an extraction column. Capital costs and operating costs were estimated, along with the revenues to be gained from selling methane and selling recovered elemental sulfur as a secondary product. Solvent regeneration would need to exceed 98% in order to keep the cost of treating a unit of natural gas equal to or less than existing industrial methods. Suggestions for cutting costs and improving process viability are made.

1. INTRODUCTION

1.1 Background and Motivation

Predictive methods for sweetening sour natural gas using bio-based solvents provide an opportunity to add value to the soybean oil industry and create an efficient and economical method for removing hydrogen sulfide from natural gas. Improvements in hydraulic fracturing (fracking) technology and increased demand for natural gas have caused a significant increase in the amount of natural gas available within the last 20 years.^{1,2} As shown in Figure 1.1, in 2000, the U.S. produced approximately 50 billion cubic feet per day of natural gas, with less than 7% of that production from hydraulically fractured wells.² As of 2015, U.S. natural gas production had risen to almost 80 billion cubic feet per day, with 67% of that produced through fracking.²

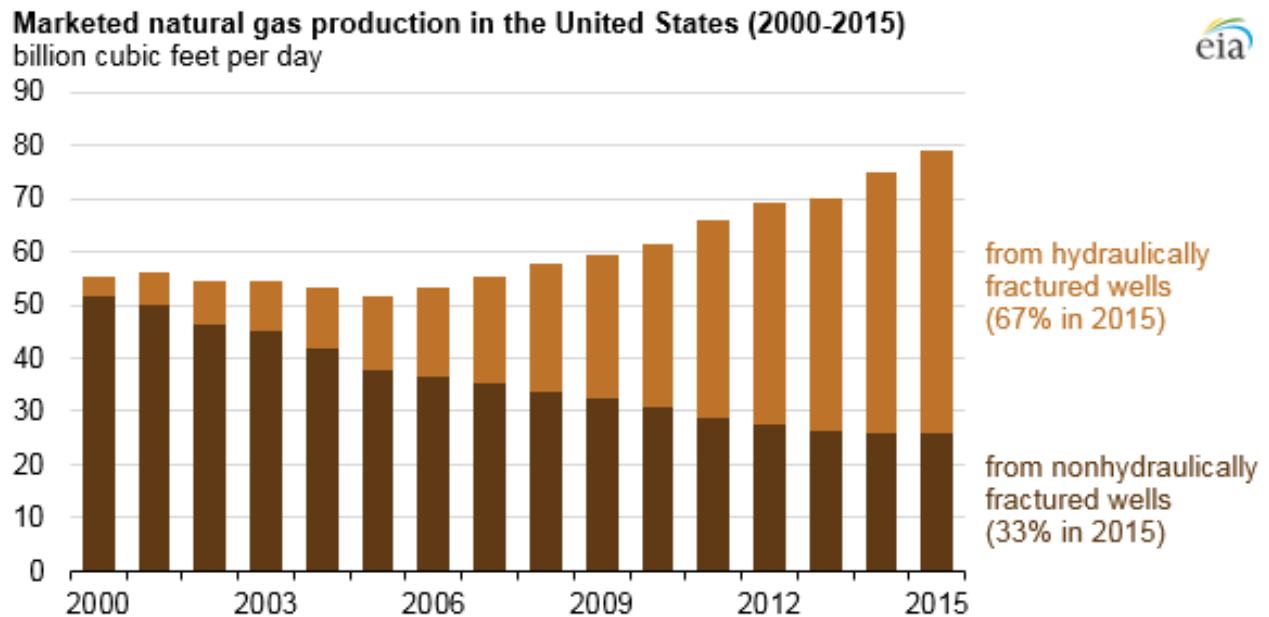


Figure 1.1. In a 2016 report, the U.S. Energy Information Administration released information regarding the impact of hydraulic fracturing on the natural gas production in the United States. It was noted that over a period of a decade, natural gas from fracking has risen to taking up two-thirds of the natural gas market, and in 2015, 90% of the natural gas produced from fracking came from tight rock formations in the lower 48 states. (Figure reproduced from “Hydraulically fractured wells provide two-thirds of U.S. natural gas production,” U.S. Energy Information Administration, 2016.²)

As the market became saturated with natural gas, prices dropped, rendering natural gas a viable competitor with other fuels such as coal.³ In addition to economically competing with coal, natural gas is considered more environmentally friendly than coal, as it releases about 50% less carbon dioxide into the atmosphere.⁴ Natural gas is also of interest in transportation fuels, as it releases up to 11% less greenhouse gases than traditional gasoline.⁵ However, the shale gas reservoirs targeted by fracking often have high concentrations of hydrogen sulfide (H_2S), up to hundreds of parts per million.¹ Natural gas contaminated with sulfur – in the form of H_2S – is commonly referred to as sour gas, and has H_2S concentrations greater than 5.7 mg/m^3 (4 ppmv) at standard temperature and pressure.⁶ H_2S is a naturally-occurring impurity that is difficult to remove, and is highly corrosive and can damage natural gas processing and transportation equipment.⁷ It is also highly hazardous and acutely toxic to humans even at levels as low as 1 ppm, affecting respiration and the central nervous system.^{8,9} Additionally, combustion of sour gas releases sulfur dioxide to the atmosphere, causing acid rain, and combustion of sour gas poses several risks to the environment and human health.¹⁰ However, flaring – burning of sour gas at the wellhead – is a common practice when the H_2S levels are high enough that economic transportation and sweetening methods are considered impractical.¹¹ Industrially, H_2S is typically removed through an amine treatment process known as sweetening. Generally, amine gas treatment uses a variety of alkylamines to absorb H_2S and CO_2 from streams of sour gas, yielding a stream of gas free of these contaminants and an amine solution containing the absorbed gases.^{12–15} This is an energy intensive process that requires increased energy as contaminant concentrations increase,¹² and there is a demand for new technology for removing H_2S from natural gas. Other removal strategies include membrane filtration,^{16,17} adsorption through ionic liquids,^{18–25} and other lab-scale sulfur adsorption methods.²⁶ These alternatives have failed to be implemented due to low removal efficiency or economic viability. There is an unmet need for a simple, cost-effective method to remove the hydrogen sulfide from natural gas, which could be widely implemented and is economically viable.

The present research evaluates the feasibility of using conventional soybean oil or high-oleic soybean oil to remove hydrogen sulfide from natural gas. Soybean oil is a readily available bioresource, and other vegetable oils are known to be capable of binding sulfur compounds.^{27,28} The unsaturated fatty acids found in soybean oils offer several potential binding sites for sulfur.

While laboratory experiments can be costly and time-consuming, predictive models that examine interactions at a molecular level can be efficient tools for solvent screening and choosing initial key process parameters. Examining a two-phase system composed of natural gas and soybean oil using molecular modeling to predict how hydrogen sulfide will partition between the two phases can allow for more rapid proof-of-concept and evaluation of the feasibility of such an endeavor. A molecular modeling approach based on statistical thermodynamics known as the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to simulate the partitioning of the target molecule (hydrogen sulfide) between the liquid (soybean oil) and gas (methane) phases. The COSMO-RS predictive model has been used to predict partitioning of target molecules in a variety of liquid-liquid^{29–35} and vapor-liquid^{36,37} systems. This *a priori* approach to predicting the partition coefficient (K) allows for more rapid determination of optimal process parameters (temperature, pressure, concentration) and reduction of experimental effort (time, resources). Preliminary results predicted K values between 0.0002 – 0.0006 at temperatures ranging from 25 – 100 °C at atmospheric pressure; K values less than 1 and approaching 0 are indicative of near-complete removal of the hydrogen sulfide from the natural gas. This will be a novel use of high-oleic soybean oil as a bio-solvent for cleaning natural gas and will potentially impact the economics of the soybean and gas industries.

1.2 Overview & Objectives

Conventional soybean oil and high-oleic soybean oil are abundantly available in Indiana and other Midwestern states, which contribute largely to the 4.3 billion bushels of soybeans and 22.6 billion pounds of soybean oil produced in the U.S. in 2016.³⁸ High-oleic soybean oil has a fatty acid profile of 65 – 85% oleic acid, an unsaturated fatty acid which may be able to effectively bind sulfur. The unsaturated fatty acids in soybean oils may allow them to act as extraction solvents for the removal of hydrogen sulfide from natural gas. This starting hypothesis is supported by studies demonstrating that vegetable oils are able to absorb sulfur.^{27,28} The long-term goal of this project is to address the challenges of removing hydrogen sulfide impurities from natural gas and improve quality of natural gas obtained through fracking. The primary research objective is to utilize molecular modeling as a tool for developing a new use of high-oleic soybean oil as a universal solvent to provide an environmentally conscientious solution to removing hydrogen sulfide from natural gas. The underlying rationale is that an approach that begins on a fundamental,

molecular level will be best suited for developing methods for removing the hydrogen sulfide from natural gas as close to the wellhead as possible. The objectives include theoretical modeling using the Conductor-like Screening Model for Real Solvents (COSMO-RS) to develop a method that can be used in the soybean and gas industries.

- Objective #1** *Use molecular modeling to develop a hydrogen sulfide removal method using high-oleic soybean oil.* The COSMO-RS approach will be used to predict how H₂S partitions between the gas and oil.
- Objective #2** *Conduct physical experiments to compare to the model and determine bio-oils capacity for sorbing H₂S.* Physical absorption experiments and development of isotherms will be compared to model data and be used to determine feasibility of using soybean oils as extraction solvents.
- Objective #3** *Investigate the economic feasibility of using bio-oil solvents for extracting H₂S from natural gas.* Extraction column design, equilibrium stage analysis, and modeling of a bio-oil extraction system will be investigated to determine the maximum cost of using soybean oil and regenerating it to stay competitive with other methods.

The proposed research is creative and original in addressing the challenge of removing hydrogen sulfide from natural gas by studying the compounds at a molecular level. It is also a unique use of the COSMO-RS method in studying gas/liquid partitioning behavior at a molecular level to design a large-scale processing method. While the COSMO-RS method has been demonstrated to robustly simulate the behavior of molecules in the gas phase and liquid phase, the present work is unique in utilizing COSMO-RS to develop a solvent system that utilizes high-oleic soybean oil and other co-solvents in order to remove impurities from a gas. This research also proposes a novel use of high-oleic soybean oil as a solvent for removal of hydrogen sulfide from natural gas, which will add value to the soybean industry. This bio-based solvent system will improve the environmental impact of fracking and natural gas combustion.

This study demonstrates a new use for high-oleic soybean oil as a bio-based, environmentally friendly solvent for cleaning natural gas. This could lead to increased use of natural gas in

transportation fuels, which releases less carbon dioxide to the atmosphere than traditional gasoline. The two-fold result of finding a new use for high-oleic soybean oil and new gas sweetening solvents could have a positive impact on the natural gas and soybean industries if use of soybean oil bio-solvents proves economically viable.

1.3 Summary of Work

Chapter 2 provides an overview of the current literature regarding natural gas sweetening methods and technologies, COSMO-RS theory and uses, and availability and characteristics of high-oleic soybean oil and other seed oils. Chapter 3 outlines the methods used in both theoretical and physical experiments designed to meet the objectives of this work. Chapter 4 details the findings from assessing the viability of using high-oleic soybean oil as an H₂S extraction solvent using *in silico* methods and physical experiments to find the partition coefficient and develop absorption isotherms. Chapter 5 provides insight into the economic feasibility of using high-oleic soybean oil or soybean oil as gas sweetening solvents by estimating column dimensions and capital costs and includes a sensitivity analysis relating solvent regenerative power to the limit for the cost of treating a unit of sour natural gas. Chapter 6 explores temperature effects on partitioning and the use of seed oils other than high-oleic soybean oil, as well as reviewing literature on converting captured H₂S to other sulfur species. Chapter 7 summarizes the findings and conclusions and offers recommendations for future work.

2. LITERATURE REVIEW

2.1 Removal of Hydrogen Sulfide from Sour Natural Gas

2.1.1 Challenges

Utilization of natural gas harvested through fracking is impeded by the presence of hydrogen sulfide. H_2S is naturally occurring and commonly found in natural gas at concentrations up to hundreds of parts per million.¹ Natural gas is considered sour when the concentrations of H_2S exceed 5.7 mg/m^3 , or greater than 4 ppmv at standard temperature and pressure.⁶ H_2S removal is critical because it is highly corrosive and hazardous to human health.⁷⁻⁹ Over time, H_2S damages processing and transportation equipment, and poses a serious danger to gas workers, as it is acutely toxic at levels as low as 1 ppm.^{8,9} Treating sour gas – including transporting, processing, and removing the contaminants – requires significant energy input often rendering it economically infeasible, which results in a common practice called flaring. Flaring is the burning of sour gas at the wellhead, which releases sulfur dioxide and other toxins to the atmosphere.¹¹ Although there are environmental restrictions on these practices, it is generally considered more environmentally conscientious to flare the sour gas rather than release it – with all the methane – to the atmosphere. However, the sulfur dioxide formed contributes to acid rain and poses its own risks to the environment.¹⁰ For these reasons, there is a demand to find a method for H_2S removal as close to the wellhead as possible.

2.1.2 H_2S Removal Methods

Various methods have been developed for the desulfurization of natural gas, with different degrees of successful industrial implementation. Amine gas treating is one of the most common industrial processes for removing H_2S and CO_2 from streams of sour natural gas, but other methods including membrane filtration and use of ionic liquids or zeolites have also been investigated as shown in Table 2.1.

Table 2.1. Overview of industrial processes used for absorbing contaminant gases from natural gas streams.

Process		Commercial development	Solvents or reactive chemicals	Regeneration	Description	Sources
chemical absorption processes	Amine gas treating	widely used	monoethanolamine (MEA), diethanolamine (DEA), diisopropylamine (DIPA), diglycolamine (DGA), methyldiethanolamine (MDEA), other proprietary amines	A stripping tower and heat exchanger are used to increase temperature and force heat dissociation of the amines so they can be recycled; amine degradation products must be removed	Amines absorb H ₂ S and CO ₂ to form amine salts which easily dissociate when temperature is increased and pressure is dropped	Korpys & Wojcik, 2014 ³⁹ ; Butwell et al., 1982 ⁴⁰ , Stewart, 2014 ⁴¹
	Hot carbonate processes	Benfield, Catacarb, Giammarco-Vetrocoke	Potassium carbonate	CO ₂ is necessary for regeneration of the potassium carbonate in the stripping tower	Potassium carbonate absorbs H ₂ S and CO ₂ ; proprietary processes use catalysts to increase rate of reaction and prevent corrosion	Stewart, 2014 ⁴¹ ; Rahimpour & Kashkooli, 2004 ⁴² ; Ghosh et al., 2009 ⁴³ ; Cullinane & Rochelle, 2004 ⁴⁴
physical adsorption processes	Rectisol	Lurgi, Linde	Methanol	Methanol is regenerated in two stages: flashing via pressure reduction, then cooled	At temperatures as low as -80 °C methanol is used as a solvent in a multi-stage absorber; results in selective separation of gases	Korpys & Wojcik, 2014 ³⁹ ; Kohl & Nielsen, 1997 ⁴⁵ ; Korens et al. 2002 ⁴⁶
	Selexol	Allied Chemical Corp., UOP LLC	Dimethylethers of polyethylene glycol	Multiple flashing stages release absorbed hydrocarbons; flashed gases are compressed and recycled	Provides pure streams of CO ₂ by effectively removing H ₂ S	Korpys & Wojcik, 2014 ³⁹ ; Kohl & Nielsen, 1997 ⁴⁵ ; Korens et al., 2002 ⁴⁶
	Fluor	The Fluor Corp.	Propylene carbonate	Pressure reduction causes desorption	Low temperature absorption; Can lower from 50% CO ₂ to 1-2% CO ₂	Korpys & Wojcik, 2014 ³⁹
	Purisol	Lurgi AG, Air Liquide	N-methylpyrrolidone	Flashing and compression force desorption	High solubility of H ₂ S and low solubility of CO ₂ , so it can selectively remove H ₂ S in the presence of CO ₂	Korpys & Wojcik, 2014 ³⁹ ; George & Bowles, 2011 ⁴⁷

Table 2.1 continued.

Process		Commercial development	Solvents or reactive chemicals	Regeneration	Description	Sources
Hybrid processes	Sulfinol	Shell	Sulfolane	Cooling, condensation and compression	Absorption of H ₂ S, CO ₂ , COS, mercaptans	Korpys & Wojcik, 2014 ³⁹ ; Korens et al., 2002 ⁴⁶
	Flexsorb SE and PS	ExxonMobil	Amines and FLEXSORB	Improved regeneration compared to sulfinol	Non-selective; reduces solvent circulation rate and reboiler duty	Korpys & Wojcik, 2014 ³⁹
Ionic Liquids	Variety of ILs	n/a	Imidazolium-based ionic liquids	Lab-scale and in silico studies seek to examine solubility of H ₂ S and CO ₂ in different ionic liquids	Ionic-liquids are developed in which H ₂ S and CO ₂ are highly soluble	Karadas et al., 2010 ¹⁸ ; Shokouhi et al., 2010 ¹⁹ ; Jalili et al., 2009 ²⁰ ; Shiflett et al., 2010 ²¹ ; Pomelli et al., 2007 ²³
Gas permeation	Membrane filtration	n/a	Pressure-driven membrane separation of H ₂ S and CO ₂ using polycarbonate and polyimide membranes	n/a	Useful for treating small volumes of gas with H ₂ S concentrations less than 100 ppm	Alexander & Winnick, 1994; Baker, 2002; Tabe-Mohammadi 1999
Solid bed processes	Molecular sieves	Primarily used for small gas streams or subsequent to other processes	Porous crystalline solids with localized polar charges	Hot sweet stripping gases break the ionic bonds, removing the H ₂ S and H ₂ O	Pores allow molecules the size of H ₂ S, H ₂ O, and CO ₂ to enter; polar H ₂ S and H ₂ O form weak ionic bonds with the charge sites	Stewart, 2014 ⁴¹ ; Kuznicki et al., 2000 ⁴⁸ ; Liu et al., 2005 ⁴⁹ ; Tomita et al., 2004 ⁵⁰
	Iron sponge	n/a	Ferric oxide	Ferric sulfide is oxidized with air to produce sulfur and regenerate the ferric oxide	Wood chips coated with ferric oxide are used as the packing material in a solid bed reaction vessel; gas flows downward and H ₂ S reacts with the ferric oxide to form ferric sulfide and water	Stewart, 2014 ⁴¹ ; Anerousis & Whitman, 1985 ⁵¹ ; Cherosky & Li, 2013 ⁵²
	Zinc oxide	Rarely used	Zinc oxide	The zinc sulfide is not regenerated to zinc oxide, and is a heavy metal salt that is difficult to dispose of	Zinc oxide granules in a solid bed form zinc sulfide and water	Stewart, 2014 ⁴¹ ; Carnes & Klabunde, 2002 ⁵³ ; Wang et al., 2008 ⁵⁴

The gases removed by different treatment processes are shown in Table 2.2. Removal of H₂S and CO₂ is typically desirable, while removal of carbonyl sulfide (COS) and carbon disulfide (CS₂) can complicate the regeneration steps in some cases.⁴¹

Table 2.2. Gases removed by different gas sweetening processes.⁴¹

Process	Gases Removed			
	H ₂ S	CO ₂	COS	CS ₂
MEA	X	X	X	X
DEA	X	X	X	X
MDEA	X			
DGA	X	X	X	X
DIPA	X	X	X	
Hot carbonate	X	X	X	X
Rectisol	X			
Sulfinol	X	X	X	X
Selexol	X	X	X	X
Fluor	X	X	X	X
Membrane	X	X		
Molecular sieve	X	X	X	X
Iron sponge	X			
Zinc oxide	X			

2.1.2.1 Amine Gas Treating

Industrially, H₂S is typically removed through an amine treatment process known as sweetening. Generally, amine gas treatment uses a variety of alkylamines to absorb H₂S and CO₂ from streams of sour gas, yielding a stream of gas free of these contaminants and an amine solution containing the absorbed gases.^{12–15} A simplified schematic of this process is shown in Figure 2.1. Monoethanolamine, diethanolamine, methyldiethanolamine, and diglycolamine solutions of 20–50% are commonly used for removing H₂S and CO₂, and the solutions are chosen based on the concentrations of the contaminants in the natural gas.^{12–15} Subsequent processing of the H₂S using the Claus process can convert the H₂S to elemental sulfur.⁵⁵ However, amine gas treating has high energy demands that increase as the concentration of the contaminants increase,¹² which sometimes renders removal either ineffective or economically unviable when contaminant concentrations are high.

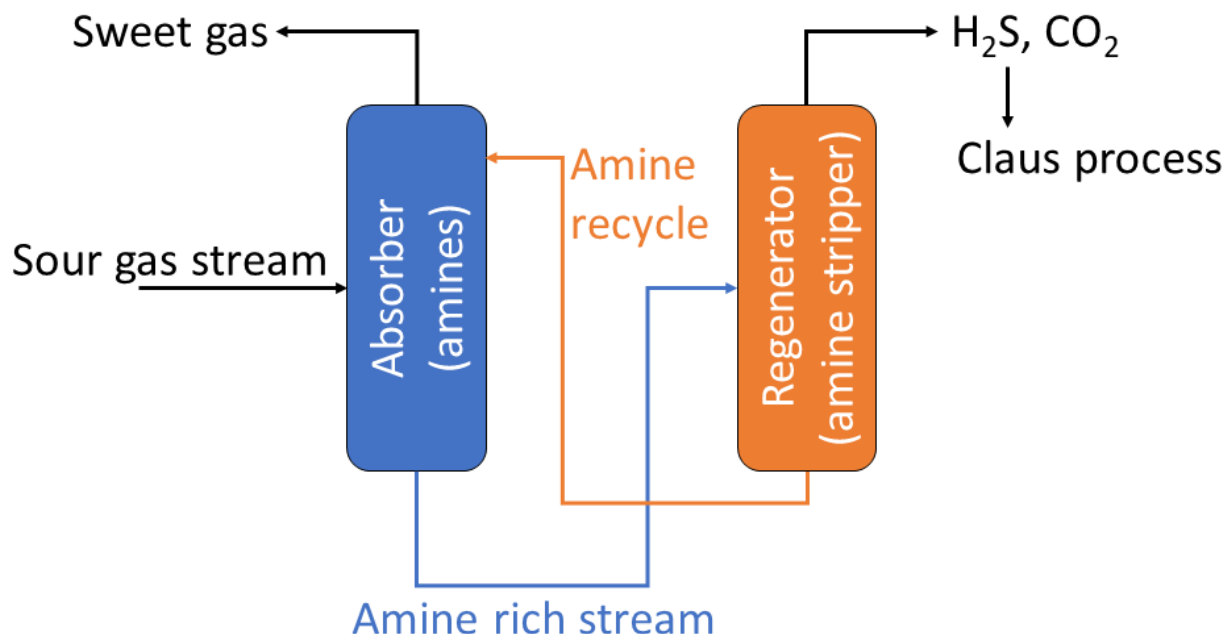


Figure 2.1. Simple schematic of an amine gas sweetening process. Sour natural gas streams are often scrubbed of hydrogen sulfide and carbon dioxide via amine gas stripping. The sour gas stream enters an absorber of alkylamines, which separates out a stream of “sweet gas” from an amine rich stream containing H_2S and CO_2 . The alkylamines are regenerated through a process that strips off the H_2S and CO_2 , so that the alkylamines can be recycled. From there, H_2S can be broken down into hydrogen and sulfur, useful chemical building blocks.

Absorption of acid gases by amine solutions occurs due to the partial pressure differential between the liquid and vapor phases.⁴¹ The reactions are usually reversible by manipulating temperature and pressure, which allows the acid gases to be stripped off the amines and the amine solution recycled.⁴¹ The absorbing towers can be trayed towers or conventional packing towers.⁴¹ Different amine solutions are compared in Table 2.3.

Table 2.3. Comparison of amine solutions used in amine gas treating.^{39–41}

Amine and wt% in aqueous solution	Advantages	Disadvantages
Monoethanolamine (MEA) 15 – 20%	Very stable primary amine; no degradation or decomposition; reversible reactions with H ₂ S and CO ₂	Reacts with COS and CS ₂ forming salts and inhibiting MEA regeneration in the stripping column; foams easily
Diethanolamine (DEA) 25 – 35%	All reactions (including those with COS and CS ₂) can be reversed under normal stripping column conditions	Less alkaline than MEA, requires stronger solution/higher loading
Diglycolamine (DGA) 50 – 70%	Primary amine with low vapor pressure, which decreases amine losses; reactions with COS and CS ₂ can be reversed easily	Proprietary process – Fluor Econamine
Diisopropanolamine (DIPA) Unknown	Secondary amine similar to DEA, but reportedly with lower energy consumption; pressure control can be used to preferentially remove H ₂ S or CO ₂	Proprietary process – Shell ADIP
Methyldiethanolamine (MDEA) 40 – 50%	Tertiary amine; removes H ₂ S but not CO ₂ ; significantly less expensive than MEA or DEA	Can be advantageous or disadvantageous depending on if the CO ₂ content of the feed gas and treated gas is of concern

Monoethanolamine (MEA) is one of the most common and widely-used solvents in gas sweetening.^{39–41} MEA is a very stable primary amine which will not degrade or decompose at temperatures up to its normal boiling point.⁴¹ Reactions with MEA can be reversed in the stripping column by heating the stream to 118 °C at 69 kPa, releasing H₂S and CO₂ to the vapor phase and regenerating the MEA.⁴¹ One concern in using MEA is its reaction with carbonyl sulfide (COS) and carbon disulfide (CS₂).⁴¹ In such a case, the MEA cannot be regenerated at normal stripping column temperatures and MEA is consumed from the process.⁴¹ This necessitates use of a reclaimer to remove the contaminant salts.⁴¹

Diethanolamine (DEA) is a secondary amine, so it is less alkaline than MEA, and a stronger solution is necessary to treat the sour gas.⁴¹ It is more advantageous to use DEA when COS and CS₂ are present, because although DEA will react with them, the DEA can still be regenerated at normal stripping column temperatures.⁴¹

Diglycolamine (DGA) is a primary amine similar to MEA. It is used in the Fluor Econamine process.^{41,56} It has an advantage over MEA in that reactions with COS and CS₂ are easily reversible.⁴¹ It also has lower vapor pressure, which means lower amine losses.⁴¹

Diisopropanolamine (DIPA) is a secondary amine similar to DEA. It is used in the Shell ADIP process.³⁹⁻⁴¹ It reportedly has lower energy consumption than DEA systems.⁴¹ It preferentially removes H₂S at low pressures and CO₂ at high pressures, which is a useful control unique to this amine.⁴¹

Methyldiethanolamine (MDEA) is a more recently popular gas sweetener that selectively removes H₂S when CO₂ is present.³⁹⁻⁴¹ It also significantly reduces treatment costs (if CO₂ removal is not needed).⁴¹ MDEA is a tertiary amine. At pressures from 5500 – 6900 kPa, it can remove H₂S levels to concentrations acceptable within pipelines.⁴¹ However, up to 60% of the CO₂ will flow through the absorber without being removed.⁴¹ MDEA is particularly advantageous in creating a concentrated H₂S acid gas stream to be sent to a Claus recovery process, but the remaining gas will have high CO₂ content.⁴¹

2.1.2.2 Hot carbonate

Processes using potassium bicarbonate (KHCO₃) are typically referred to as hot carbonate systems and are similar to amine gas treating schemes but using potassium carbonate solutions rather than amine solutions.^{41,42} Regeneration is only possible in the presence of CO₂ so these processes should not be used for H₂S removal if CO₂ is not also present and in need of removal.⁴¹ To achieve pipeline quality gas, a secondary treatment is often required to reduce the H₂S levels below 4 ppm.⁴¹ High temperatures in the absorber are necessary to keep the potassium bicarbonate soluble, and so dead spots and plugging from precipitation are often problems.⁴¹ Corrosion inhibitors must also be added to reduce the corrosive effects of hot potassium carbonate solutions on carbon steel vessels.⁴¹ Proprietary systems often include catalysts which increase the reaction rates in the absorber and stripper and decrease corrosion.^{41,43,44}

2.1.2.3 Physical absorbents

Unlike chemical absorbent processes, physical absorbents are based on gas solubility instead of chemical reactions, and gas solubility is a function of temperature and gas partial pressure.⁴¹ A variety of organic solvents are used to absorb the acid gases, and regeneration is typically carried out by flashing to lower pressures or stripping off with inert gas.⁴¹ A significant disadvantage of physical absorbents is their high affinity for C^{3+} hydrocarbons, so hydrocarbon-rich gas cannot be economically treated with physical absorbents.⁴¹ Physical absorbents are advantageous when selective H_2S removal is necessary and when partial pressure of acid gases in the feed gas is higher than 345 kPa.⁴¹

Rectisol was developed by Lurgi and Linde and uses methanol.^{39,41,45,46} This process is operated at low temperatures and although it has been applied to purification of natural gas, it is not commonly used.⁴¹

The Sulfinol process is a proprietary process developed by Shell.^{39,41,46} Sulfolane® (tetrahydrothiophene) is a physical solvent mixed with DIPA (a chemical solvent) and water to make the Sulfinol® solution.^{39,41,46} Presence of Sulfolane® allows for higher acid gas loadings compared to amine systems.^{39,41,46} Advantages include a lower energy of regeneration which reduces the cost per unit of acid gas treated.^{39,41,46}

The Selexol process uses the dimethylether of polyethylene glycol and is licensed by UOP.^{39,41,45,46} Selexol® is selective for sulfur compounds but can also remove up to 85% of CO_2 .⁴¹ DIPA is often added to remove CO_2 to meet pipeline specifications.

The Fluor Solvent process is a physical absorption process using propylene carbonate to remove CO_2 , H_2S , CS_2 , COS , and C^{3+} hydrocarbons from natural gas streams.^{39,41} This system requires larger than average absorption towers and high circulation rates in order to produce pipeline quality gas.⁴¹ Favorable characteristics of propylene carbonate include the high degree of solubility for CO_2 , low solubility for light hydrocarbons (C_1 , C_2), and its noncorrosive properties.⁴¹

2.1.2.4 Ionic Liquids

Development of ionic liquids (ILs) as tailorable solvents and absorbents has led to research into their use for absorbing H_2S from natural gas.^{18–25} The tunable properties of ILs and negligible vapor pressure make them particularly well-suited to optimizing removal of H_2S from a natural gas stream.¹⁸ In a few cases, they were found to be more effective than amine treatment methods.^{22,24} However, the primary drawback is that an IL may work very well for a particular concentration of H_2S , but not nearly as well for other concentrations of H_2S or in combination with other concentrations of contaminants. The inability to find one IL to serve as a universal solvent for removing H_2S from natural gas streams makes this method extremely difficult to widely implement.

In conclusion, amine gas treating is used by the natural gas industry, but is sometimes ineffective and uneconomical, driving a need for a simple, cost-effective method to remove the hydrogen sulfide. While a variety of methods have been found to work at small scales or for certain concentrations of contaminants, a more universal and cost-effective treatment method is still needed.

2.1.2.5 Membrane Filtration

Membrane filtration systems have been studied for use in removing contaminants from natural gas.^{16,17,57} However, these systems have been shown to be most effective at removing CO_2 but not necessarily H_2S , and are most effective for smaller producers that produce less than 5 million standard cubic feet per day.¹⁷ At smaller production levels, membrane technology is more cost-effective than amine treatment; when production exceeds 5 million scfd, amine systems are more economically viable.¹⁷ The primary inhibitor to adoption of membrane technology is ineffective removal of H_2S , particularly in lowering H_2S concentrations below 100 ppm.⁵⁷ One study found an electrolyte membrane could achieve up to 81% removal of H_2S from a gas mixture containing 2000 ppm H_2S ,¹⁶ but this technology has not been adopted at an industrial scale.

2.1.2.6 Molecular sieves

In a molecular sieve process, a packed bed utilized porous crystalline solids which contain locally charged sites in the pores.^{41,48-50} The pore size must be small enough to prevent entry of hydrocarbons and typically allows entry of H₂S, H₂O, and CO₂.⁴¹ Polar water and H₂S form weak ionic bonds with the charged sites, and the crystalline solids can be regenerated by flowing through hot gas which breaks the ionic bonds and removes the H₂S and H₂O.^{41,48-50} Molecular sieves work best in processing small gas streams and are typically used as a secondary step with other processes.⁴¹

2.1.2.7 Iron sponges

An iron sponge process for treating sour natural gas is a type of solid bed processed in which the sour gas stream flows through a fixed bed of solid particles, and the acid gases are held in the bed.^{41,51} The iron sponge process utilizes iron oxide to convert H₂S to iron sulfide and water (shown in Reactions 2.1 and 2.1), and is a viable process for treating gas with H₂S concentrations below 300 ppm operating at pressures below 3500 kPa.⁴¹ Iron sponges are designed to only remove H₂S, not CO₂ or other acid gases.



Successful conversion of H₂S to iron sulfide relies on careful pH control (8-10) and temperature control (< 110 °C), and sufficient water vapor in the system.^{41,51} The solid bed material is constructed by treating wood chips (or similar materials) with ferric oxide to create high surface area of ferric oxide.^{41,51,52} Regeneration of the solid material is performed by slowly introducing air to the reaction vessel and allowing it to oxidize the ferric sulfide, forming sulfur and ferric oxide.⁴¹ The regeneration reactions are highly exothermic and if not carefully controlled, the wood chips may ignite.⁴¹

2.1.2.8 Zinc oxides

Zinc oxide processes utilize granular zinc oxide in a solid bed to react with H₂S, forming zinc sulfide and water as shown in Reaction 2.3.^{41,53,54}



The reaction is diffusion controlled, with temperatures greater than 120 °C increasing diffusion and the reaction rate.⁴¹ Channeling in the solid bed is a concern in this process, so typically the solid beds are designed to be long and thin to decrease chances of channeling.⁴¹ This method is rarely used because the spent bed of zinc sulfide is a heavy metal salt that is difficult to dispose of.⁴¹

2.1.2.9 Summary of H₂S Removal Methods

Despite the many methods for sweetening sour natural gas, amine gas treating remains the most common method due to low solvent cost, high solvent regenerative power, and the success of the process in producing sweet gas that meets requirements for pipeline injection. However, there is a desire and a need to develop a method that uses bio-based solvents rather than harsh chemicals, which is economically feasible, less energy intensive, able to treat feed gas with a range of H₂S concentrations, and could compete with existing methods.

2.1.3 Emerging Practices for Treating Biogas

Biogas, a form of methane developed through fermentation of organic matter such as food waste or agricultural materials, is an emerging form of renewable energy.⁵⁸ Like natural gas, biogas is of interest for use as a replacement for transportation fuels as well as for heat and power.⁵⁸ Because it can be produced from waste materials such as food waste, biomass, and agricultural residues, it is of great interest for replacing natural gas.⁵⁸ However, much like natural gas, biogas often has high concentrations of contaminants, such as H₂S, CO₂, and others including water, nitrogen, oxygen, halocarbons, and methyl siloxanes.⁵⁸⁻⁶⁰ Much like ‘sour natural gas’ is ‘sweetened’ to natural gas, ‘biogas’ is ‘upgraded’ to ‘biomethane’ for use as fuel. Table 2.4 compares the composition of the three methane-based fuels: natural gas, biogas, and biomethane.

Table 2.4. Comparison of composition of biogas, biomethane, and natural gas.^{61–63}

Gas composition	Biogas	Biomethane	Natural Gas
Methane	40-75%	94-99.9%	93-98%
Carbon Dioxide	15-60%	0.1-4%	1%
Nitrogen	0-5%	< 3%	1%
Oxygen	< 2%	< 1%	-
Hydrogen	< 1%	Traces	-
Hydrogen Sulfide	0 – 20,000 ppm	< 10 ppm	Traces
Ammonia	0 – 500 ppm	Traces	-
Ethane	-	-	< 3%
Propane	-	-	< 2%
Siloxane	Traces	-	-
Water	1-7%		

In the process of upgrading biogas to biomethane, carbon dioxide and hydrogen sulfide, the two largest contaminants, must be removed. A scheme for biogas production is shown in Figure 2.2.

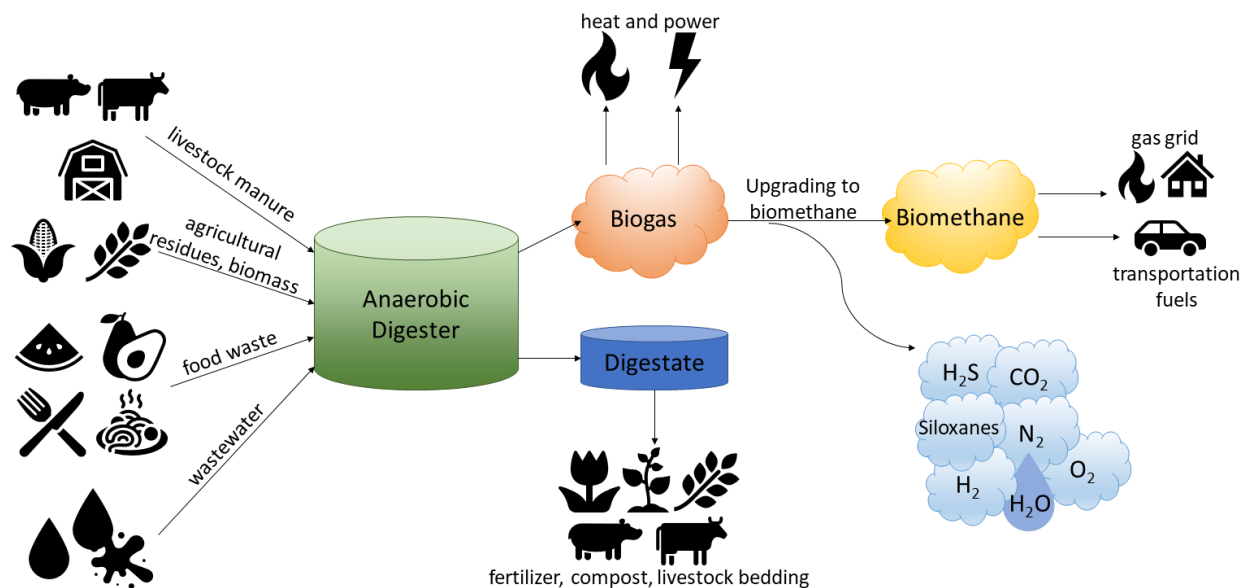


Figure 2.2. Process for producing biogas and biomethane from livestock manure, agricultural residues, biomass, food waste, and wastewater, through anaerobic digestion. Modified from the Environmental and Energy Studies Institute Biogas Fact Sheet.⁶⁴

The composition of biogas is largely dependent on the feedstock(s) used and the anaerobic digestion procedure.^{58–60} In creating technology and processes for upgrading biogas to biomethane, the greatest challenge to overcome is designing a process that is effective for dealing with widely variable methane composition in the biogas input streams, as well as widely variable concentrations of contaminants such as H₂S and CO₂.^{58–60} Use of biomethane in transportation fuels or injected into the natural gas power grid is preferable to combustion of biogas for heat and power, because biomethane is more efficient.⁵⁸ Several methods are being researched for removal of H₂S from biogas as part of the process for upgrading biogas to biomethane.^{58,59,72,60,65–71}

2.1.3.1 Biological H₂S Removal from Biogas

Research into biological methods for removing H₂S from biogas seek to develop economical and environmentally friendly alternatives to chemical desulfurization.⁵⁹ A summary of biological H₂S removal methods is shown in Table 2.5.

Table 2.5. Summary of biological methods for removing H₂S from biogas.^{60,65–68}

Method	Description	Advantages	Disadvantages
Biofiltration/ Biotrickling filtration	Sulfur-oxidizing bacteria (SOB) in a packed bed/column oxidize H ₂ S to other sulfur species	Reduce H ₂ S levels from thousands of ppm to hundreds of ppm; control of sulfur species formed by controlling what SOBs are used	Does not contribute to CO ₂ removal and dual-treatment methods are preferred; sulfur formation clogs system
<i>In situ</i>	Lithoautotrophic microaerophilic SOBs grow on the walls of the headspace of the anaerobic digester and convert H ₂ S to sulfur	No need for desulfurization downstream from the digester, no need for extra modules or supports for the SOBs	Requires carefully controlled conditions for the microorganisms to grow and convert H ₂ S to S; tank needs cleaned periodically to remove sulfur build-up
Microalgae photobioreactors	Microalgae and SOBs are used in combination in photobioreactors for fixing CO ₂ and H ₂ S	H ₂ S conversion to sulfate is near 100%; removes CO ₂ and H ₂ S simultaneously	Cost and needs of the microalgae and photobioreactors

Biotrickling filtration is a method that circulates biogas through a packed bed containing sulfur oxidizing bacteria (SOB).^{59,60,73,74} The aerobic SOB are immobilized in the packed bed and grown as a biofilm on plastic supports, providing high surface area for H₂S contacting.^{58,59} Biogas and air enter the bottom of the packed column and flow upwards; a nutrient wash trickles from top to bottom and provides nutrients to the microorganisms while also washing out products formed.⁵⁸ Oxidation products include sulfur, sulfate, and sulfuric acid; sulfur clogging the packed bed is of concern.^{58,59,73,74} Biotrickling methods have been successfully used to scrub biogas of H₂S concentrations up to 12,000 ppm.^{59,74} Key parameters that must be considered when designing this type of system include oxygen mass transfer, type of diffuser, retention and residence times, and H₂S concentrations in the feed gas.⁵⁹

In situ H₂S removal relies on lithoautotrophic microaerophilic SOBs to grow on the walls of the anaerobic digestion tank in the headspace, which convert H₂S to sulfur and create a buildup of sulfur on the inside of the tank.^{60,68} This method requires carefully controlled conditions to create microaerobic conditions in the headspace of the tank for the SOBs to grow, and the tanks must be cleaned periodically to remove the sulfur build-up.^{60,68}

Methods have been developed to use microalgae and SOB_s in photobioreactors to remove CO₂ and H₂S in one unit operation of a biogas upgrading process.^{60,65–67} Photosynthetic microalgae fix CO₂ and provide oxygen needed by the SOB_s to convert H₂S to sulfate.⁶⁰

2.1.3.2 Chemical H₂S Removal from Biogas

Despite interest in using biotechnology to treat biogas and upgrade it to biomethane, chemical methods (including sorption and precipitation) continue to prevail industrially, primarily due to being long-established in gas sweetening.⁶⁰ A comparison of methods is shown in Table 2.6.

Table 2.6. Chemical methods for removing H₂S from biogas.^{60,69–71} More information about chemical removal of gaseous H₂S can be found in *Section 2.1.2*.

Type of method	Method	Advantages	Disadvantages	Reduce H ₂ S to:
<i>In situ</i> in the biogas digester	Addition of iron salts (FeCl ₂ or FeCl ₃)	Requires only an iron salt storage tank and pump to add directly to digester	High cost of reagents	150 ppm
Packed adsorption modules	Packed with iron oxide, zinc oxide, or activated carbon	Fast oxidation kinetics	High cost of regeneration and/or replacement of adsorbent materials	1 ppm
Chemical absorption	Organic solvents like in conventional gas sweetening	Well-established kinetics and methods	Use of harsh chemicals (in some cases)	Varies based on solvents/ methods

Addition of iron sulfide salts is an *in situ* method for removing H₂S from biogas in the digester. Iron's affinity for forming iron sulfide has been taken advantage of to create conditions for *in situ* precipitation of iron sulfide in biogas digesters.^{60,69–71} Iron chloride salt can be added to the digester and will dissociate and mix with H₂S to form FeS, an insoluble iron sulfide salt.^{60,70} The primary advantage of this method is it only requires an iron salt storage tank and pump to achieve.⁶⁰ The primary disadvantage of this method is the high cost of the iron chloride salts.⁶⁰

Similar to iron sponges and zinc oxide methods in conventional gas sweetening (*Sections 2.1.2.7 and 2.1.2.8*), packed columns containing iron oxide or zinc oxide are sometimes used to remove H₂S from a biogas stream as part of the upgrading process.^{60,69,70,72} An advantage is high removal of H₂S, down to 1ppm, and fast oxidation kinetics.⁶⁰ A disadvantage is the high costs regenerating and/or replacing the adsorbent materials.⁶⁰

Other chemical absorption methods for removing H₂S from biogas are similar to those used in conventional natural gas sweetening processes, relying on organic solvents to remove H₂S and stripping the solvents of H₂S (and other acid gases) to recover H₂S and regenerate the solvents. These methods are well-outlined in *Section 2.1.2*.

2.2 Conductor-like Screening Model for Real Solvents

2.2.1 Theory

The Conductor-like Screening Model for Real Solvents (COSMO-RS) is commonly used to study solvation phenomena, including the partitioning of molecules in vapor-liquid and liquid-liquid systems.⁷⁵ It has an advantage over other solvation models in utilizing a statistical thermodynamics approach to analyze interacting surfaces.⁷⁶ COSMO-RS is capable of predicting a variety of thermodynamic properties, including vapor pressure, solubility, activity coefficients, and more.³⁷ For a solute molecule *X* (in this study, hydrogen sulfide), COSMO calculates a quantity known as the ideal screening energy, ΔX , as the difference between the solute's energy in vacuum vs. in a conducting continuum. The screening energy is calculated for tiny surface segments of the molecule to develop a surface charge density. The surface charge density is then used to create a σ -profile, which is a probability distribution of the screening charge densities of the surface segments. Using the COSMOthermX software, the σ -profiles of the molecules are used to calculate chemical potential of molecules in a mixture, and the chemical potential can be converted to the activity coefficient and partition coefficient. The primary advantage of the COSMO-RS method is that only molecular structure of the solvents and solutes and knowledge of the phase composition in a two-phase system are needed in order to calculate the partition coefficient.

2.2.2 Applications

COSMO-RS is used to study a variety of solvation-related questions, but most relevant to this research is the use of COSMO-RS in predicting partition coefficients. Several studies, including studies in this research group,^{29–31} have utilized COSMO-RS to predict partition coefficients of a variety of molecules in liquid-liquid systems,^{32–35} and have verified the accuracy of COSMO-RS predictions using the experimental shake-flask method and liquid chromatography. COSMO-RS has also been used to study vapor-liquid systems and behavior of molecules at vapor-liquid equilibrium.^{35,36,77–82}

2.2.3 Vapor-Liquid Equilibrium Studies

COSMO-RS has been used to study the behavior of a variety of systems at vapor-liquid equilibrium,^{35,36,77–82} but most pertinent to this research are studies using COSMO-RS to study fatty acids in biodiesel⁷⁹ and separating hydrogen sulfide from methane.⁸²

COSMO-RS has been used to calculate LLE and VLE phase equilibria of refining operations for enzymatic biodiesel production.⁷⁹ Biodiesel produced from soybean feedstocks was modeled as a weighted sum of five fatty acid components: palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. The BP-TZVP parameterization set was used and models were ran at temperatures up to 130 °C, and the study found reasonable agreement between COSMO-RS predictions and experimental data.⁷⁹

Another study focused on using COSMO-RS to screen ionic liquids for separating hydrogen sulfide from methane and ethane.⁸² While ionic liquids are not of interest in this study, the use of COSMO-RS to evaluate H₂S solubility in methane, and the approach and parameterization used in this paper, are relevant and useful to this study. Density functional theory was applied using the BP-TZVP parameterization set in COSMOthermX and the solubility of H₂S in methane and other gases was calculated. Semi-empirical equations were developed that provide a correlation between the COSMO-RS predictions and experimental solubility collected from a variety of sources, so that solubility of H₂S can be accurately and confidently predicted when experimental solubility is not available.⁸²

2.2.4 Software Workflow

HyperChem, Turbomole (TmoleX), and COMSOtherm (COSMOthermX) can be used in a workflow shown in Figure 2.3 to model a biphasic system using only molecular structures and phase composition data as input.

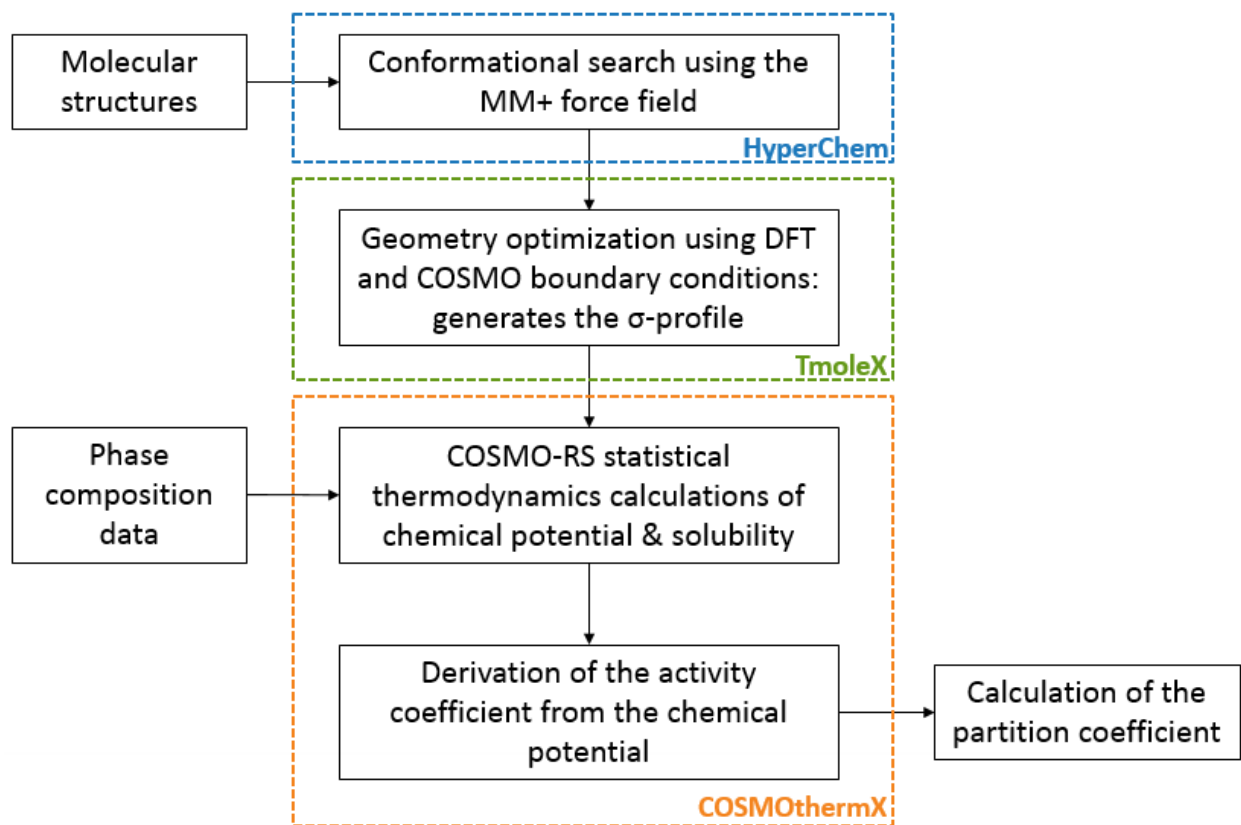


Figure 2.3. A workflow starting only with molecular structures and phase composition data can be used to calculate the partition coefficient of (a) solute(s) in a biphasic liquid-liquid or liquid-vapor system, based on the COSMO-RS theory.

2.3 Soybean Oil

Soybean and high-oleic soybean oil are abundantly available in Indiana and other Midwestern states, which contribute largely to the 4.3 billion bushels of soybeans and 22.6 billion pounds of soybean oil produced in the U.S. in 2016.³⁸ Both high-oleic soybean and conventional soybean oil contain unsaturated fatty acids (oleic and linoleic, respectively), which may be capable of binding sulfur. The unsaturated fatty acids in these oils make them promising extraction solvents for the removal of hydrogen sulfide from natural gas.

2.3.1 Resource Availability

The United States and in particular midwestern states, such as Indiana, produce billions of pounds of soybean oil annually.⁸³ Approximately 10% of soybeans harvested are converted to soybean oil. Annual U.S. production of soybeans and soybean oil is shown in Figure 2.4.

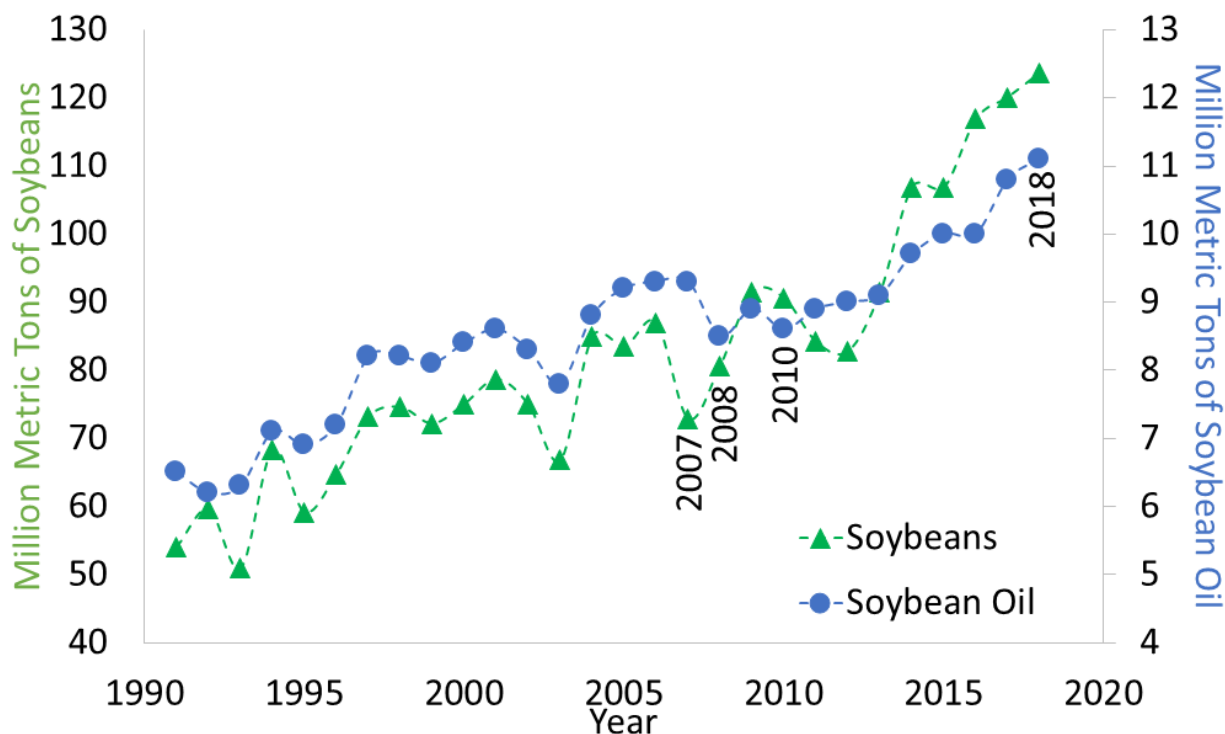
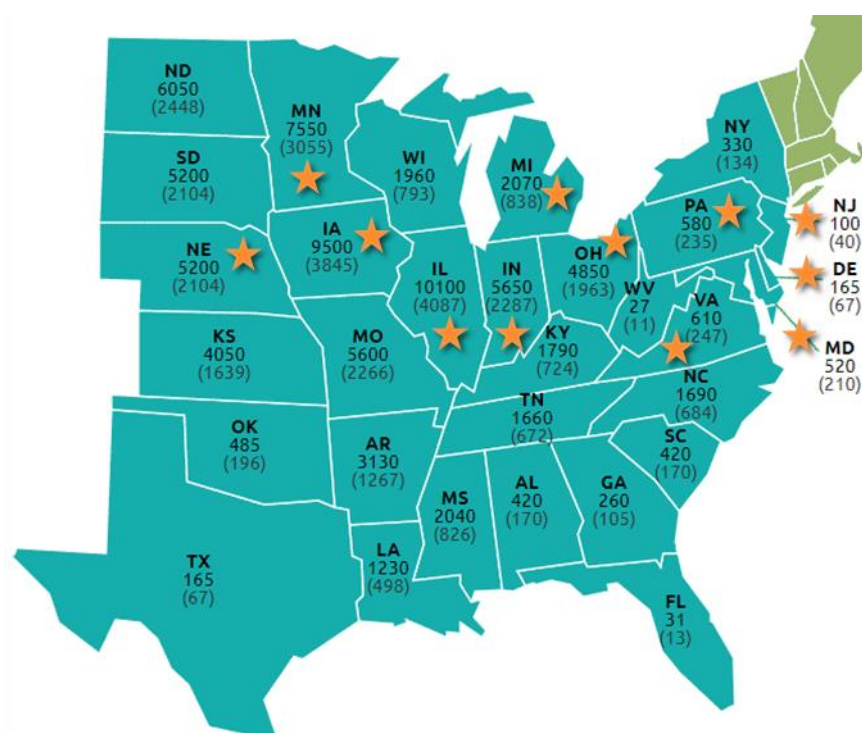


Figure 2.4. U.S. soybean and soybean oil production in million metric tons, 1991 – 2018. Data from The American Soybean Association 2019 SoyStats report.⁸³

Soybean oil accounts for 55% of vegetable oil consumption in the United States, with canola oil taking 14% of the market share and other vegetable oils taking less than 10% each.⁸³ 68% of soybean oil is used in food products, 25% in biodiesel and for bioheat, and 7% goes to industrial uses including solvents, paints, plastics and cleaners.⁸³ The U.S. Soybean Check-off advertises a “Fuel vs. Food: You don’t have to choose” message, indicating a national effort to find new industrial and non-food uses of soybean oils.⁸⁴ Additionally, the American Soybean Association and soybean checkoff groups intend to increase the amount of high-oleic soybeans harvested and production of high-oleic soybean oil by 2023.³⁸ Figure 2.5 shows a map of states with their production of soybean oil and indicates the states targeted for increased production of high-oleic soybeans.



U.S. Soybean **Area Planted by State** 2016
Thousand Acres (Thousand Hectares)

Figure 2.5. This map adapted from the SoyStats 2017 report shows the number of acres (hectares) of soybeans planted by state. In 2016, 500,000 acres of high-oleic soybeans were planted. The states marked with stars are targets in the U.S. Soybean Checkoff's initiative to have 18 million acres of high-oleic soybean planted by 2023.³⁸

2.3.2 Comparison of Soybean Oil and High-Oleic Soybean Oil

High-oleic soybean oil is derived from soybean varieties that produce higher amounts of oleic acid than the other fatty acids found in soybean and most oilseeds. A comparison of the fatty acid profile for soybean oil (SBO) and high-oleic soybean oil (HOSBO) is shown in Table 2.7. Soybean oil is high in linoleic acid, while high-oleic soybean oil has decreased linoleic acid content and oleic acid in the range of 65 – 85 weight percent depending on the variety or brand.^{38,84,85}

Table 2.7. Fatty acid composition of soybean oil (SBO) and high-oleic soybean oil (HOSBO) by weight percent. Oleic, linoleic, and α -linolenic acid are all unsaturated C18 molecules with 1, 2, and 3 double bonds respectively. Palmitic and stearic acid are saturated fatty acids.⁸⁵

Carbon bonds:		Weight %		
double bonds	Fatty acid	SBO	HOSBO	Molecular weight
C16:0	palmitic	11.0	6.0	256.42
C18:0	stearic	4.0	3.0	284.48
C18:1	oleic	22.0	85.0	282.46
C18:2	linoleic	55.0	4.0	280.45
C18:3	α -linolenic	8.0	2.0	278.43

Some of the reasons for the U.S. soybean growers' efforts toward increasing production of high-oleic soybeans is due to interest in high-oleic soybean oil as a healthier product when used in frying and cooking, and as a more stable product when used in industrial applications such as in paints and lubricants.^{85–88} A comparison of some properties of SBO and HOSBO are shown in Table 2.8.

Table 2.8. Similarities and differences between conventional soybean oil (SBO) and high-oleic soybean oil (HOSBO).^{86–88}

Conventional SBO & HOSBO	Conventional SBO	HOSBO
<ul style="list-style-type: none"> • Low cost • Grown and produced domestically • Excellent source of fat 	<ul style="list-style-type: none"> • Grown across the U.S. and globally • Good source of omega-3 fatty acids • Works well in salad dressings and cooking oils, which make up 40% of domestic use 	<ul style="list-style-type: none"> • Produced only in the United States • Extended fry life • Increased oxidative stability • Improved nutritional profile – approved heart healthy claim by FDA • Used in commercial baking and frying

2.3.3 Sulfur Binding Potential of Fatty Acids

As shown in Table 2.7, soybean oil and high-oleic soybean oil are primarily comprised of palmitic, stearic, oleic, linoleic, and α -linolenic acids. A number of studies, largely in the field of food chemistry, have examined the ability of different vegetable oils and fatty acids to bind elemental sulfur and sulfides such as H_2S . These studies are summarized in Table 2.9.

Table 2.9. Various studies in food chemistry and other fields have explored the binding of elemental sulfur and sulfides using different types of vegetable oils and fatty acids.

Vegetable Oil	Fatty acid %						Sulfur compounds absorbed	References
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Erucic		
Soybean	12.8	4.3	22.5	53.8	6.5	-	S; H_2S	Cowan <i>et al.</i> , 1946 ²⁸ ; Endisch <i>et al.</i> , 2013 ⁸⁹ ; Schwab & Gast, 1968 ⁹⁰
Canola	4.8	1.9	57.8	20.4	12.6	2.4	S; H_2S	Cowan <i>et al.</i> , 1946 ²⁸ ; Endisch <i>et al.</i> , 2013 ⁸⁹
Linseed	7.0	4.0	20.0	14.0	55.0	-	S; H_2S	Cowan <i>et al.</i> , 1946 ²⁸ ; Schwab & Gast, 1968 ⁹⁰
Oleic Acid	-	-	100	-	-	-	S	Westlake, 1946 ²⁷
Palm	41.9	6.4	41.2	10.5	-	-	S; H_2S	Endisch <i>et al.</i> , 2013 ⁸⁹

2.3.4 Comparison with other Seed Oils

Conventional soybean oil and high-oleic soybean oil not only share many characteristics with each other but are also very similar in terms of fatty acid composition, flavor profile, oxidative stability, and other qualities to other seed oils such as canola, sunflower, and palm oils.^{85,87,88,91–93} A comparison of the fatty acid profiles of conventional SBO, HOSBO, canola and sunflower oils are shown in Table 2.10.

Table 2.10. Fatty acid composition of conventional soybean oil (SBO), high-oleic soybean oil (HOSBO), canola oil, sunflower oil, and palm oil.^{85,93}

Fatty acid	Molecular weight	Carbon bonds: double bonds	Weight %				
			SBO	HOSBO	Canola	Sunflower	Palm
palmitic	256.42	C16:0	11.0	6.0	4.9	6.2	36.7
stearic	284.48	C18:0	4.0	3.0	1.6	3.7	6.6
oleic	282.46	C18:1	22.0	85.0	33.0	25.2	46.7
linoleic	280.45	C18:2	55.0	4.0	20.4	63.1	8.6
α -linolenic	278.43	C18:3	8.0	2.0	7.9	0.2	0.3
gadoleic	310.51	C20:1	-	-	9.3	-	0.2
erucic	338.57	C22:1	-	-	23.0	-	-

In addition to comparing the fatty acid profile, other characteristics can be compared as well, and are compared in Table 2.11.

Table 2.11. Characteristics and comparison between conventional soybean oil (SBO), high-oleic soybean oil (HOSBO), canola oil, sunflower oil, and palm oil.^{38,85,88,93}

Characteristic	SBO	HOSBO	Canola	Sunflower	Palm
Available acreage (US)	85 million	18 million by 2023	1.74 million	1.6 million	35 million global
Flavor profile	Neutral	Neutral	Neutral to grassy	Mild, pleasant flavor	Nearly flavorless
Relative Oxidative Stability	Low	Highest	Medium	Lowest	High
Market/Uses	Bottled cooking oil, frying	Baking, frying	Bottled cooking oil, dressings, frying	Snack foods	Margarine, baked goods
Price to customers	Average	Expensive	Average	Most expensive	Most economical
Kinematic Viscosity (mm²/s, 40 °C)	4.2	4.1	4.4	4.2	4.5
Iodine Value (g I₂/100g)	128	85.9	109	132	57
Acid Value (mg KOH/g)	0.14	0.12	0.16	0.15	0.12

High-oleic seed oils – including high-oleic soybean oil and high-oleic canola oil – are gaining traction in food processing due to their improved oxidative stability, more neutral flavor profiles, extended fry life.^{86–88} High-oleic soybean oil has been approved to be labeled as “heart healthy” by the FDA, and growing consumer interest in healthy products and U.S. produced goods provides more market opportunities for high-oleic soybean oil.^{86–88} The higher oxidative stability of high-oleic soybean oil also increases interest in industrial uses such as paints and solvents.^{86–88}

Although palm oil is the most commonly used in food products globally, has a nearly flavorless taste profile and is extremely low cost,^{86,87} increased consumer awareness of deforestation and other perceived negative practices of palm oil production has led to some consumer-driven interest in replacing palm oil with suitable alternatives in products,^{94,95} Although sunflower oil has many favorable qualities including high-oleic acid content and sustainable production processes, production of sunflower oil is far lower than that of other seed oils and sunflower oil is by far the most expensive.^{86–88,96,97}

3. MATERIALS & METHODS

3.1 Molecular Modeling with COSMO-RS

To model a bi-phasic system consisting of a gas phase (methane or nitrogen), liquid phase (soybean oil, high-oleic soybean oil, or some other combination of fatty acids), and predict the partitioning of H₂S between the two phases, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used. COSMO-RS is described in detail in *Chapter 2 Section 2*, and a software workflow as shown in Figure 2.3 was used.

First, HyperChem (release 8.0, Hypercube, Inc.)⁹⁸ was used to draw the two-dimensional structures of the acids, methane, and hydrogen sulfide molecules. The three-dimensional structures of each molecule were generated under the Molecular Mechanics + (MM+) force field, which includes molecular dynamics calculations. Conformations of the five fatty acids found in soybean oils (stearic, palmitic, oleic, linoleic, α -linolenic) were generated using the conformational search feature. The number of conformations generated is dependent on the parameters chosen, including limits on the energy range and root mean square error (RMSE). Conformations were considered duplicates if energy was within 0.05 kcal/mol and the maximum acceptable energy criterion was set to 1 kcal/mol above best. The RMS error was restricted to 0.25 Å and the number of accepted conformers was limited to 30. The number of conformers found for each acid was as follows: 30 palmitic acid, 1 stearic acid, 18 oleic acid, 30 linoleic acid, 2 α -linolenic acid conformers.

Next, TmoleX (Version 3.4, COSMOlogic GmbH & Co. KG, Germany)⁹⁹ was used to process all of the conformations, using a combination of density functional theory and statistical thermodynamics to calculate the screening charge density of the surface of each molecule, which is then saved as a σ -profile. The calculations in TmoleX utilize the Becke-Perdew functional and triple zeta valence polarized (TZVP) basis set for density functional theory.¹⁰⁰ B-P is a density functional theory model proposed by Becke¹⁰¹ and TZVP is a basis for molecular calculations.¹⁰² The average screening charge density, σ_m , is then used to calculate the σ -profile, which represents the probability of a surface segment having a screening charge density of σ_m . The σ -profiles generated by TmoleX represent the probability distribution of the screening charge densities of the

surface segments. Only molecular structure and a few basic constants are needed in order to calculate the σ -profile, which is a major advantage of using COSMO-RS. Figure 3.1 shows the σ -profile for one conformer of oleic acid.

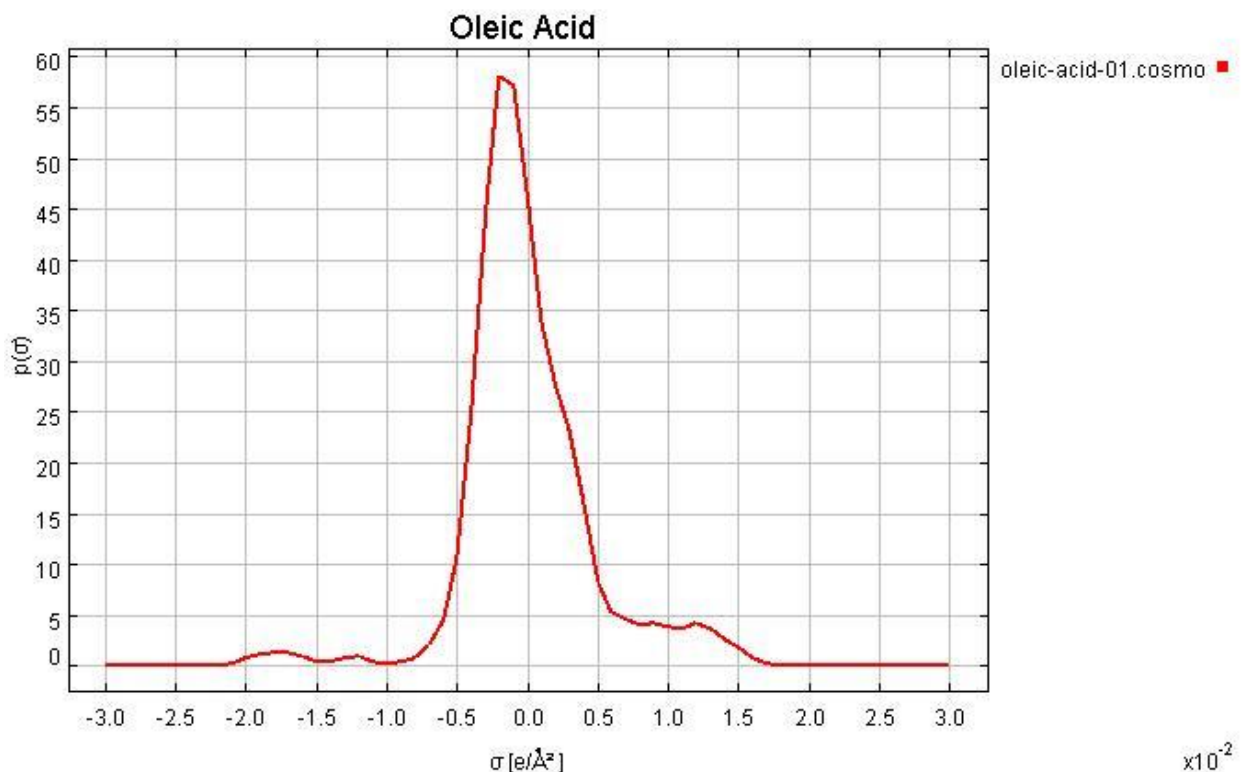


Figure 3.1. σ -profile of oleic acid lowest energy conformation, generated by TmoleX.

Additionally, TmoleX generates a more qualitative way of examining the molecules in the form of a σ -surface, as shown in Figure 3.2. The σ -surface is a visual representation of the σ -profile and represents the screening charge density of the surface of the molecules.

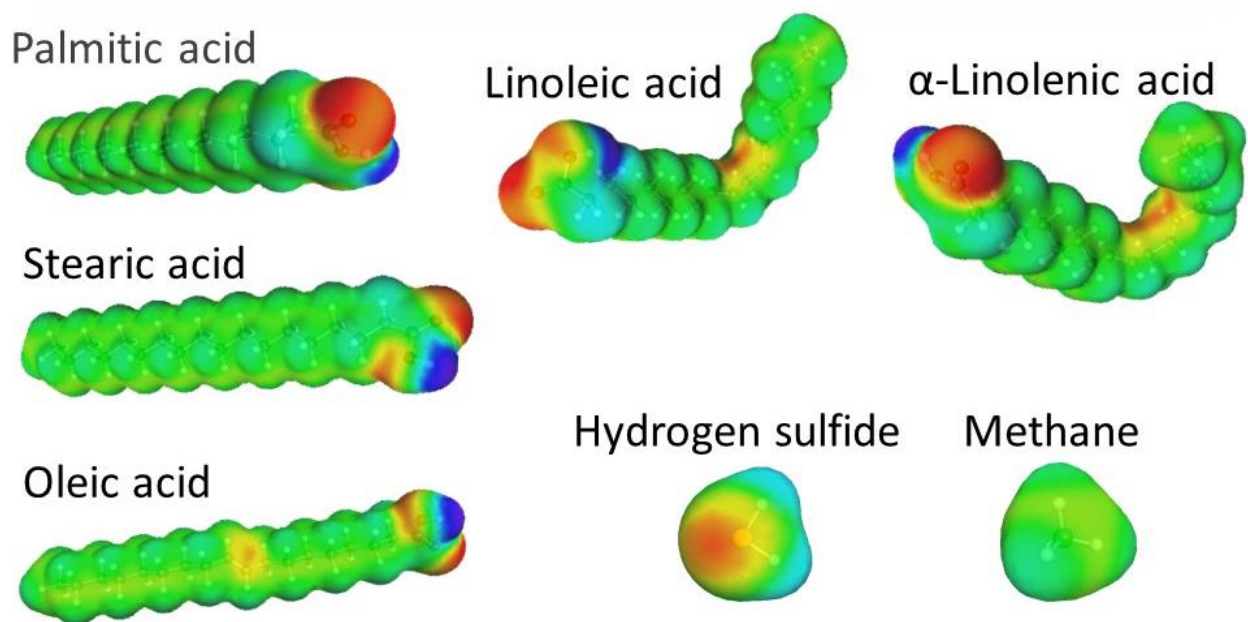


Figure 3.2. σ -surfaces for the five fatty acids found in soybean oils, as well as for hydrogen sulfide and methane. These σ -surfaces were generated by TmoleX and visualized using COSMOview.

Although the surface appears continuous, it is an illustration of tiny surface segments, each of which has their own screening charge density, potential for interactions, and which can be quantitatively examined in the σ -profile or qualitatively examined in the σ -surface. Blue areas represent where the molecule is likely to be a hydrogen bond donor and red areas are where the molecule is likely to be a hydrogen bond acceptor.

Finally, the σ -profiles generated by TmoleX are imported into COSMOthermX (Version 13, COSMOlogic GmbH & Co. KG, Germany)¹⁰³ and used to simulate molecular interactions in the two-phase system. COSMOthermX is used to calculate the activity coefficient of hydrogen sulfide in each phase, and then the partition coefficient is calculated as the ratio of the activity coefficients multiplied by the molar volume of each phase. The soybean oil fatty acid mass fractions (Table 2.7) were used as the lower phase. The activity coefficient was calculated using the activity coefficient tab in COSMOthermX, using all conformers and using only the lowest energy conformers. There was negligible difference, indicating using the lowest energy conformation should be sufficient. The upper phase was modeled as 100% methane. The partition coefficient (K) was derived from the activity coefficients using Equation 3.1.

$$K_i^{UL} = \frac{\gamma_i^L}{\gamma_i^U} \times \frac{\sum x_i^L v_{0j}}{\sum x_i^U v_{0j}} \quad (3.1)$$

In Equation 3.1, γ_i is the activity coefficient of H₂S in the upper (U) and lower (L) phases at infinite (i) dilution, and $\frac{\sum x_i^L v_{0j}}{\sum x_i^U v_{0j}}$ is the ratio of the molar volumes of each phase.

3.2 Development of H₂S Gas Bubbling Systems

3.2.1 First iteration: 1L Gas Bubbler

The first round of physical experiments was conducted using a setup as shown in Figure 3.3. A 1L glass gas-wash bottle was used as a sort of bubble column, which is advantageous as the mass transfer and fluid dynamic characteristics of such configurations are well understood.^{104,105} The gas-wash bottle was filled with 900 mL of soybean oil and the headspace flushed with nitrogen gas. A compressed gas cylinder containing methane with 4 ppm hydrogen sulfide was obtained from American Welding & Gas, Inc., Lafayette, IN. The compressed gas was used to flow gas into the gas-wash bottle, and the methane/hydrogen sulfide gas assumed to displace the nitrogen. Outlet gas from the gas-wash bottle was collected with intention to be analyzed using gas chromatography (GC) or gas chromatography – mass spectrometry (GC-MS).

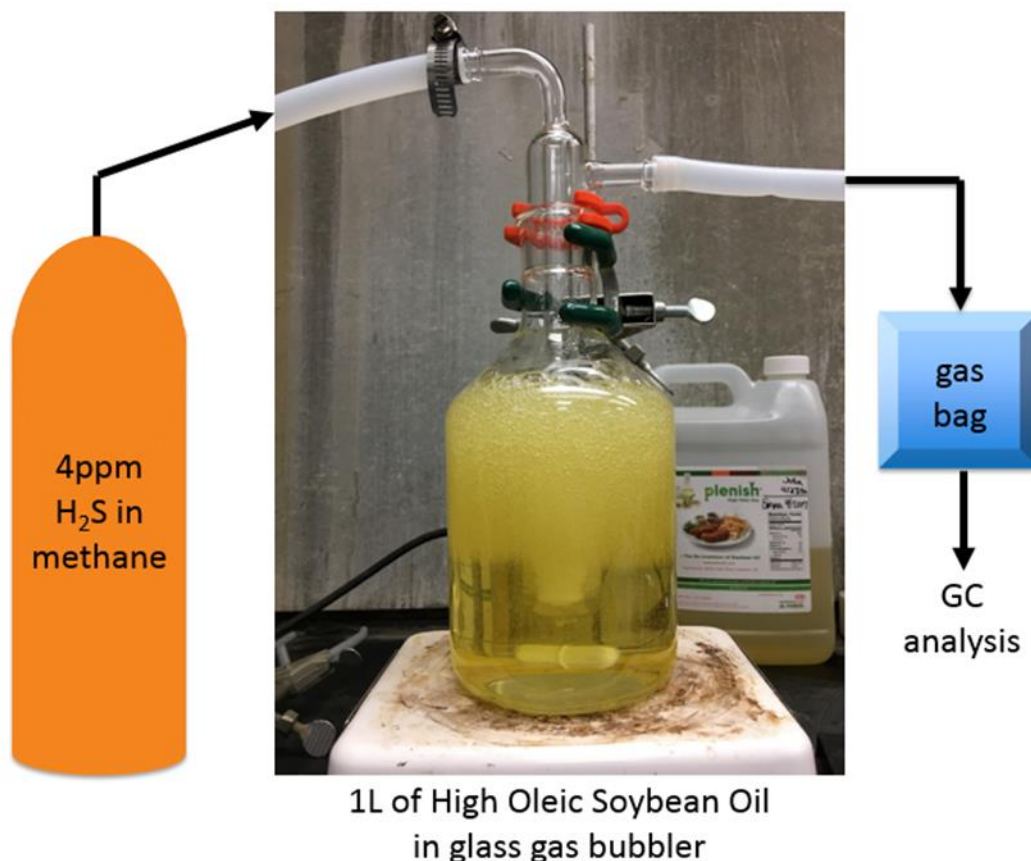


Figure 3.3. Experimental setup for bubbling CH₄/H₂S mixture through soybean oil. Initially, these experiments will be conducted at standard temperature and pressure, with temperature controlled using a water-bath as necessary.

The intention of these experiments was to determine the effectiveness of the soybean oil in removing the hydrogen sulfide from the methane, and use gas chromatography (GC) to analyze the hydrogen sulfide concentrations in the methane after bubbling it through the soybean oil, and analyze sulfur species in the soybean oil as well. Preliminary runs using this apparatus found a decrease from 4 ppm to 2 – 3 ppm H₂S in the outlet gas after passing through the soybean oil for five minutes and being collected in a gas bag at ambient conditions; this was completed in triplicate and the inlet and outlet gas' H₂S content was measured using a BIOGAS 5000 portable gas analyzer (Landtec North America, Dexter, MI, USA). However, in the course of these preliminary experiments, several experimental design flaws were found. Despite many attempts and collaboration with technicians and chemists from Agilent Technologies, there was an inability to successfully detect H₂S and/or insufficient distinction between CH₄ and H₂S peaks using GC or GC-MS techniques on the available equipment (including available instruments, columns, and

detectors). There was also an inability to develop a method for detecting H₂S/sulfur species in the soybean oil using available equipment and instrumentation. This method utilized large volumes of soybean oil which were then presumed to be contaminated/containing H₂S, in addition to using large volumes of gas. There was also insufficient resolution of the H₂S detection on the BIOGAS 5000 Analyzer (1ppm H₂S resolution) and concern that 4ppm was not a high enough starting concentration of H₂S, and that explosive methane gas was hazardous to be using in the lab. Based on all these concerns, experimental design shifted toward using small volumes in glass headspace bottles and in silicone dip tubes, as described in Sections 3.2.2 and 3.2.3.

3.2.2 Equilibrium Extraction of H₂S in Glass Headspace Bottles

To control the scale of experiments and volume of materials used, as well as to understand the equilibrium conditions for the system, studies were developed using 150 mL glass headspace bottles. Calibration cylinders of 40 ppm H₂S in balance Nitrogen (Ideal Calibrations, LLC, Melvindale, MI) were used rather than H₂S in methane for safety reasons and based on availability of gas handling equipment and protective safeguards. High-oleic soybean oil (Archer Daniels Midland Company, Frankfort, IN), soybean and canola oils (purchased locally, Great Value brand, Walmart Inc.), sunflower oil (purchased locally, Spectrum Naturals brand, Fresh Thyme Market), heptane and 1-hexene (Sigma-Aldrich) and water (deionized in-house) were used as solvents. 50 mL of solvent was added to a glass headspace bottle (150 mL), which was then sealed with a rubber septum and aluminum crimp-cap. Ambient air was removed via syringe. Gas (~100 mL) containing 40 ppm H₂S in nitrogen was introduced at a rate of 0.25 L/min to the bottle. The setup is depicted in Figure 3.4.

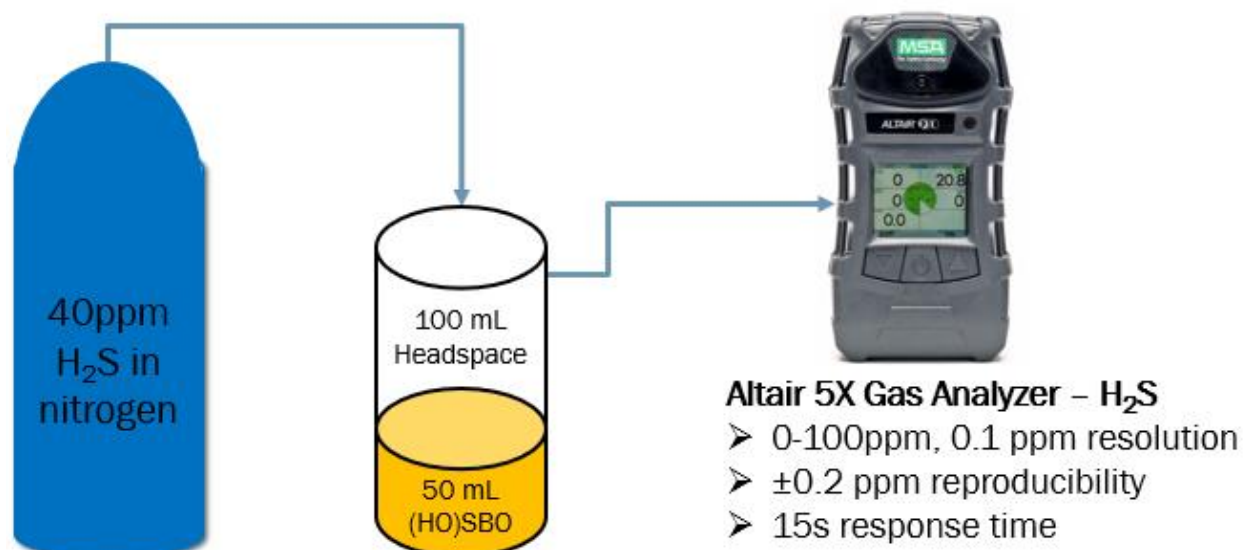


Figure 3.4. Setup for equilibrium extraction studies of H₂S between nitrogen gas and a liquid phase comprised of soybean oil (SBO), high-oleic soybean oil (HOSBO), or other solvents. Each sample experienced a residence time between 0 – 60 minutes that included no mixing (0 minutes), shaking by hand (up to 1 minute), or 200 rpm in an incubator shaker (15 – 60 minutes). At the conclusion of the residence time, the Altair 5X was used to determine the concentration of H₂S in the headspace.

The gas cylinder was connected to the bottle via 1/8" tubing and an 18-gauge needle. Samples were taken in triplicate for each solvent and each temperature under study at residence times ranging from 0 – 60 minutes. The 0 time-point samples had no forced mixing and the samples with residence times less than 1 minute were vigorously hand shaken. All other samples were placed in an incubator shaker at 200 rpm. The bottles were then connected to an Altair 5X Gas Analyzer (Ideal Calibrations, LLC, Melvindale, MI) and analysis of H₂S remaining in the gas phase was determined as described in 3.3: *Analysis of H₂S*.

3.2.3 Saturation Studies and Isotherm Modeling

To determine the saturation limits and capacity for removing H₂S from a gas phase, experiments were designed to collect data for isotherm modeling. Solvents under study included soybean oil (SBO), high-oleic soybean oil (HOSBO), canola oil, sunflower oil, heptane, 1-hexene, and water. 40 mL of solvent was added to a 50 mL conical tube with a silicone dip tube (Chemglass Life Sciences, LLC). Gas containing 40 ppm H₂S in nitrogen was added at an assumed constant flow rate for 30 minutes. The setup is depicted in Figure 3.5.

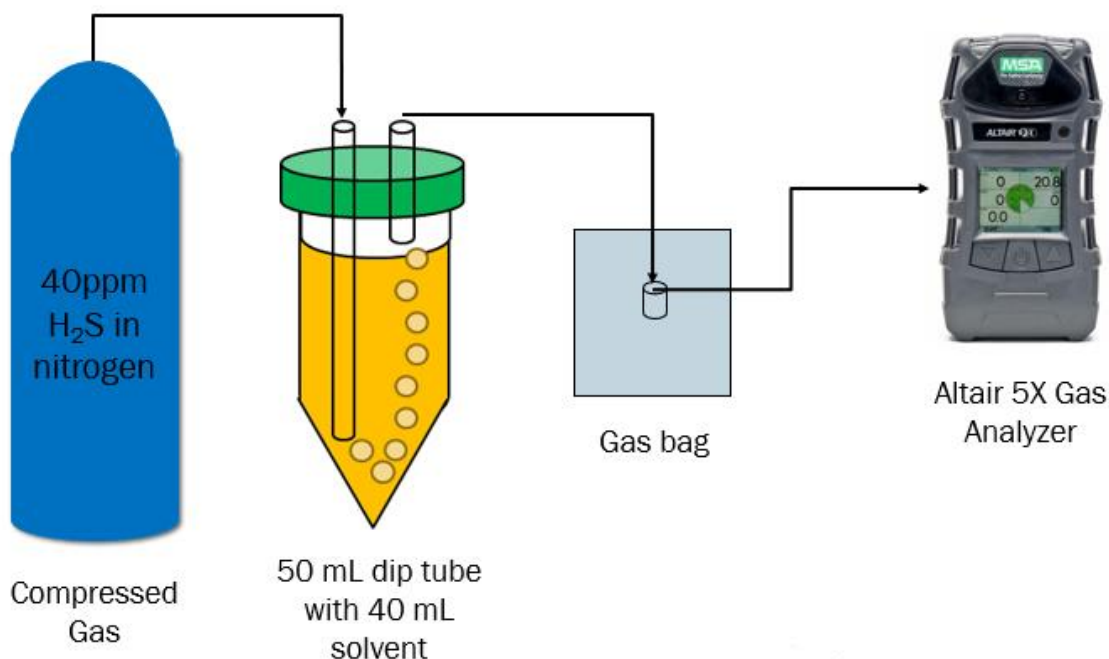


Figure 3.5. Setup for H₂S extraction studies and isotherm data collection.

The outlet gas was collected in a gas bag every 1 minute for 15 minutes and every 5 minutes for an additional 15 minutes, for a total of 30 minutes of gas bubbling through one solvent sample. This was conducted in triplicate for each solvent at each temperature under investigation. The Altair 5X Gas Analyzer was used to determine the amount of H₂S remaining in the outlet gas and the difference between inlet and outlet was assumed to be trapped in the solvent. The data was then used for Langmuir and Freundlich isotherm modeling and determination of adsorption capacity for H₂S.

3.3 Analysis of H₂S – Gaseous and Dissolved

An Altair 5X gas analyzer (rented, Ideal Calibrations, LLC, Melvindale, MI) was used to measure H₂S concentration in inlet and outlet gases. To confirm the concentration of H₂S in the inlet gas, gas from the cylinder was flowed into a Tedlar PVF 1.6L gas sampling bag (Saint-Gobain Chemware) and then the Altair 5X sampled gas from the gas bag. This was repeated in triplicate and conducted before each set of experiments. The mass of H₂S introduced to each solvent could then be calculated using the concentration and known volume of gas. The Altair 5X included sensors for LEL (%), CO (ppm), O₂ (ppm), and H₂S (ppm). In particular, the low concentration

H₂S sensor it was equipped with had a range of 0 – 100 ppm with 0.1 ppm resolution and ± 0.2 ppm reproducibility. The Altair 5X required approximately 30 seconds to return a reading for each sample and for each sample the highest LEL (%), CO (ppm), and H₂S (ppm) values and lowest O₂ (%) values were recorded. Simple mass balance as in Equation 3.2 was used to determine the mass of H₂S presumed to be trapped in the solvent, and after conversion to concentration (using known volumes) the experimental partition coefficient, K_{exp} , was calculated using Equation 3.3.

$$H_2S_{(inlet\ gas)} = H_2S_{(outlet\ gas)} + H_2S_{(accumulated\ in\ solvent)} \quad (3.2)$$

$$K_{exp} = \frac{[H_2S]_{outlet\ gas}}{[H_2S]_{accumulated\ in\ solvent}} \quad (3.3)$$

3.4 Economic Analyses

For seed oils such as conventional soybean or high-oleic soybean oil to be viable extraction solvents for removing H₂S from sour natural gas, the cost of doing so would need to be less than or equal to conventional processes for treating sour natural gas.

Amine gas treating, explored in Section 2.1.2.1, is the most common industrial method for treating sour gas. Use of alkylamines solvents enable an adsorption and stripping cycle where alkylamines absorb H₂S and CO₂ and these gases are stripped off so the amine solvents can be regenerated and re-used.

To design a soybean oil (or other bio-oil) based system that would function similarly to amine gas treating and be economically competitive, the first step is construction of equilibrium stage diagrams and design of an extraction column. Experimentally determined partition coefficients for H₂S in soybean and high-oleic soybean oil were used.¹⁰⁶ A 1000 kmol/h feed gas flow rate was chosen to be on par with flow rates used industrially for treating sour gas using amine gas treating. In order to account for a variety of feed gas concentrations, feed gas concentrations of 40 ppm (2.6 mol%) and 400 ppm (20 mol%) H₂S in methane were used in simulations with 99.9% removal of H₂S as the target. A graphical solution¹⁰⁷ was used to determine the number of equilibrium stages necessary and the Kremser method^{107,108} was used to evaluate the percent of H₂S removed at each stage, up to 15 stages. To design a column to meet such specifications, flooding capacity and column diameter were calculated. The cost of a carbon steel trayed column

was calculated using the desired specifications and the relationship between equipment size, material, and cost developed in Table A-1 in Turton et al. 2012.¹⁰⁹ The Chemical Engineering Plant Cost Index was used to adjust to current prices in 2020.¹¹⁰ Solvent cost was calculated as a function of plant annual downtime and a sensitivity analysis relating solvent regenerative power to the cost of treating gas was determined.

4. ASSESSING VIABILITY OF SOYBEAN OILS TO REMOVE HYDROGEN SULFIDE FROM NATURAL GAS¹

4.1 Abstract

A combination of *in silico* and benchtop experiments were implemented to assess how soybean oils could remove hydrogen sulfide (H₂S) – a corrosive and toxic impurity – from natural gas. The rise of hydraulic fracturing (i.e. fracking) in the United States has increased both the use of and interest in natural gas, but natural gas extracted via fracking is increasingly concentrated with H₂S. The present work is a proof-of-concept study to evaluate the viability of conventional and high-oleic soybean oils to extract H₂S. The Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict the partition coefficient (K_{mod}) of the target molecule (H₂S) between the liquid (soybean oil) and gas phases. This predicted K_{mod} values were below 0.0005 at temperatures ranging from 10 – 100 °C at atmospheric pressure; K_{mod} values approaching 0 are indicative of near-complete removal of the H₂S from the gas. Experiments resulted in K_{exp} values below 0.2 in bi-phasic gas/oil systems, residence times < 15 minutes. Isotherm models demonstrated the saturation limits of the soybean oils as compared to water and heptane. This proof-of-concept study and novel use of soybean oils as bio-solvents for sweetening natural gas has potential to positively impact the soybean and natural gas industries.

4.2 Introduction

In silico molecular modeling was used to determine the extent to which soybean oil or high-oleic soybean oil can perform as a bio-based extraction solvent to remove hydrogen sulfide (H₂S) from sour natural gas. Success of a soy-based bio-solvent has potential for high-impact application in both the soybean and natural gas industries. As technology for hydraulic fracturing (fracking) and harvesting natural gas from shale reservoirs has improved over the last two decades, more natural gas has become available, particularly in the United States, leading to increased use of natural gas as a fuel source.^{1,2} As of 2015, 67% of the U.S. natural gas production of 2.3 billion m³/day is

¹ Reprinted with permission from Brace, E. C.; Engelberth, A. S. Assessing Viability of Soybean Oils to Remove Hydrogen Sulfide from Natural Gas. *ACS Sustain. Chem. Eng.* **2020**, *Just Accepted*. <https://doi.org/10.1021/acssuschemeng.0c01991>¹⁰⁶ Copyright 2020 American Chemical Society.

produced through fracking.² As natural gas saturated the market, prices dropped, which has enabled natural gas to compete with coal as a fuel source.³ Natural gas is also considered a more environmentally friendly fuel source, as its combustion releases about 50% less CO₂ into the atmosphere compared to coal and fewer greenhouse gases than traditional gasoline.⁵ One issue inhibiting natural gas from dominating the fuel industry is that shale gas reservoirs are more concentrated with H₂S, up to hundreds of parts per million.¹ Sour gas – defined as natural gas with greater than 4 ppmv H₂S – should not be combusted as is, because H₂S is acutely toxic to humans and presents several hazards to the environment.^{8–10} H₂S is highly corrosive and costly to remove, causing major damage to processing and transportation equipment.⁷ Although sweetening of sour gas through amine gas treating is a well-established industrial process, it is also energy intensive.¹² Sour gas is commonly burned at the wellhead (a process known as flaring) when high H₂S concentrations make sweetening methods uneconomical.¹¹ There is a demand for a technology to provide a cost-effective, environmentally conscientious solution to remove H₂S from sour gas.

The present research is a proof-of-concept study focused on evaluating the feasibility of removing H₂S from natural gas using soybean oils – both conventional and high-oleic – as the extraction solvent. The U.S. produced more than 10.2 billion kg of soybean oil in 2016,³⁸ and the soybean industry seeks new uses of soybean oil and high-oleic soybean oil. In the United States, 68% of soybean oil is used in food products, 25% is converted to biodiesel, and 7% (as of 2018) is used in industrial uses including paints, lubricants, solvents, inks, and other products.⁸⁴ The U.S. Soybean Checkoff continues to seek innovative uses of soybean oil converted to other industrial products, including environmentally friendly solvents.⁸⁴ Vegetable oils have a demonstrated ability to bind with sulfur compounds,^{27,28} and the unsaturated nature of fatty acids in soybean oils offers increased potential binding sites for sulfur. Predictive *in silico* models examining these compounds (H₂S, natural gas components, soybean oil) on a molecular level offer low-cost and expeditious process for fundamental research into the feasibility of using soybean oil as an extraction solvent. Molecular modeling allows for rapid solvent screening and selection of initial process parameters, thereby informing experimental design and process scale-up. To understand how H₂S will partition in a two-phase system composed of soybean oil and natural gas, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to simulate partitioning of the target molecule (H₂S) between the liquid (soybean oil) and gas (methane) phases. The COSMO-RS model has

been used to predict partitioning of target molecules in a variety of liquid-liquid^{29,31–35} and vapor-liquid^{36,37} systems. This *a priori* approach to predict the partition coefficient (K) allows for more rapid determination of initial process parameters (temperature, pressure) and reduction of experimental effort (time, resources). The present study employs a novel use of soybean oil as a bio-solvent for sweetening gas, and has potential for scale-up to an industrial process which would impact the economics of the soybean and gas industries.

4.3 Experimental Methods

4.3.1 Reagents and Equipment

Calibration cylinders of 40 ppm H₂S in balance nitrogen were obtained from Ideal Calibrations (Ideal Calibrations, LLC, Melvindale, MI). High-oleic soybean oil was obtained from ADM (Archer Daniels Midland Company, Frankfort, IN) and soybean oil was purchased locally (Great Value brand, Walmart Inc.). Analysis of the inlet gas and outlet gas was performed using an Altair 5X Gas Detector equipped with a low concentration H₂S sensor. The Altair 5X was rented from Ideal Calibrations (Ideal Calibrations, LLC, Melvindale, MI). Tedlar PVF 1.6L gas sampling bags (Saint-Gobain Chemware), 18-gauge needles (Becton Dickinson & Co.), and nylon barbed luer locks (Cole-Parmer) were also used in the equilibrium studies. Omnitop 50 mL Sample Tubes with 18-inch c-flex inlet and silicone dip tube (Chemglass Life Sciences, LLC) and Tedlar PVF 1.6 L gas sampling bags (Saint-Gobain Chemware) were used in the saturation and isotherm studies.

4.3.2 *In Silico* Approach: COSMO-RS

The COSMO-RS method allows for calculation of the partition coefficient, K , of a solute between two phases. This predictive method is advantageous in that it only requires molecular structures of the solute and solvent molecules and composition of the phases as inputs for prediction.^{37,75} No experimental data is required for prediction, although experimental data can be used to inform reiterations of the model after the initial process conditions are determined. A methodology for using COSMO-RS and related software to predict partition coefficients has been outlined by Hopmann *et al.*^{33,34} and demonstrated in a variety of studies including biomolecules^{29,31,32,35} and separating H₂S from methane.⁸² To use this methodology, the liquid phase was modeled as a

mixture of five fatty acids that are the primary components of soybean oil, as shown in Table 4.1. It was initially hypothesized that high-oleic soybean oil (HOSBO), with its > 80% of an acid with one double bond, would afford a high degree of unsaturated bonds for binding H₂S. However, based on the fatty acid compositions shown in Table 4.1, the ratio of double bonds in conventional soybean oil (SBO) to HOSBO is approximately 1.5:1 and is attributed to the high percent of linoleic acid found in SBO.

Table 4.1. Fatty acid composition of soybean oil (SBO)¹¹¹ and high-oleic soybean oil (HOSBO)⁸⁵.

Carbon bonds: double bonds	Fatty acid	Weight %		Molecular weight
		SBO	HOSBO	
C16:0	palmitic acid	11.0	6.0	256.42
C18:0	stearic acid	4.0	3.0	284.48
C18:1	oleic acid	22.0	85.0	282.46
C18:2	linoleic acid	55.0	4.0	280.45
C18:3	α -linolenic acid	8.0	2.0	278.43

HyperChem (release 8.0, Hypercube, Inc., Gainesville, FL) was used to generate the three-dimensional structures of the fatty acid molecules using the Molecular Mechanics + (MM+) force field. The conformational search feature was used to generate up to 30 of the lowest energy conformations of each acid. Molecules were considered to be duplicates if energy was within 0.05 kcal/mol and the maximum acceptable energy criterion was set to 1 kcal/mol above best. The RMS error was restricted to 0.25Å and the number of accepted conformers was limited to 30. TmoleX (Version 3.4, COSMOlogic GmbH & Co. KG, Germany) was used to generate the σ -profile representations of screening charge density for each conformation of the acids and for the H₂S, methane, and nitrogen gas molecules. The Becke-Perdew (B-P) functional and triple zeta valence polarized (TZVP) basis sets for density functional theory were applied.^{101,102} Finally, COSMOthermX (Version 13, COSMOlogic GmbH & Co. KG, Germany) was used for calculation of chemical potential and the activity coefficient based on the σ -profiles generated in TmoleX. The mass fractions of the acids in soybean oil were input as the composition of the liquid lower phase; the upper phase was modeled as 100% methane or 100% nitrogen. The partition coefficient (K_{mod}) was derived from the activity coefficients (γ_i) of H₂S in the upper (U) and lower (L) phases at infinite (i) dilution, as shown in Equation 4.1. The activities are multiplied by a ratio of the

weighted sum of the molar volumes of each phase – where x_i is the molar fraction of solute i and v_{0j} is the molar volume of each pure compound – in each phase.

$$K_{mod}^{UL} = \frac{\gamma_i^L}{\gamma_i^U} \times \frac{\sum x_i^L v_{0j}}{\sum x_i^U v_{0j}} \quad (4.1)$$

The activity coefficient of H₂S at temperatures from 10 – 100 °C were predicted for the liquid phase, and from 10 – 100 °C at 1 atm for the gas phase.

4.3.3 Equilibrium Extraction of Hydrogen Sulfide Using Headspace Bottles

For the preliminary, proof-of-concept studies, the experiments are intended to verify the theoretical results rather than to comprehensively optimize the process. For this reason, all experiments were carried out at atmospheric pressure and 25 °C. Soybean oil (50 mL) was added to a glass headspace bottle (150 mL), which was then sealed with a rubber septum and aluminum cap. Ambient air was withdrawn using a syringe. Gas (100 mL) containing 40 ppm H₂S in nitrogen was introduced at a rate of 0.25 L/min to each bottle, by connecting the gas cylinder to the bottle via 1/8” tubing and an 18 gauge needle. Samples were taken in triplicate for residence times of 0, 0.5, 15, 30, 45, and 60 minutes, resulting in 18 HOSBO samples and 18 SBO samples. The 0 time-point samples had no forced mixing, and the 0.5 minute time-point samples were vigorously shaken by hand for 0.5 minutes before reading the H₂S gas concentration. The 15, 30, 45, and 60 minute samples were placed in an incubator shaker at 25 °C and 200 rpm. The bottles were then connected to the Altair 5X with an 18 gauge needle and tubing, and the highest H₂S reading from the Altair 5x during an approximately 30 second sampling period was recorded. The 2:1 gas to oil ratio was used to provide sufficient gas for the Altair 5X to generate an accurate reading.

4.3.4 Analysis of H₂S Remaining in the Gas Headspace

The Altair 5X was used to measure the concentration of H₂S in the gas from the gas cylinder, by flowing gas from the cylinder into a Tedlar PVF 1.6L gas sampling bag (Saint-Gobain Chemware) and then from the gas bag to the Altair 5X (the gas could not flow directly from the cylinder to the detector via tubing because the flow rate of the cylinder regulator and the Altair 5X are not equivalent). In three repeated tests, the Altair 5X measured the H₂S in the supply gas to be 30 ppm. The mass of H₂S entering each vial was calculated using the measured H₂S concentration

along with the known volume of gas (100 mL) that was injected into each bottle. The Altair 5X was connected via an 18-gauge syringe and tubing to each headspace bottle after gas addition and used to read the concentration of the H₂S gas in the headspace of the bottle after agitated contact with soybean oil. The Altair 5X was equipped with sensors to read LEL (%), CO (ppm), O₂ (%) and H₂S (ppm). For each bottle, an approximately 30 second sampling period was observed and the highest LEL (%), highest CO (ppm), lowest O₂ (%), and highest H₂S (ppm) values were recorded. The headspace volume was still assumed to be 100 mL and as such the H₂S (ppm) values were converted to masses of H₂S gas and a mass balance was performed to determine the mass and concentration of H₂S in the soybean oil of each bottle, and these values were then used to calculate experimental partition coefficients, K_{exp} , using Equation 4.2.

$$K_{exp} = \frac{\text{Concentration } H_2S \text{ in the gas phase}}{\text{Concentration } H_2S \text{ in the oil phase}} \quad (4.2)$$

4.3.5 Saturation and Isotherm Modeling Studies

To determine the adsorption capacity of the soybean oils and other solvents, further experiments were carried out to collect data for isotherm modeling. All experiments were carried out at atmospheric pressure and 25 °C. Solvent (40 mL) – soybean oil, high-oleic soybean oil, water, or heptane – was added to a 50 mL conical tube with a silicone dip tube (Chemglass Life Sciences, LLC). Water was chosen as a comparative solvent to the soybean oils due to the known solubility of H₂S in water.¹¹² Heptane was chosen as a second comparative solvent as it differs in both structure (straight chain versus branched) and saturation as compared to the fatty acids in soybean oils. Gas containing 40 ppm H₂S in nitrogen was introduced at an assumed constant flow and the outlet gas that passed through the solvent was collected in a gas bag. The concentration of H₂S collected in the gas bag was determined using an Altair 5X gas analyzer as described in the previous section. Concentration was recorded every minute for the first 15 minutes and then every 5 minutes for the last 15 minutes (for a total of 30 minutes of gas bubbling) and was repeated in triplicate for each solvent tested. Assuming a closed system and no loss of H₂S, the concentration and mass of H₂S sorbed (accumulated) using a simple mass balance as in Equation 4.3.

$$H_2S_{(input \text{ gas})} = H_2S_{(output \text{ gas})} + H_2S_{(accumulated \text{ in solvent})} \quad (4.3)$$

The amount of H₂S in the inlet gas in each 1-minute interval was assumed to be equal (constant flow rate) and the amount of H₂S in the 5-minute intervals was assumed to be five times as much. Sorption data was then used for Langmuir and Freundlich isotherm modeling and determination adsorption capacity for H₂S.

4.4 Results and Discussion

4.4.1 Theoretical Determination of the Partition Coefficient

The partition coefficient (K_{mod}) of H₂S in a two-phase system comprised of methane or nitrogen (gas phase) and soybean oil, high-oleic soybean oil, or heptane (liquid phase) was calculated using the COSMO-RS theoretical method. Methane was used to represent natural gas, which typically has a methane concentration > 90%. The oil phase composition was based on the weight percent of the five fatty acids (Table 4.1). Additional simulations were performed using other fatty acid combinations, as shown in Figure 4.1, to determine how bond saturation contributed to partitioning. The temperature of the theoretical models was varied from 10 to 100 °C and pressure was set at atmospheric. Figure 4.1 displays the observed relationship between degree of bond saturation and partitioning. It is evident from Figure 4.1 that as the number of double bonds increase – from palmitic acid with zero double bonds in its carbon backbone to α -linolenic acid with three double bonds – the capacity to accommodate H₂S increases.

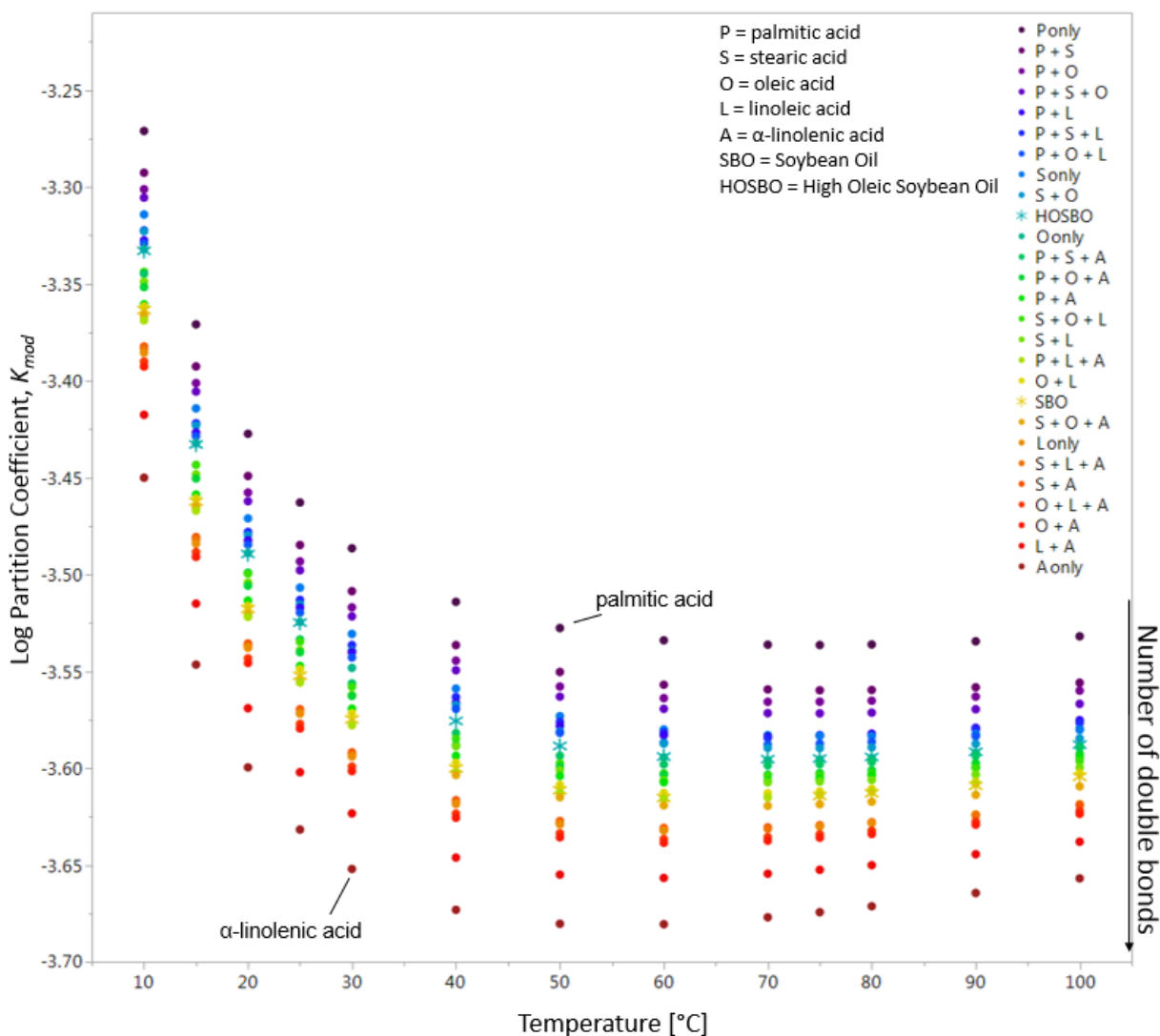


Figure 4.1. The theoretical partition coefficient for palmitic acid (P), stearic acid (S), oleic acid (O), linoleic acid (L), α-linolenic acid (A), and many combinations thereof, were calculated using the COSMO-RS method and Equation 4.1. The high-oleic soybean oil (HOSBO) and soybean oil (SBO) data used a phase composition based on the weight % of the fatty acids as shown in Table 4.1. All other combinations were even distributions, e.g. P + L + A was 33% each of palmitic, linoleic, and α-linolenic acids. These predictions indicate that the fatty acids that have the most double bonds provide the most binding opportunities for H₂S, and have lower logK values, indicating near-full removal of the H₂S from the methane gas phase.

From the theoretical calculation of the partition coefficient of H₂S in the model systems, it is shown that SBO and HOSBO have similar capacity for binding H₂S. The predicted performance of the soybean oils falls within the continuum of soybean model acids. Tukey's test was performed ($\alpha = 0.05$) and concluded there was no statistically significant difference between the log K_{mod} values

from 40 – 100 °C, indicating there would likely be no improvement to partitioning by applying heat to the system.

In an effort to be able to suitably compare K_{mod} to K_{exp} , the initial inclination was to experiment using H₂S in methane gas. However, this particular experiment proved to be infeasible from a safety aspect: compressed methane gas containing H₂S poses substantial risk in the laboratory. A safer substitute was nitrogen containing H₂S. To ensure that results from the substitute gas would be comparable, K_{mod} was determined for H₂S in both methane and nitrogen for SBO and HOSBO (Figure 4.2).

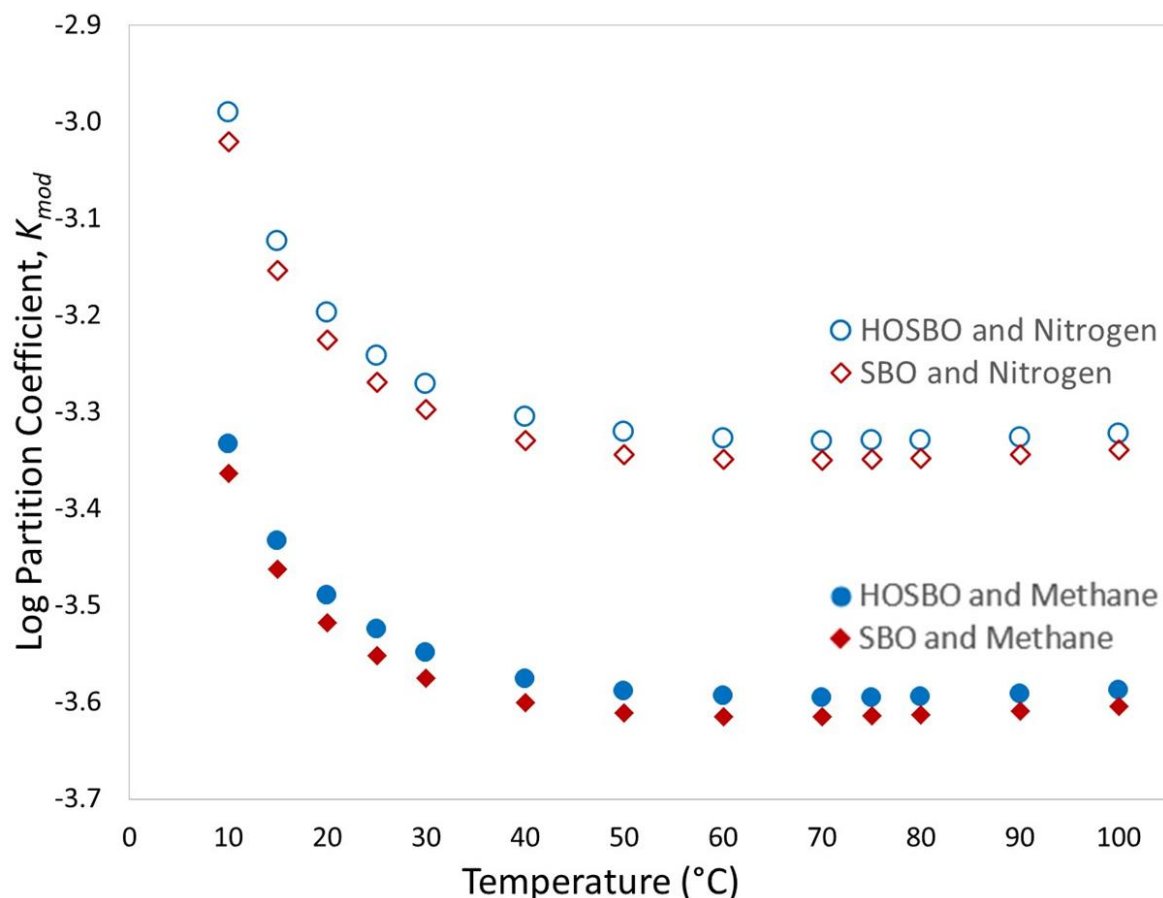


Figure 4.2. Theoretical partition coefficients for H₂S in systems containing soybean oil (SBO) or high-oleic soybean oil (HOSBO) and methane or nitrogen were calculated using COSMO-RS and Equation 4.1. Results indicate that SBO and HOSBO have similar binding capacity for H₂S, and that not only does H₂S prefer soybean oils over methane, but also prefers them over nitrogen. The closer the partition coefficient is to zero (the more negative log K is), the higher the probability of finding the H₂S in the oil phase rather than the gas phase.

Results of the model shown in Figure 4.2 indicates that the nitrogen-based systems have a higher partition coefficient. Due to the favorable prediction of methane system partition coefficients, which were even lower than K_{mod} for the nitrogen systems, it was confirmed that experimental validation could be performed using the safer alternative – H₂S in nitrogen. The theoretical calculations provided confidence that partitioning of H₂S out of the gas phase and into the oil would be even more favorable in a methane or natural gas system than what was determined experimentally with nitrogen. Thus, nitrogen was deemed to be a suitable safe proxy for experimentation.

4.4.2 Experimental Determination of the Partition Coefficient

To evaluate the feasibility of using soybean oil to remove gaseous H₂S, physical experiments were carried out in triplicate as described in the methods. The H₂S remaining in the gas phase after contact and mixing with SBO or HOSBO was analyzed using an Altair 5X gas detector with a low concentration H₂S sensor. Mass balance was used to determine the concentrations of the H₂S in the oils, and the partition coefficient was then calculated using Equation 4.2. The resulting K_{exp} is shown in Figure 4.3.

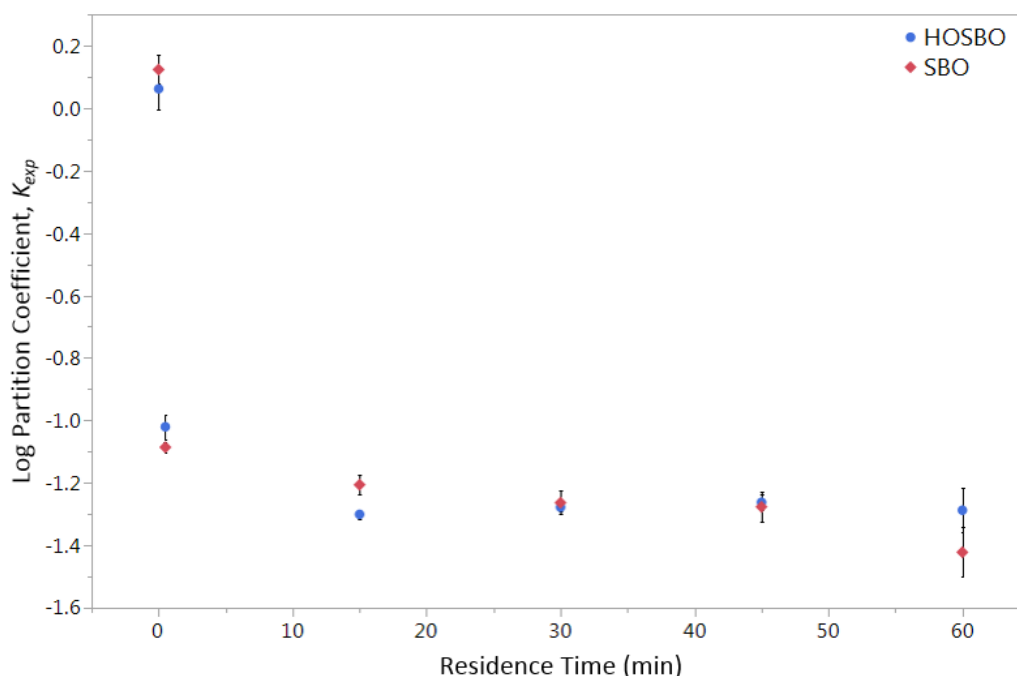


Figure 4.3. Partitioning of H₂S in a nitrogen gas and soybean oil (SBO) or high-oleic soybean oil (HOSBO) system. Experiments were carried out in triplicate with H₂S concentration in each phase determined at time 0 (contact with the oil, no mixing), 30 seconds (hand shaken for 30 seconds), and at 15, 30, 45, and 60 minutes (incubator shaker at 200 rpm and 25 °C). The experimentally determined partitioning shows no statistically significant difference between HOSBO and SBO for binding the H₂S, and no statistically significant difference between residence times of 0.5-60 minutes, indicating equilibrium is quickly attained.

The experiments were carried out only at 25 °C based on the implication from the *in silico* model that heating the system would have trivial impact on partitioning. The zero time-point samples showed a statistically significant difference between using SBO and HOSBO (Student's T-test, $\alpha=0.05$). However, there was no significant difference overall in partitioning based upon oil type (Tukey's test, $\alpha=0.05$) and no significant difference in residence times from 0.5 minutes to 60 minutes (Tukey's test, $\alpha=0.05$), indicating rapid attainment of equilibrium. Experimentally determined partition coefficients for 15 – 60 minute residence times are shown along with the predicted partition coefficients in Figure 4.4.

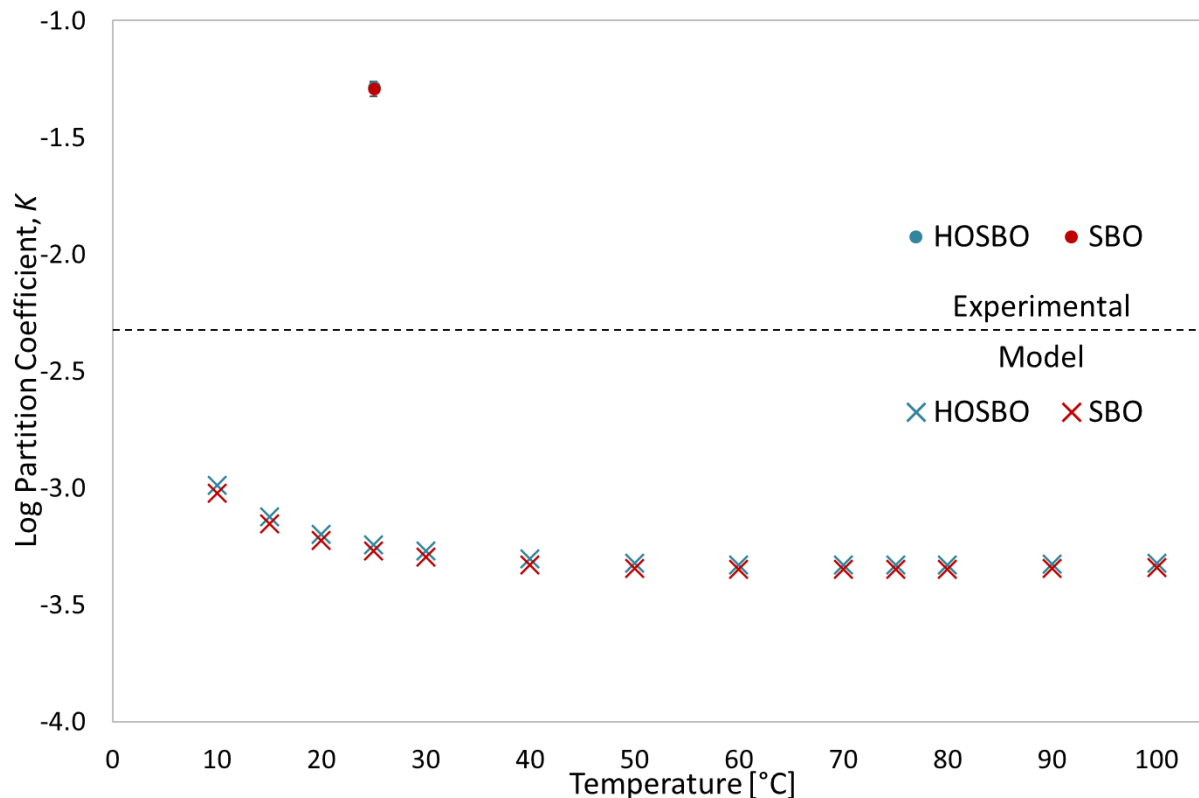


Figure 4.4. Comparison of theoretical and experimental partition coefficients for H₂S in nitrogen and soybean oil (SBO) or high-oleic soybean oil (systems). The lower log K is, the better the partitioning. Although experimental partition coefficients are not as low as predicted, > 90% removal of the H₂S from the gas can be achieved within 15 minutes of mixing with a 2:1 gas:oil ratio.

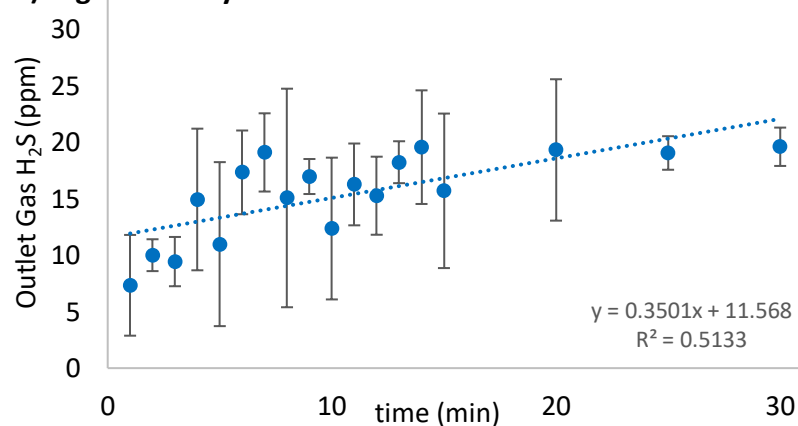
While K_{exp} are higher than K_{mod} , experiments point to > 90% removal of H₂S from the gas phase by the soybean oil, at an initial gas to oil ratio of 2:1 and a temperature of 25 °C within 15 minutes of contact. This indicates 1L of sour gas could potentially be treated with 0.5L of soybean oil and achieve 90% or better removal of the H₂S. The noteworthy K_{exp} indicates that SBO or HOSBO are viable bio-solvent candidates for removing H₂S from carrier gas. Partitioning of H₂S out of methane and into soybean oil is more strongly predicted than it was for nitrogen, and it is expected that experiments would confirm this prediction.

4.4.3 Saturation Studies and Isotherm Modeling

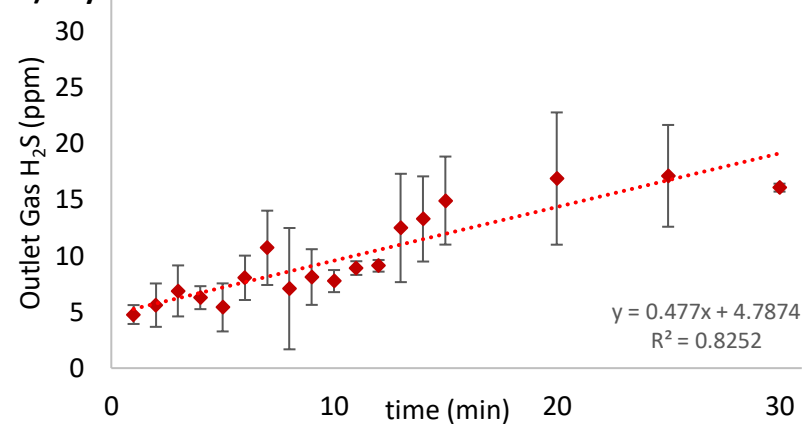
In an effort to validate that the difference between the inlet and outlet concentrations of H₂S could be correctly attributed to H₂S entrapment within the oil, H₂S was bubbled through high-oleic soybean oil, soybean oil, water, and heptane as described in *Saturation and isotherm modeling*

studies. Concentration of H_2S in the inlet gas was determined by the Altair 5x gas analyzer to be 30ppm and the concentration in the outlet gas is shown in Figure 4.5. Throughout the duration of the experiment, the concentration of H_2S in the outlet gas increased; this is likely due to solvent saturation (i.e. once the solvent is saturated with H_2S , then any H_2S added beyond saturation point will be immediately released in the outlet).

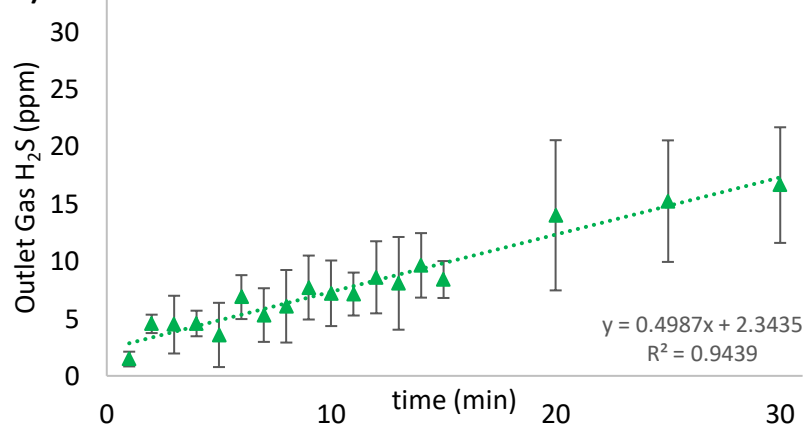
a) High-oleic Soybean Oil



b) Soybean Oil



c) Water



d) Heptane

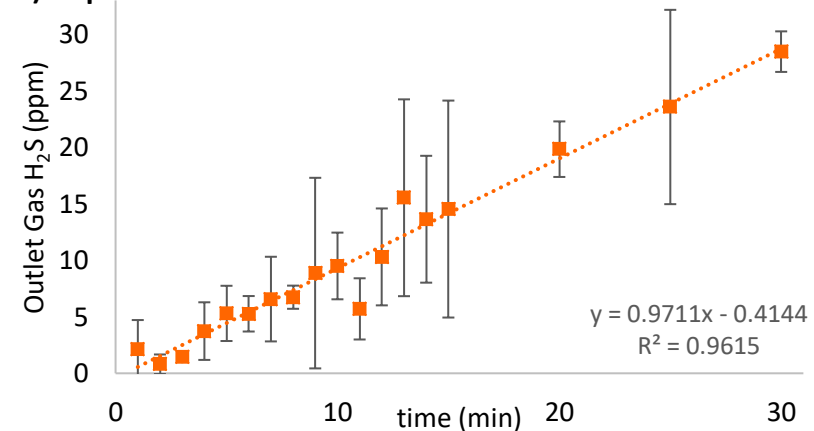


Figure 4.5. 30ppm H_2S was bubbled through 40 ml of solvents (a) high-oleic soybean oil (b) soybean oil (c) water and (d) heptane in triplicate at assumed constant flow rate. The outlet gas was collected in a gas bag and the concentration of outlet gas H_2S determined every minute from 1 – 15 minutes and every five minutes from 15 – 30 minutes. The error bars represent the standard deviation. As more H_2S was bubbled through each solvent, less of the H_2S was trapped by the solvent and more of simply passed through and was measured in the outlet gas. Soybean oil and high-oleic soybean oil seemed to reach saturation after about 20 minutes while higher saturation limits were observed for water and heptane.

Using mass balance (Equation 4.3) to determine the total amount of H₂S that had been introduced to the solution and the adsorbed concentration, the experimental data were fit to both Langmuir and Freundlich isotherm models. Although Langmuir and Freundlich isotherm models were developed for adsorption of gases or liquids by solids, Langmuir and Freundlich isotherms have been fit to study gas/liquid interactions.¹¹³ The Langmuir (4.4) and Freundlich (4.5) equations are given as:

$$\text{Langmuir isotherm} \quad q_e = \frac{bQ_0C_e}{1 + bC_e} \quad (4.4)$$

$$\text{Freundlich isotherm} \quad q_e = K_f C_e^n \quad (4.5)$$

where q_e is the adsorbed H₂S (mg/L solvent) and C_e is the equilibrium concentration of H₂S in solution (mg/L solvent). In the Langmuir isotherm equation b (L/mg) is the Langmuir adsorption constant, and Q_0 (mg/g) is the maximum amount of the adsorbed H₂S. In the Freundlich isotherm equation, $K_f((\text{mg/g})\text{L/mg})^{1/n}$ is the Freundlich adsorption constant and n is the Freundlich linearity constant. The parameters for these models are shown in Table 4.2 and the fitted models are plotted with the experimental data in Figure 4.6.

Table 4.2. Isotherm parameters for H₂S in different adsorbing solvents using the Langmuir (Equation 4.4) and Freundlich (Equation 4.5) isotherm models. In all cases the H₂S adsorption was better explained by the Langmuir model with R^2 values ranging from 0.952 – 0.970 compared to R^2 values ranging from 0.888 – 0.928 for the Freundlich model. The isotherm models are also plotted vs the experimental data in Figure 4.6.

Adsorbent	Langmuir isotherm parameters			Freundlich isotherm parameters		
	Q_0	b	R^2	K_f	n	R^2
High-oleic soybean oil	1.16	0.843	0.952	0.504	0.515	0.888
Soybean oil	2.00	0.608	0.963	0.719	0.586	0.913
Water	2.38	0.537	0.970	0.793	0.610	0.928
Heptane	1.96	0.730	0.962	0.784	0.548	0.902

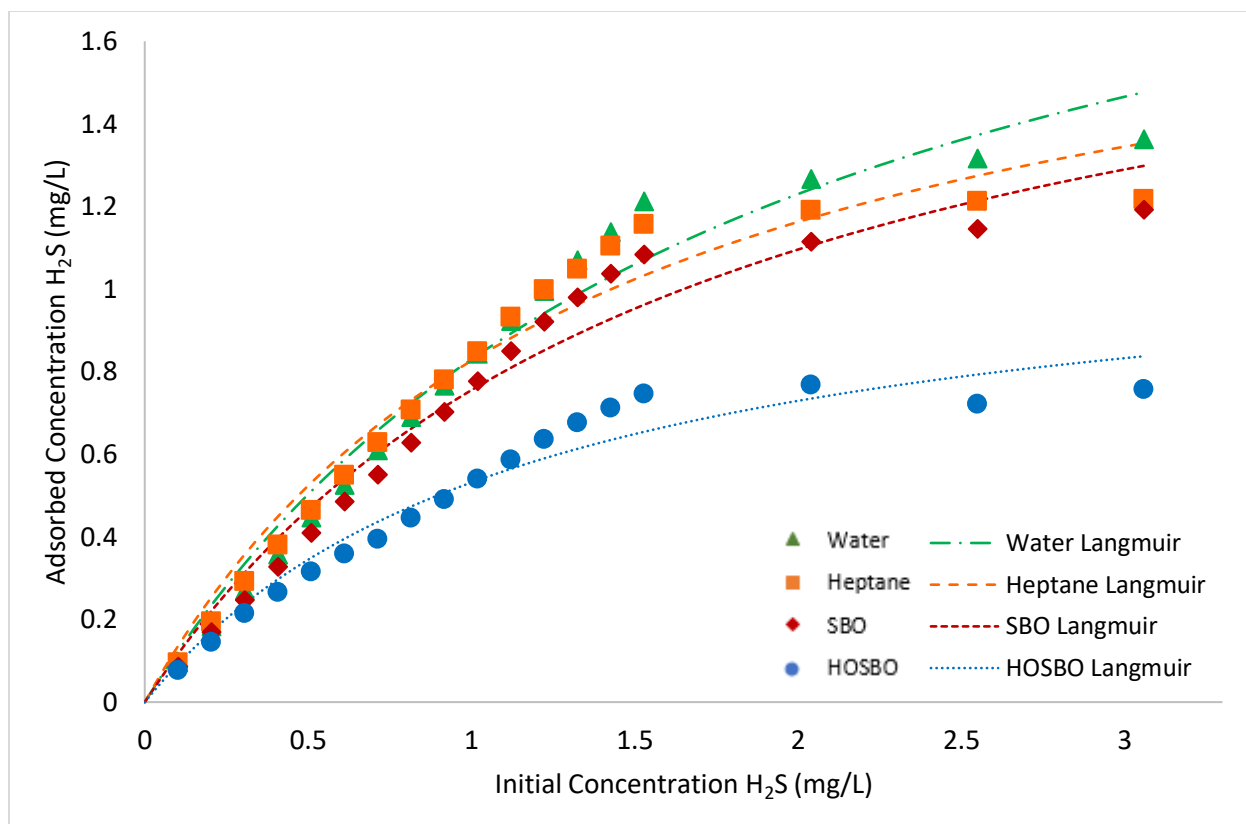


Figure 4.6. The concentration of adsorbed H₂S versus the input concentration of H₂S (from a compressed gas form) in four different solvents: water, heptane, soybean oil (SBO) and high-oleic soybean oil (HOSBO) is shown. Langmuir isotherm parameters (Table 4.2) were fitted to the experimental data and used to develop the Langmuir isotherm models shown here. A lower adsorption capacity for H₂S in high-oleic soybean oil than soybean oil is in line with more favorable partitioning into soybean oil as discussed in Figures 4.1 – 4.3.

The experimentally determined adsorption isotherms and corresponding Langmuir adsorption models indicate that water has the highest saturation limit for H₂S and that high-oleic soybean oil has the lowest. Although water may have a high saturation limit for H₂S, the cost of using water, downstream separations challenge, and the undesirability of using a valuable natural resource to trap H₂S makes it an undesirable and unlikely solvent for use in sweetening sour gas. The maximum adsorption capacity Q_0 is also related to K_{exp} in that Q_0 is the ratio of the adsorbed H₂S to the total H₂S concentration in the system; K_{exp} is the ratio of the H₂S adsorbed to the H₂S not adsorbed and exiting the system in the gas phase. Thus higher Q_0 values also correspond to higher K_{exp} values. Both the theoretical and experimental partitioning (Figures 4.1 – 4.4) and the experimental isotherm development (Figures 4.5 and 4.6) indicate that SBO has a slight advantage over HOSBO in terms of being capable of binding H₂S. The experimental findings align with the

findings presented in Figure 4.1 in that it appears that H₂S binding capacity to the soybean-based oils is correlated with the number of available double bonds. Further investigation into other fatty acid-based oils is recommended to more fully understand these phenomena.

4.4.4 Comparison with Current Technologies

To fully understand technoeconomic viability of this process, scale-up experiments and simulations would need to be conducted. Based on the initial findings presented here, it is possible that 1L of sour natural gas could have $\geq 90\%$ H₂S removal using 0.5L of soybean oil. Based on 2018 average prices of U.S. soybean oil,⁸³ this would cost \$0.30 for treating 1L of gas. In comparison, traditional amine sweetening costs are very low, around \$0.03 per 1L of gas. However, the technoeconomics of using soybean oil as a biosolvent could be improved through further investigation or through a multi-stage process with soybean oil regeneration and recycle. A key element of developing this proof-of-concept work into a viable process will include developing methods to remove the H₂S from the oil and downstream conversion to sulfur or sulfate building blocks. There are reported methods for removing H₂S from solution and conversion to sulfur or sulfate for commodity chemicals,¹¹⁴ and this will be critical for regeneration of the soybean oil (so that it can be recycled and so the process generates minimal waste oil), as well as improving the economic viability of the process by converting the H₂S recovered to value streams.

4.5 Conclusion

To meet the energy and transportation sectors' demands for natural gas, new methods are needed to remove H₂S from natural gas sources. Soybean oil and high-oleic soybean oil, which are abundantly available in the United States, offer an opportunity as bio-solvents for removing H₂S from sour gas. This proof-of-concept study demonstrates a 2:1 nitrogen gas:soybean oil mixture with 30 ppm of H₂S in the gas phase demonstrated a $> 90\%$ removal of H₂S from the gas phases within a residence time of 15 minutes, which indicates that equilibrium is quickly attained. Further studies into isotherm development revealed a slightly higher binding capacity for soybean oil as compared to high-oleic soybean oil. The experimental results of this study demonstrate that soybean oil and high-oleic soybean oil perform similarly well in binding gaseous H₂S, and *in silico* models indicate the partitioning may be more favorable in methane/soybean oil systems. This

proof-of-concept study indicates soybean oil could perform well as an extraction solvent for removing H₂S from natural gas.

4.6 Acknowledgements

The authors thank the funding opportunity from Indiana Soybean Alliance (ISA 16056097) and Indiana Hatch Project No. IND010677.

5. ESTIMATING AN ACHIEVABLE TARGET PRICE TO REGENERATE BIO-OILS POST HYDROGEN SULFIDE REMOVAL²

5.1 Abstract

Bio-oils such as conventional soybean, high-oleic soybean, canola, and sunflower offer valuable use as bio-solvents for removing hydrogen sulfide (H_2S) from natural gas. Preceding bench-scale studies indicate that greater than 90% of H_2S can be removed from a gas stream; economic analysis of such a process is necessary to determine solvent regenerative power required and price limits on a to-be-determined solvent regeneration scheme. With a goal of processing 1000 kmol/h of sour gas and removing 99.9% of H_2S from gas streams with various feed concentrations, design of an absorption unit to process natural gas using bio-oils as the absorbing solvent was carried out through equilibrium stage analysis. A graphical method combined with the Kremser method found a trayed tower with 14 stages, a 2 m diameter and 8.5 m height, could successfully meet these goals with a bio-solvent flow rate of 120 kmol/h. Capital costs were centered on the price of an extraction column designed to meet the desired throughput. Comparison to conventional amine gas treating was used to set a limit for the cost of treating a unit of gas, and sensitivity analysis of the relationship between solvent regeneration and re-use and cost of treating the gas. The economic viability of the process depends on capability of regenerating and recycling more than 98% of the soybean oil bio-solvent to compete with amine gas treating, the most popular industrial method.

5.2 Introduction

The use of bio-oils – conventional soybean, high-oleic soybean, canola, and sunflower – to remove hydrogen sulfide (H_2S) from a gaseous mixture has been demonstrated¹⁰⁶ and has potential for use in the natural gas industry to sweeten gas as it is extracted. High concentrations of H_2S in natural gas render it sour, with sour gas defined as natural gas containing anywhere from 4 ppmv to thousands of parts per million H_2S .¹¹⁵ Bio-oils have demonstrated the ability to remove up to 90%

² Reprinted with permission from Brace, E. C.; Engelberth, A. S. Estimating an Achievable Target Price to Regenerate Bio-Oils Post Hydrogen Sulfide Removal, *ACS Sustain. Chem. Eng.* **2020**, Submitted.¹⁴⁷ Copyright 2020 American Chemical Society.

of gaseous H_2S from a gas stream at the bench-scale¹⁰⁶ and could be used in a scheme similar to the industrially prevalent amine gas treating methods.^{116,117}

In an effort to evaluate if further investigation into bio-oils as gas sweetening agents could yield a viable process, the economic feasibility must be assessed. The present work aims to determine the number of stages required to remove 99.9% of H_2S from methane feed gas with varying concentrations of H_2S , to examine the capital costs, determine the required regenerative power of the bio-oil solvent, and ultimately determine the maximum price of and the equipment necessary to regenerate and recycle the bio-oils to be competitive with currently implemented gas processing methods.

5.3 Methods

In considering the price of using bio-oils as extraction solvents for treating sour gas and removing H_2S , the cost of such a process would need to be less than or equal to the existing industrial processes for treating sour natural gas. To draw such a comparison, the factors that impact the cost of the process must be verified. By constructing equilibrium stage diagrams an extraction column can be designed, which can then be used to estimate capital cost. Sensitivity analysis, with respect to bio-oil solvent regeneration capability, can also reduce cost and aid in understanding what the cost ceiling for gas treatment to compete with conventional methods would be. Recovered sulfur could be a lucrative byproduct, as sulfur is valued at more than \$200/ton as a chemical building block.¹¹⁸ As a baseline comparison, the overall cost can be set equal to the current cost of amine gas treatment; from there, the total maximum cost of bio-oil solvent regeneration/sulfur recovery units can be calculated and the feasibility of developing a process within those cost constraints can be evaluated.

To construct the equilibrium stage diagrams, experimentally determined partition coefficients for H_2S in each bio-oil were used.¹⁰⁶ Feed gas concentrations of 40 and 400 ppm H_2S in nitrogen were examined with 99.9% removal of H_2S as the target. A 1000 kmol/h gas feed rate was applied for all simulations, which is on par with flow rates and volumes used industrially in amine gas treating. A graphical solution method¹⁰⁷ was used to determine the number of equilibrium stages necessary for removing 99.9% of the H_2S from different feed gas concentrations using soybean oil or high-

oleic soybean oil as the sorption solvent. The Kremser method^{107,108} was then used to evaluate the percent of H₂S absorbed at each theoretical equilibrium stage for different absorbent flow rates and feed gas compositions: the parameters used are shown in Table 5.1.

Table 5.1. Flow rates and compositions used for graphical and Kremser methods of equilibrium stage analyses.

Parameter	Value
Feed gas flow rate	1000 kmol/h
Feed gas composition	40 ppm (2.6 mol%) or 400 ppm (20 mol%) H ₂ S
Sorbent flow rate	96 – 250 kmol/h
Sorbent composition	100% bio-oil: soybean or high-oleic soybean

To set a maximum total price, comparisons were drawn between similar amine gas treating and other processes employing an absorption unit and solvent regeneration and recycle units.^{115–118} Industrially popular amine gas treating works similar to the scheme proposed here, with alkylamines (most commonly diethanolamine or monoethanolamine) acting as an H₂S and CO₂ absorbent in an extraction column, while the gases are stripped off in a stripping column to regenerate the amine solvents.^{116,117,119}

5.4 Results & Discussion

Economic evaluation of processing sour natural gas using bio-oils is necessary in determining economic viability of such a process before taking efforts to scale up a bench-scale process. Methods to regenerate and recycle the bio-oils and recover sulfur are not yet fully understood, so a total price for the process is set equal to that of existing technologies (such as amine gas treating). After subtracting capital costs and solvent costs from the total price limit, the maximum cost of solvent regeneration and sulfur precipitation was calculated. Discussion regarding the feasibility of developing a process to meet these cost constraints is included.

This study aims to investigate the number of stages necessary for 99.9% removal of H₂S from varying feed gas concentrations, the price of the extraction column and initial solvent cost, the

potential revenue through conversion of H_2S and sale of sulfur, and impact of solvent lifetime and regeneration. Figure 5.1 shows a schematic of the proposed process.

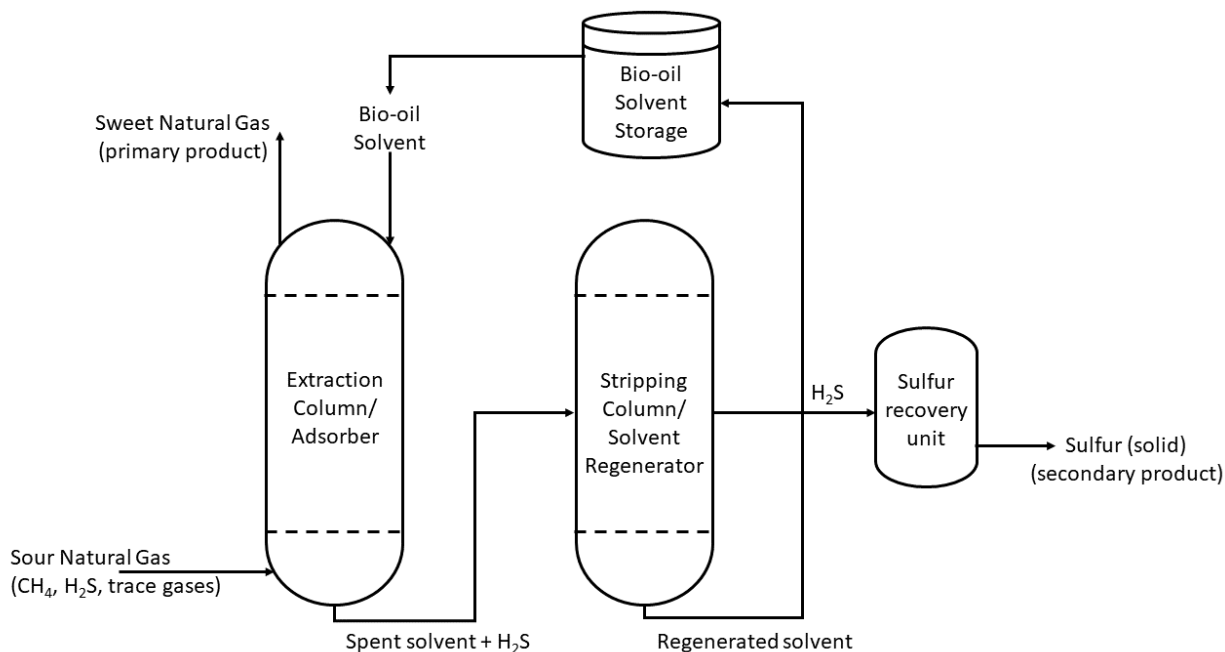


Figure 5.1. Schematic diagram of a potential process using bio-oil as an extraction solvent to remove H_2S from sour natural gas. An extraction column and solvent cost will be the primary initial costs and will be used to set a limit on how much the solvent regeneration/sulfur recovery units could cost in order for the total process to be economically viable.

5.4.1 Estimation of Stages and Efficiency for Recovering H_2S as Concentration Varies

To determine the number of stages necessary for handling sour natural gas using bio-oil extraction solvents, varying concentrations of H_2S in methane were examined (Table 5.1 in *Methods*). A graphical method was implemented to determine the optimal flow rates of the liquid absorbent feed and the number of stages required to achieve 99.9% removal of H_2S from the feed gas. Partition coefficient values (K) for soybean oil (SBO, $K = 0.08$) and high-oleic soybean oil (HOSBO, $K = 0.1$) were previously experimentally determined for H_2S partitioning in bio-oils.¹⁰⁶ Two concentrations of H_2S were chosen for study: 40 ppm, a proximate value for the bench scale equilibrium experiments, and 400 ppm, to evaluate ability to sweeten sour gas streams at the more concentrated end of the spectrum. H_2S (40 ppm) corresponds to a 2.6 mol% H_2S in methane and 400 ppm H_2S corresponds to a 20 mol% H_2S in methane. Figure 5.2 shows the absorption model framework for graphical evaluation.

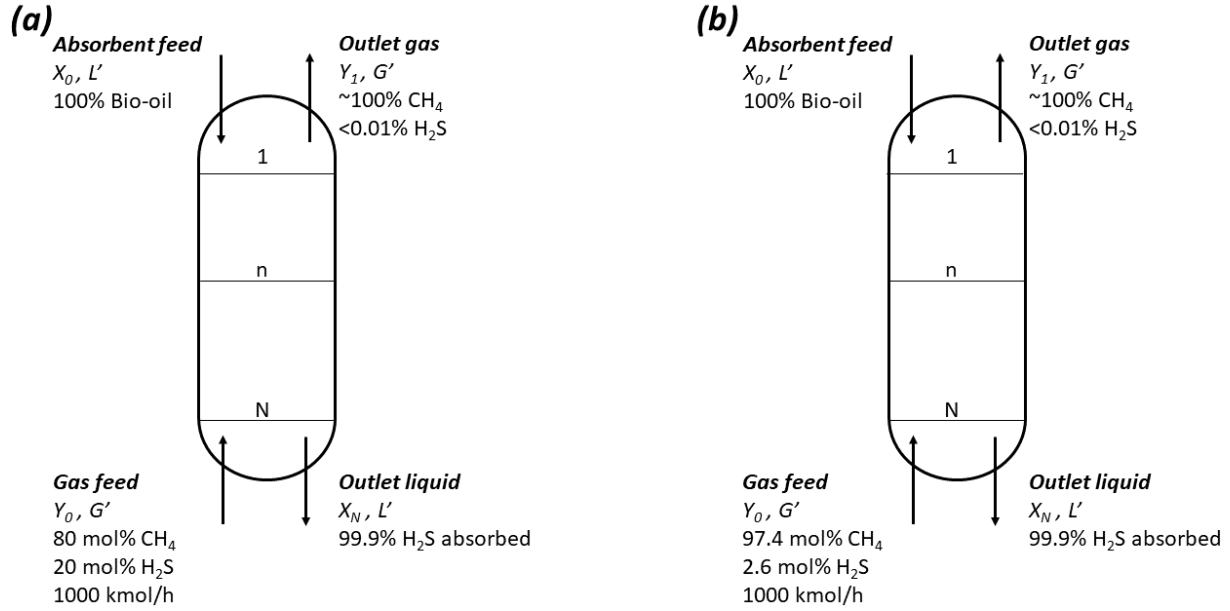


Figure 5.2. A tray column absorption unit operation with a gas feed of either (a) 20 mol% H_2S ($\sim 400\text{ppmv}$) or (b) 2.6 mol% H_2S ($\sim 40\text{ppmv}$). Based on a feed gas flowrate of 1000 kmol/h, the absorbent flow rate L' and number of stages N necessary to achieve 99.9% removal of the H_2S from the gas feed was determined using a graphical method.

Equations 5.1 – 5.3 were used to determine the minimum absorbent flow rate, L'_{min} , the optimum absorbent flow rate, $1.5L'_{min}$, and the operating lines. The minimum absorbent flow-rate, Equation 5.1, is a function of the partition coefficient K_N and the flow rate G' of the gas feed. The optimum absorbent flow rate, L' , in Equation 5.2, is recognized to be a multiple of the minimum absorbent flow rate, L'_{min} , and is typically estimated to be close to optimal at $1.5 \times L'_{min}$.¹⁰⁷ Depending on which multiple of L'_{min} is chosen for L' , different operating lines can be graphed according to Equation 5.3.

$$\text{Minimum absorbent flowrate} \quad L'_{min} = G'K_N \quad (5.1)$$

$$\text{Optimum absorbent flowrate} \quad L' = 1.5 \times L'_{min} \quad (5.2)$$

$$\text{Absorber operating lines} \quad X_0L' + Y_{N+1}G' = X_NL' + Y_1G' \quad (5.3)$$

The equilibrium line was constructed using an experimentally determined K_N value of 0.1 mg H_2S (gas) / mg H_2S (oil) for high-oleic soybean oil and 0.08 mg H_2S (gas) / mg H_2S (oil) for soybean oil.¹⁰⁶ The equilibrium line equation used in the graphical solutions is shown in Equation 5.4.¹⁰⁷

The concentration of H_2S in the gas (X) and the concentration in the absorbent liquid (Y) at any stage (N) is a function of the partition coefficient (K).

$$\text{Equilibrium line} \quad K_N = \frac{Y_{N+1}/(1 + Y_{N+1})}{X_N/(1 + X_{N+1})} \quad (5.4)$$

The graphical solution for (a) 20 mol% H_2S absorbed by high-oleic soybean oil, (b) 2.6 mol% H_2S absorbed by high-oleic soybean oil, (c) 20 mol% H_2S absorbed by soybean oil, and (d) 2.6 mol% H_2S absorbed by soybean oil are shown in Figure 5.3. Table 5.2 summarizes the conclusions for $1.5L'_{min}$ and N depending on the absorbent and feed concentration of H_2S .

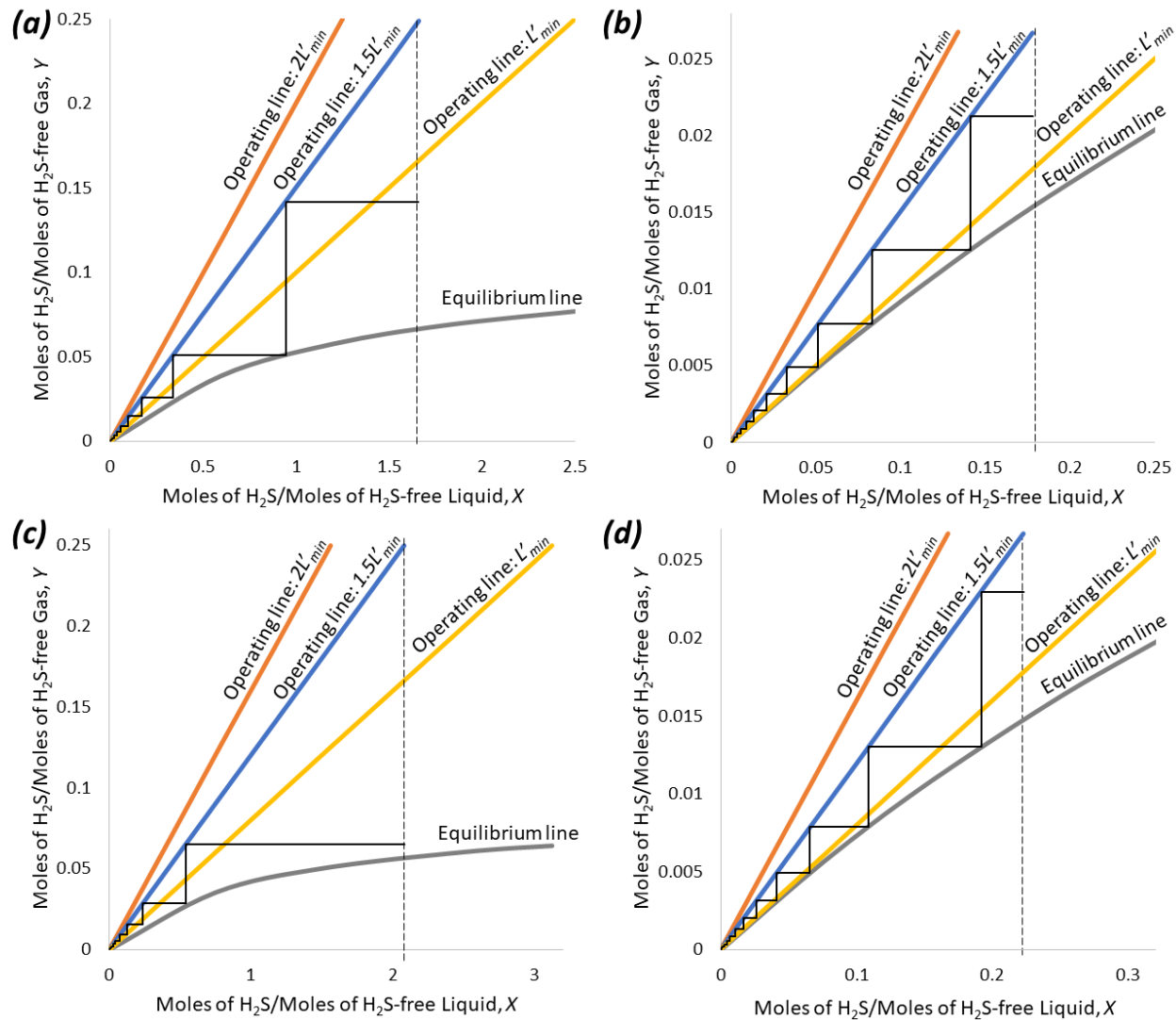


Figure 5.3. A graphical solution to determine the number of stages necessary for removing 99.9% of H_2S from a feed gas of (a) 20 mol% H_2S in methane, HOSBO; (b) 2.6 mol% H_2S in methane, HOSBO; (c) 20 mol% H_2S in methane, SBO; (d) 2.6 mol% H_2S in methane, SBO. The operating lines are based on the flow rate of the absorbent feed. The equilibrium line is based on the partition coefficient K of H_2S in the absorbent, high-oleic soybean oil, previously determined to be 0.1. The graphical solution is completed for the optimum operating line of $1.5L'_{min}$, and the number of stages N was determined to be (a) 10.2 (b) 13.3 (c) 9.6 and (d) 14.2 stages.

Table 5.2. Optimum flow rate ($1.5L'_{min}$) and number of stages (N) calculated for different feed conditions of H_2S (2.6 mol% or 20 mol%) and different absorbing liquids (HOSBO or SBO) using the graphical solution method shown in Figure 3.

$1.5 L'_{min}$ (kmol/h)	HOSBO	SBO
20 mol% H_2S	120	96
2.6 mol% H_2S	146	117

N	HOSBO	SBO
20 mol% H_2S	10.2	9.6
2.6 mol% H_2S	13.3	14.2

Additionally, the Kremser method^{107,108} was used to determine the amount of H₂S sorbed at each theoretical equilibrium stage N using Equations 5.5 and 5.6. In Equation 5.5, the separation factor (A) is a function of the absorbent flow rate (L , varied from 101 – 250 kmol/h based on the graphical solutions), the feed gas flow rate ($V = 1000$ kmol/h), and the partition coefficient (K) of the solute (H₂S) in the system. For modeling an absorption unit, the fraction of solute absorbed can be calculated as a function of the separation factor A and number of stages in the unit N as shown in Equation 5.6.

$$\text{Separation Factor} \quad A = \frac{L}{K_i V} \quad (5.5)$$

$$\text{Fraction solute absorbed} \quad \text{Fraction solute absorbed} = \frac{A^{N+1} - A}{A^{N+1} - 1} \quad (5.6)$$

Tables 5.3 and 5.4 display results for percent of solute absorbed at each stage, N , using 1-15 stages and varied absorbent flow rates, L . Table 5.3 is based on using high-oleic soybean oil ($K = 0.1$) as the absorbent while Table 5.4 shows results for conventional soybean oil ($K = 0.08$).

Table 5.3. Percent absorption of H₂S depends on the absorbent flow rate L (varied from 101 – 250 kmol/h), partition coefficient ($K = 0.1$), feed gas flow rate ($V = 1000$ kmol/h), and is shown for each stage N , up to 15 stages. The absorbent is high-oleic soybean oil. The values represent the percent of solute (H₂S) absorbed, and $\geq 99.9\%$ is shaded green, $\geq 99.0\%$ is shaded yellow, and $< 99.0\%$ is shaded orange. The target is greater than 99.9% absorption of the H₂S.

[illegible]

Table 5.4. Percent absorption of H_2S depends on the absorbent flow rate L (varied from 101 – 250 kmol/h), partition coefficient ($K = 0.08$), feed gas flow rate ($V = 1000$ kmol/h), and is shown for each stage N , up to 15 stages. The absorbent is soybean oil. The values represent the percent of solute (H_2S) absorbed, and $\geq 99.9\%$ is shaded green, $\geq 99.0\%$ is shaded yellow, and $< 99.0\%$ is shaded orange. The target is greater than 99.9% absorption of the H_2S .

[illegible]

The graphical solution had indicated 146 kmol/h would be an optimal absorbent feed flow rate when using high-oleic soybean oil. Using the Kremser method, it is evident that as absorbent flow rate increases, the number of stages required to attain 99.9% absorption of H_2S decreases. However, there may be other negative impacts of increasing solvent flow rate, such as increased solvent use and solvent cost.

Another way of examining the system is to set a flow rate and compare the amount of H_2S absorbed by the different absorbing bio-oils. In this method, the absorbent flow rate (L), feed gas flow rate (V) are fixed and the absorption factor A is dependent on the K value of H_2S in each bio-oil. Figure 5.4 shows the comparison between the bio-oil absorption capacity at different equilibrium stages for two absorbent flow rates, 125 kmol/h and 200 kmol/h.

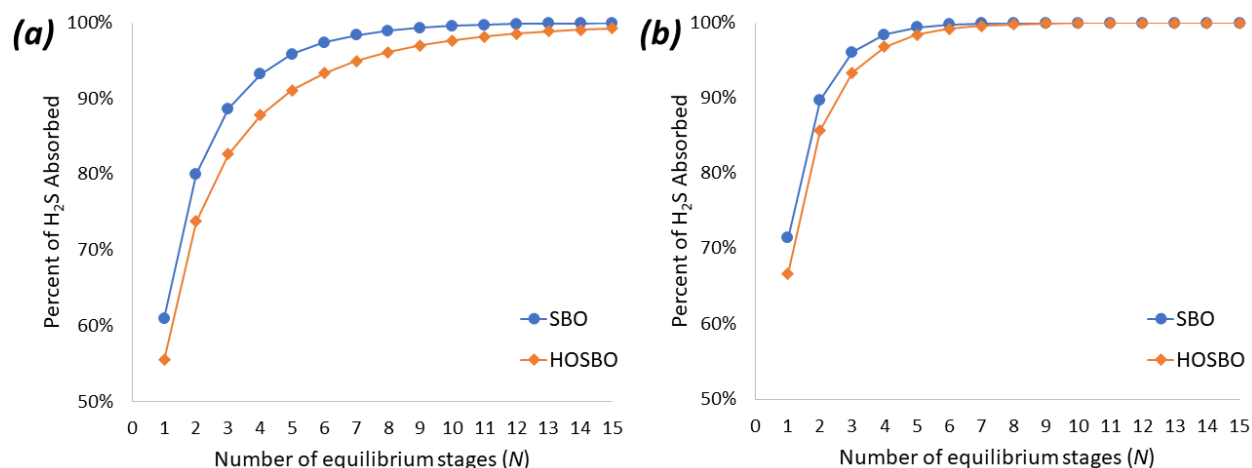


Figure 5.4. The percent of H_2S recovered at each equilibrium stage is dependent by each oil at absorbent flow rates (L) of (a) 125 kmol/h and (b) 200 kmol/h. The percent of H_2S recovered is a function of the absorbent flow rate, the feed gas flow rate ($V = 1000$ kmol/h), and the K value for H_2S in each oil (0.08 for SBO, 0.1 for HOSBO), as shown in Equations 5.5 and 5.6.

As seen in Figure 5.4 and in Tables 5.3 and 5.4, each oil is capable of attaining 99.9% H_2S absorption after some number of stages, N . In the case of the lower flow rate, as shown in Figure 5.4a, the difference between the oils is larger (root mean square deviation is 0.037) while requiring 14 stages for both oils to achieve $> 99.0\%$ H_2S sorption. At a higher flow rate (Figure 5.4b), the oils' H_2S absorption more quickly converges (root mean square deviation is 0.018) and only five stages are required to attain $> 99.0\%$ sorption of H_2S . A balance must be struck between number of stages, optimal flow rate, and the resulting bio-oil solvent use. For the remaining analysis, an

absorbent flow rate of 120 kmol/h soybean oil was chosen to limit solvent use while attaining 99.9% removal of H₂S in the least number of stages.

5.4.2 Column Design and Capital Costs

A significant cost of developing a natural gas processing facility that used bio-oils as the absorbing solvent would be the cost of the absorption unit. Based on the flow rates determined in the previous section and the size and daily processing needs of existing gas treatment methods like amine gas treating, a sieve-plate tray column is recommended as the absorption unit. Other cost considerations would include piping, installation, and any other units for solvent storage, etc.

To design an extraction column to meet the needs for 1000 kmol/h of feed gas, 120 kmol/h of liquid absorbent, and 14 trays (determined by the equilibrium stage calculations), flooding capacity of the column must be calculated.

Flooding capacity is a function of the density of the liquid and vapor phases and a flooding capacity factor, C . The calculation for flooding velocity is shown in Equation 5.7 and flooding capacity factor in Equation 5.8.

$$\text{Flooding Velocity}^{107} \quad U_f = C \left(\frac{\rho_L - \rho_V}{\rho_V} \right)^{0.5} \quad (5.7)$$

$$\text{Flooding Capacity Parameter}^{107} \quad C = F_{ST} F_F F_{HA} C_F \quad (5.8)$$

$$\text{Surface tension factor}^{107} \quad F_{ST} = \left(\frac{\sigma}{20} \right)^{0.2} \quad (5.9)$$

$$\text{Entrainment flooding capacity}^{107,120} \quad F_{LV} = \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \quad (5.10)$$

$$\text{Ratio of active tray area (A}_d\text{) to total tray area (A)}^{107,120} \quad \frac{A_d}{A} = 0.1 + \frac{(F_{LV}-0.1)}{9}, \quad 0.1 \leq F_{LV} \leq 1.0 \quad (5.11)$$

$$\text{Factor for ratio of vapor hole area to tray active area} \quad \begin{aligned} F_{HA} &= 1.0 \text{ for } A_d/A_a \geq 0.10 \\ F_{HA} &= 5(A_d/A_a) + 0.5 \text{ for } 0.06 \geq A_d/A_a \geq 0.1 \end{aligned} \quad (5.12)$$

In Equation 5.7, C is the flooding capacity parameter, ρ_L is the liquid density and ρ_V is the vapor density. The flooding capacity parameter, C , is estimated using Equation 5.8. F_{ST} is a surface tension factor, calculated as a function of the surface tension of the liquid, σ , as shown in Equation 5.9. F_F is a foaming factor, which can be assumed to be 1.0 in a system with negligible foaming.¹⁰⁷ F_{HA} and C_F are derived by first calculating F_{LV} , the entrainment flooding velocity (Equation 5.10) and the ratio of the active tray area to the total tray area (Equation 5.11). In Equation 5.10, L and V are the liquid and vapor feed flow rates respectively, M_L and M_V are the molar masses of the liquid and vapor, and ρ_L is the liquid density and ρ_V is the vapor density. Finally, Equation 5.12 can be used to calculate the factor F_{HA} . Lastly, C_F can be graphically estimated as a function of F_{LV} and plate height, which in this case was assumed to be 24 inches and gave a C_F of 0.35.^{107,120} Table 5.5 shows the parameters used in Equations 5.7 – 5.12.

Table 5.5. Parameters used in tray diameter and flooding capacity calculations for design of an absorption column.

Parameter	Parameter Value	Source (if applicable)
Temperature	298 K	-
Pressure	110 kPa	-
V , vapor flow rate	1000 kmol/h	-
L , liquid flow rate	120 kmol/h	-
M_V , molecular weight of vapor phase with 20% H ₂ S and 80% CH ₄	32.4 kg/kmol	Calculated based on feed gas composition
M_L , molecular weight of soybean oil	920 kg/kmol	Patzek 2009 ¹²¹
ρ_V , density of vapor phase with 20% H ₂ S and 80% CH ₄	1.438 kg/m ³	Calculated using ideal gas law
ρ_L , density of soybean oil	916 kg/m ³	Sahasrabudhe et al. 2017 ⁹²
F_F , foaming factor	1.0	Seader & Henley, 1998 ¹⁰⁷
σ , surface tension	29.4 dynes/cm	Sahasrabudhe et al. 2017 ⁹²
Tray height	24 inches	-
f , flooding capacity	0.8	-

Ultimately, column diameter (D_T) can be calculated using Equation 5.13 as a function of the gas flow rate (V) and molar mass (M_V), the flooding velocity (U_f) multiplied by a flooding factor (f), ratio of tray active area to area (A_d/A) and the density of the vapor phase (ρ_v). For Equation 5.13, V , M_V , and ρ_v are all given in Table 5.5. A_d/A was calculated using Equation 5.11, and U_f was calculated using Equation 5.7. The flooding capacity f must be chosen based on desired column performance. A good rule of thumb is that flooding capacity is often best around 60%, but anywhere from 40-90% is reasonable.¹⁰⁷ In this case, $f = 0.8$ is used, as that is reasonable for a gas absorption column and will help keep the column size smaller, which keeps costs lower.¹⁰⁷

$$\text{Column diameter} \quad D_T = \left[\frac{4VM_V}{fU_f\pi(1 - \frac{A_d}{A})\rho_v} \right]^{0.5} \quad (5.13)$$

Finally, column diameter was calculated as 1.96 m or 6.39 ft; for 14 trays and 24 inches between each tray, column height would be 28 ft. Using a column diameter of 2 m and column height of 8.5 m (6.4 ft and 28 ft), the total column volume would be 84.2 m³.

Equation 5.14 relates the cost of a carbon steel trayed column (C_P^0) to a column size attribute (A , volume in m³) and three constants, K_1 , K_2 , and K_3 .¹⁰⁹ The constants are obtained from Turton et al. 2012 Table A-1.¹⁰⁹ $K_1 = 3.4974$, $K_2 = 0.4485$, $K_3 = 0.1074$, and $A = 84.2$ m³.

$$\text{Equipment Cost Equation} \quad \log C_P^0 = K_1 + K_2 \log(A) + K_3 [\log(A)]^2 \quad (5.14)$$

$$\text{Cost Index Adjustment} \quad C_2 = C_1 \left(\frac{I_2}{I_1} \right) \quad (5.15)$$

However, Equation 5.14 is normalized for material pricing in 2001. To obtain an estimate for current pricing, a cost adjustment using the Chemical Engineering Plant Cost Index (CEPCI) was used. In Equation 5.15, the 2019 cost (C_2) is equal to the 2001 cost ($C_1 = C_P^0$ from Equation 5.14) multiplied by the ratio of the 2019 CEPCI ($I_2 = 607.5$) to the 2001 CEPCI ($I_1 = 394$).^{109,110} The cost of the extraction column, with the desired specifications, is estimated at \$131,600.

5.4.3 Solvent Cost

Regeneration of the solvent (soybean or high-oleic soybean oil) will be critical to lowering operating costs and developing the present method into a viable process that can compete economically with amine gas treating. The upper acceptable limit for the cost of regeneration will be explored in this discussion. Examining annual solvent cost as a function of the percent of solvent that is regenerated and recycled gives insight into the viability of using bio-oils as extraction solvents. Soybean oil is examined as a case study representative of similar costs and trends with other bio-oils.

Soybean oil availability is dependent on soybeans harvested, and about 10% (by mass) of soybeans harvested is converted into soybean oil, annually, as shown in Figure 5.5. Soybean oil accounts for 55% of vegetable oil consumption in the United States, with canola oil taking 14% of the market share and other vegetable oils taking less than 10% each.⁸³ 68% of soybean oil is used in food products, 25% in biodiesel and for bioheat, and 7% goes to industrial uses including solvents, paints, plastics and cleaners.⁸³ The U.S. Soybean Check-off advertises a “Fuel vs. Food: You don’t have to choose” message, indicating a national effort to find new industrial and non-food uses of soybean oils.⁸⁴ Soybean oil prices are shown in Figure 5.6.

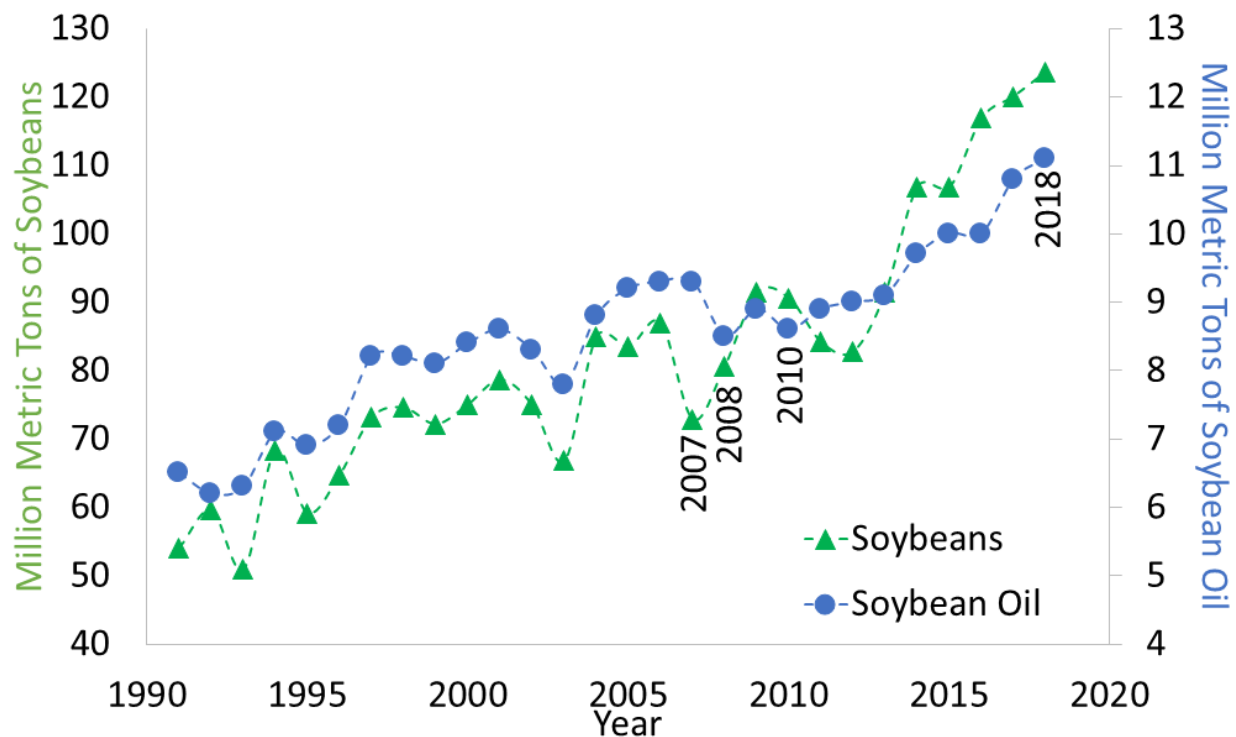


Figure 5.5. Soybean and soybean oil production in the United States, 1991 – 2018. Soybean oil production is about 10% (by mass) of soybean production overall and has continued to rise from 2010 – present.

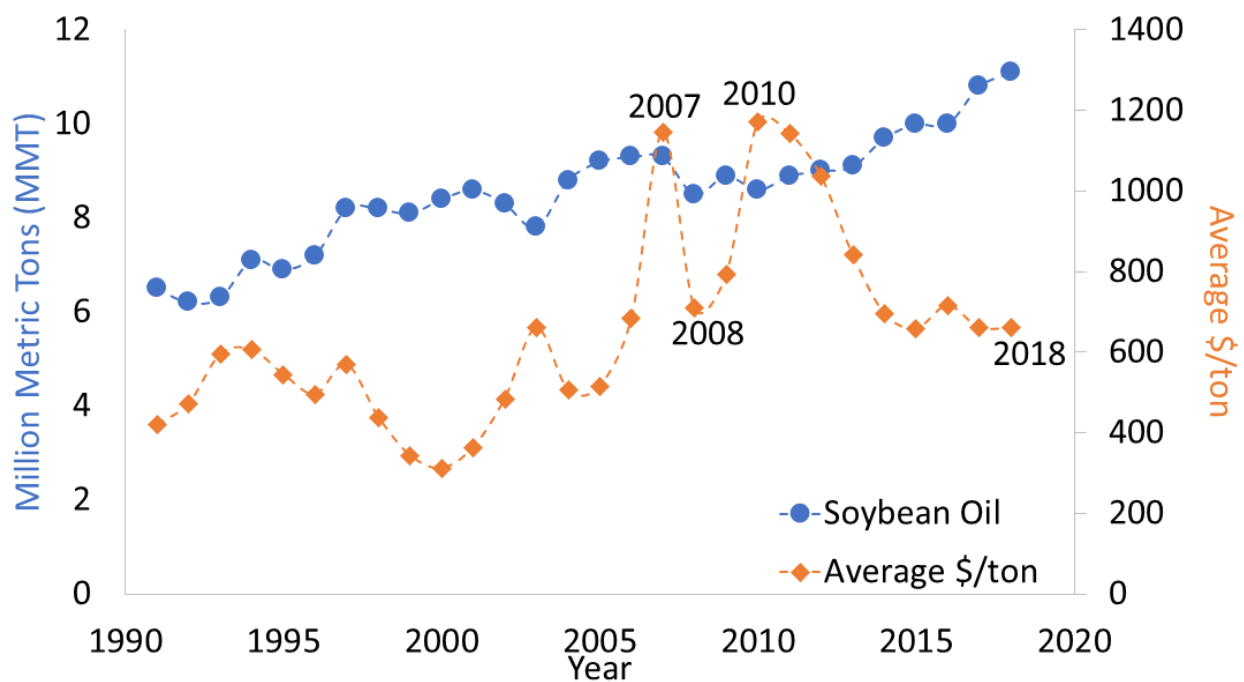


Figure 5.6. U.S. Soybean oil production and prices from 1991 – 2018.

On average from 2014 – 2018, the price of one metric ton of soybean oil was \$679, with yearly prices shown in Table 5.6. Natural gas plants typically operate year-round with 5-10% of forced downtime for maintenance and outages, both scheduled and unscheduled.¹²² Figure 5.7 shows the solvent cost in millions of U.S. dollars per year, depending on if the absorption unit is operating continuously or if the plant anticipates 5-10% of the year that the absorption unit would be offline and solvent would not be required. The price is based on the 2014-2018 average of \$679/metric ton of soybean oil but could increase in future years.

Table 5.6. U.S. soybean oil production and average \$/ton of soybean oil from 2014 – 2018. The five-year average is \$679/metric ton of soybean oil.

Year	Soybean Oil (Million Metric Tons)	Average \$/ton of soybean oil
2014	9.7	\$697
2015	10.0	\$659
2016	10.0	\$716
2017	10.8	\$661
2018	11.1	\$661

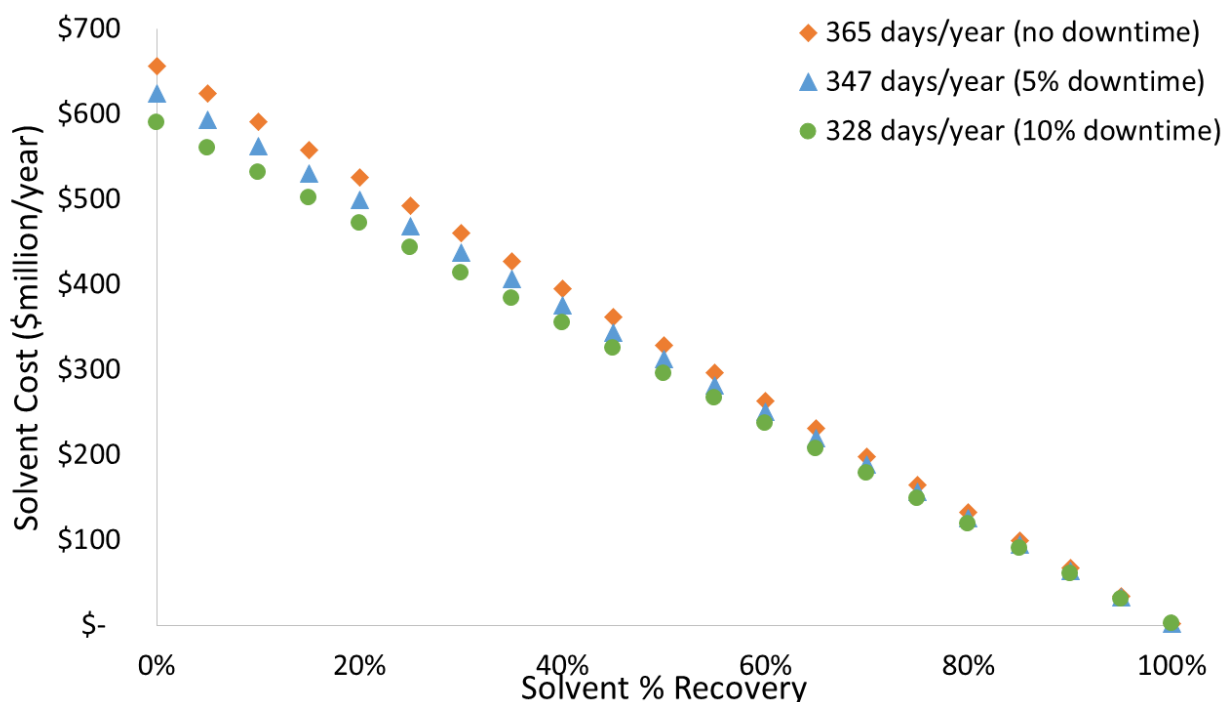


Figure 5.7. Solvent cost of using soybean oil (\$679/ton) depending on the amount of solvent that can be recovered and re-used, and the anticipated downtime of the absorption unit of the plant. For a plant operating 95% of the year, solvent cost with no recovery would amount to \$624 million/year, but even 50% of solvent recovery would result in a solvent cost of \$312 million/year.

5.4.4 Adding Value through Sulfur Recovery

In addition to post-absorption recovery of H_2S , which would require the bio-oil solvents to be regenerated and recycled, conversion of H_2S to elemental sulfur would allow for sulfur to be a secondary product of the process and generate revenue. Sulfur is a valuable chemical building block used to make sulfuric acid and other commodity chemicals and products. The annual demand for sulfur in the United States exceeds 12.7 megatons, and 36% of that is imported annually.¹¹⁸ The current selling price of sulfur is around \$200/ton, and has remained stable above \$150/ton since 2014.¹¹⁸

A relationship can be developed to predict the revenue generated in recovering and selling sulfur. This relationship is based on the selling price of sulfur (\$200/ton), the amount of sulfur recovered out of the potential amount of sulfur recovered (assumed 90%), portion of the year the plant is online (90 – 100% of the year, assuming the absorption is running at full capacity for all the time online), and the feed gas concentration of H_2S . This relationship is displayed in Figure 5.8.

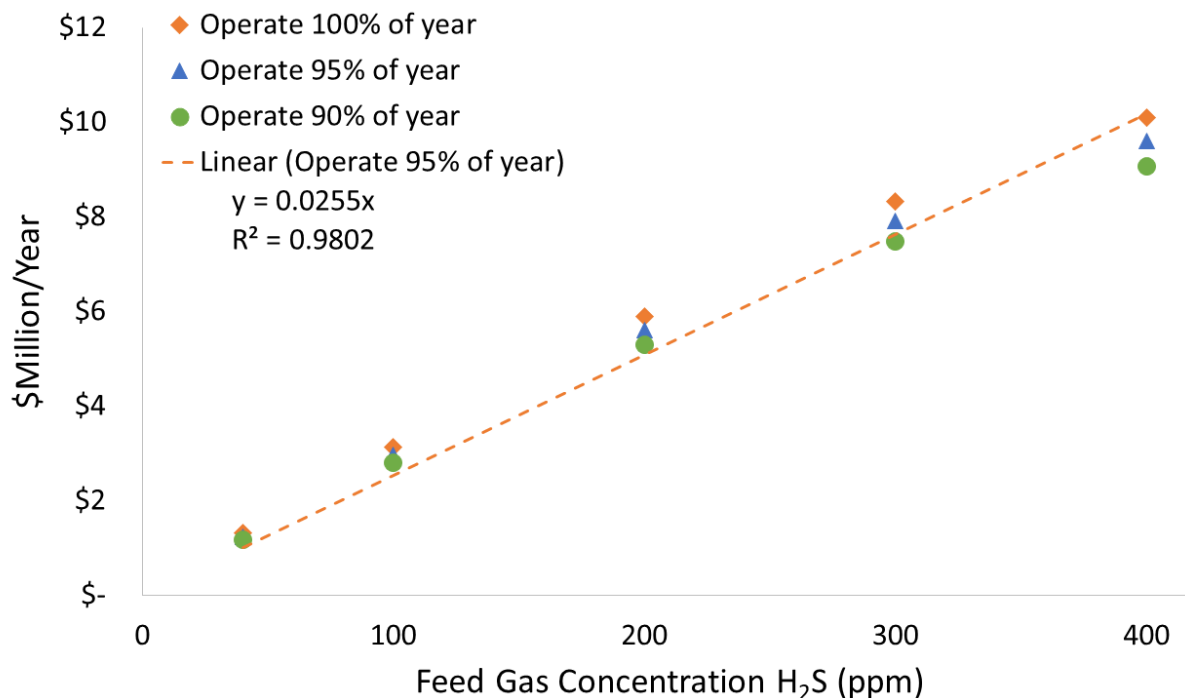


Figure 5.8. Assuming that 90% of all H₂S processed is successfully captured and converted to sulfur, revenues from \$1.2 - \$10 million annually can be anticipated from sulfur sales. This is dependent on the concentration of H₂S in the feed gas being processed throughout the year, as well as the portion of the year the plant is online and operating (assuming the absorption unit is at full capacity and online for the same percent of the year as the plant). Processing more sour gas (400 ppm) would lead to higher revenues than less sour gas (40 ppm). If the plant and absorption unit are online and full capacity 95% of the year, and the average feed gas concentration for the year was 200 ppm H₂S, an annual revenue of approximately \$5.6 million could be expected. This would correspond to selling 28,000 tons of sulfur per year.

The H₂S recovered from the natural gas must be captured and harnessed in some way, as regulations prevent the emission of this hazardous gas to the atmosphere.^{115,118} Conversion to sulfur for sale as a chemical building block is a potential lucrative option, and the Claus process for converting gaseous H₂S to elemental sulfur is well established.^{123,124}

5.4.5 Determination of the Upper Limit for the Cost of Solvent Regeneration

The amount of CH₄ available will be higher when the concentration of H₂S is lower, as shown in Figure 5.9. The most recent price for industrial natural gas is \$3.54/thousand ft³ as of February 2020¹²⁵ and is used for the revenue calculations shown in Figure 5.9, assuming that the absorption unit is able to process 1000 kmol/h of natural gas when online, and that 100% of the CH₄ in the feed gas is recovered.

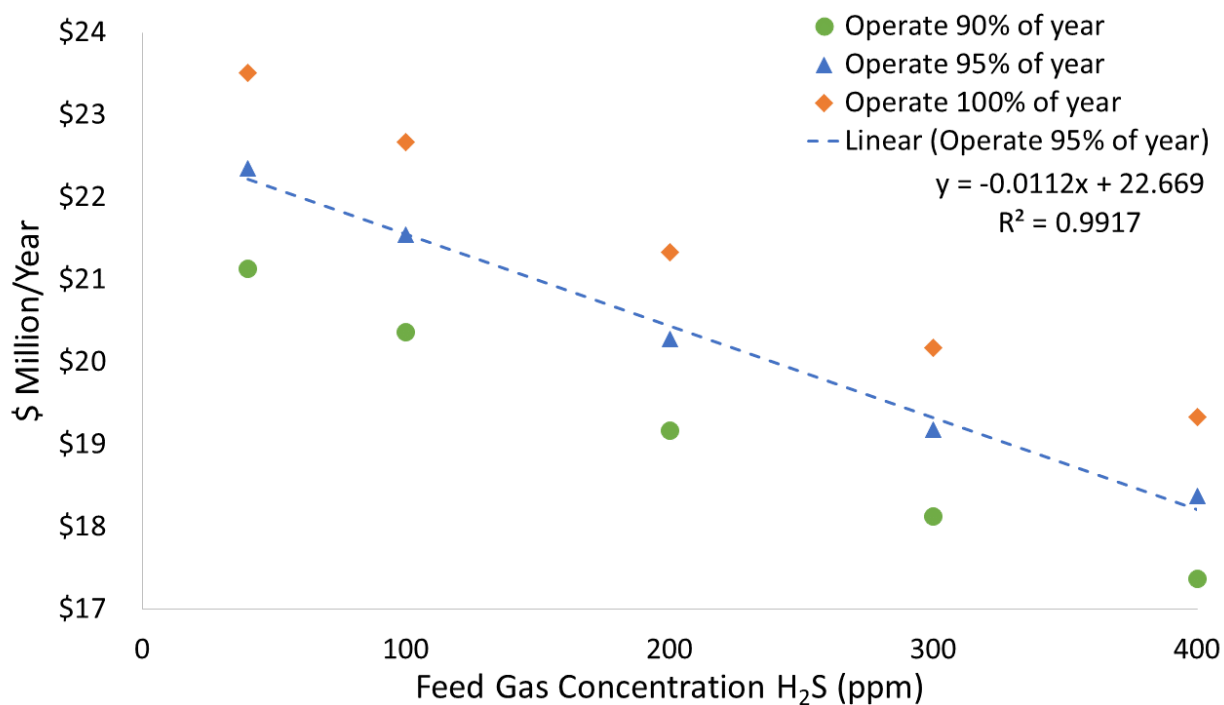


Figure 5.9. Annual revenue from processing natural gas.

However, a more sour gas gives less CH₄ but more H₂S, and overall it is more profitable to process a more sour gas (Figure 5.10). Even as the amount of near-pure methane recovered decreases, the increased recovery of sulfur makes up for the loss and in fact is more valuable.

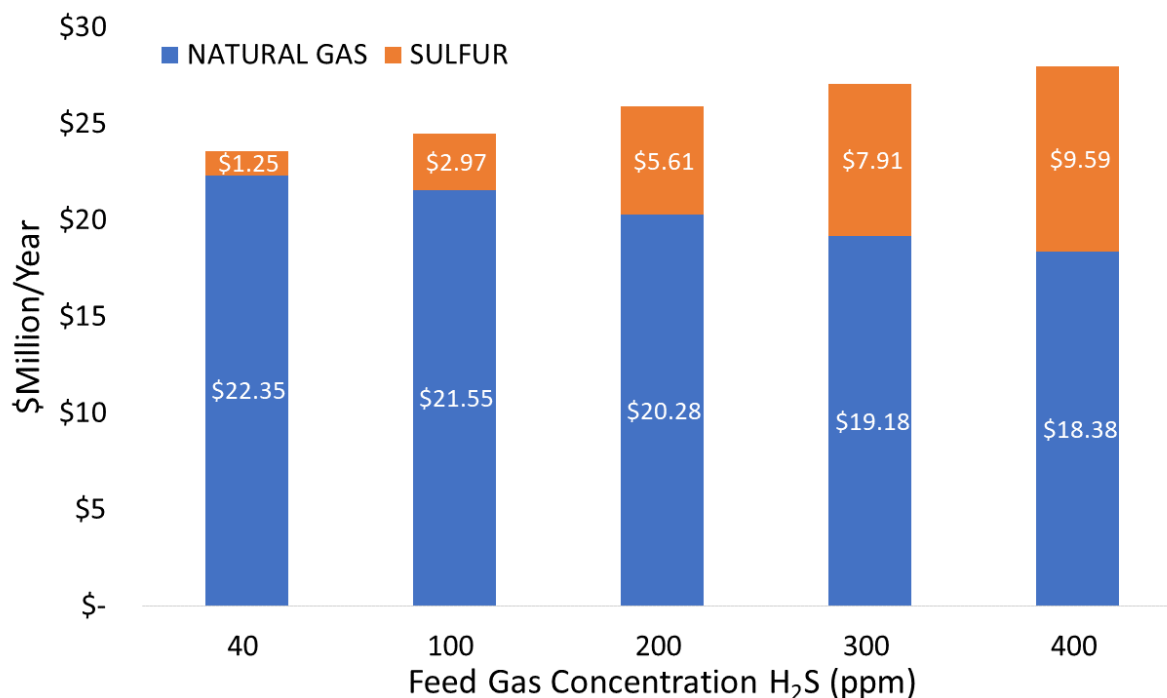


Figure 5.10. Revenue generated by the designed absorption unit operating with 5% downtime annually, 100% recovery of CH₄, and 90% recovery and conversion of H₂S to elemental sulfur. As feed gas becomes increasingly sour, although amount of sweet gas for sale will decrease, sales of sulfur will increase and increase the total revenue.

Based on 1000 kmol/h gas entering the extraction column, 5% downtime annually (but otherwise at full capacity), an average feed gas concentration of 200 ppm H₂S (with 90% sulfur recovery and 100% CH₄ recovery), and 100% solvent regenerated, costs and revenues are shown in Table 5.7.

Table 5.7. Costs and projected revenues for the designed absorption unit processing 1000 kmol/h gas with 5% downtime annually, an average feed gas concentration of 200ppm, with 100% recovery of CH₄ (primary sweet gas component) and 90% recovery and conversion of H₂S to elemental sulfur. The known costs can be used to set a limit for regeneration of the bio-solvent and precipitation of sulfur to stay competitive with other methods.

Sources			Amount
Costs	Fixed	Extraction Column	\$131,600
	Variable	Extraction Solvent	\$8,000,000 / year
	Fixed	Solvent Regeneration & Sulfur Precipitation Unit(s)	TBD
Revenues	Sweetened natural gas		\$20,280,000 / year
	Sulfur		\$5,610,000 / year

Total profits for the plant will be revenue from selling sulfur and sweet gas minus the fixed costs of capital investments, maintenance and operating costs. While the cost of the extraction column was estimated here, the maximum cost of a regeneration/precipitation unit is to be determined, there may be other costs for heat exchangers, reboilers and condensers, and other installation parts. Bryan Research & Engineering found that the absorption and stripping columns of amine gas treatment facilities typically comprise less than 45% of the fixed capital costs.¹²⁶ Another study of natural gas plants in Canada using amine gas sweetening methods found that absorbers are typically 10% of the fixed equipment cost, a regeneration/stripping column 22%, and other equipment (heat exchanger, reboiler, condenser, misc.) comprise the remainder of the costs.¹¹⁹ The study also notes that for most natural gas plants, the sweetening process only accounts for 3% of the capital expenses; liquefaction and other operations within the process account for the remainder. Calculated costs for capital expenses are shown in Table 5.8. In comparison, an amine gas sweetening plant of the same scale would have a solvent cost of approximately \$6.5 million/year, depending on the amine solution used.

Table 5.8. Capital expenditures and operating expenditures based on the design of the absorption column, solvent cost, and volumes of gas processed annually. Relationships based on empirical data collected from Canadian natural gas plants and described in the literature¹¹⁹ are used to calculate costs of equipment and labor.

Capital Expenditures	\$ USD	Calculation method
Equipment Costs	\$43,866,508	
Sweetening Equipment Costs	\$1,316,000	Absorption is 10% of total sweetening equipment costs
Absorption Equipment	\$131,600	Calculated based on column size, type, number of trays
Solvent Regeneration & Sulfur Precipitation Equipment	\$289,520	22% of sweetening costs
Heat Exchangers & Reboilers	\$736,960	56% of sweetening costs
Misc.	\$210,560	16% of sweetening costs
Other Equipment	\$42,550,667	Sweetening is 3% of total equipment costs; other costs come from liquefaction
Labor Costs	\$263,200,000	6x equipment costs
<hr/>		
Operating expenditures		
Solvent (99% recovery)	\$8,000,000/year	Calculated based on soybean oil prices, as shown in Figures 5.6 and 5.7.

Based on a study of Canadian natural gas plants, natural gas is typically processed at a cost of \$8/GJ – where \$4/GJ is allocated to pipeline/source costs, leaving \$4/GJ for actual treatment and liquefaction of the gas to be sold as liquefied natural gas. Based on the simple model in Table 5.8, which roughly estimates the capital costs and neglects all parts of operating expenditures other than solvent recovery, and assuming the plant has only 5% downtime but otherwise runs at maximum capacity, a continuous cash flow diagram is shown in Figure 5.11.

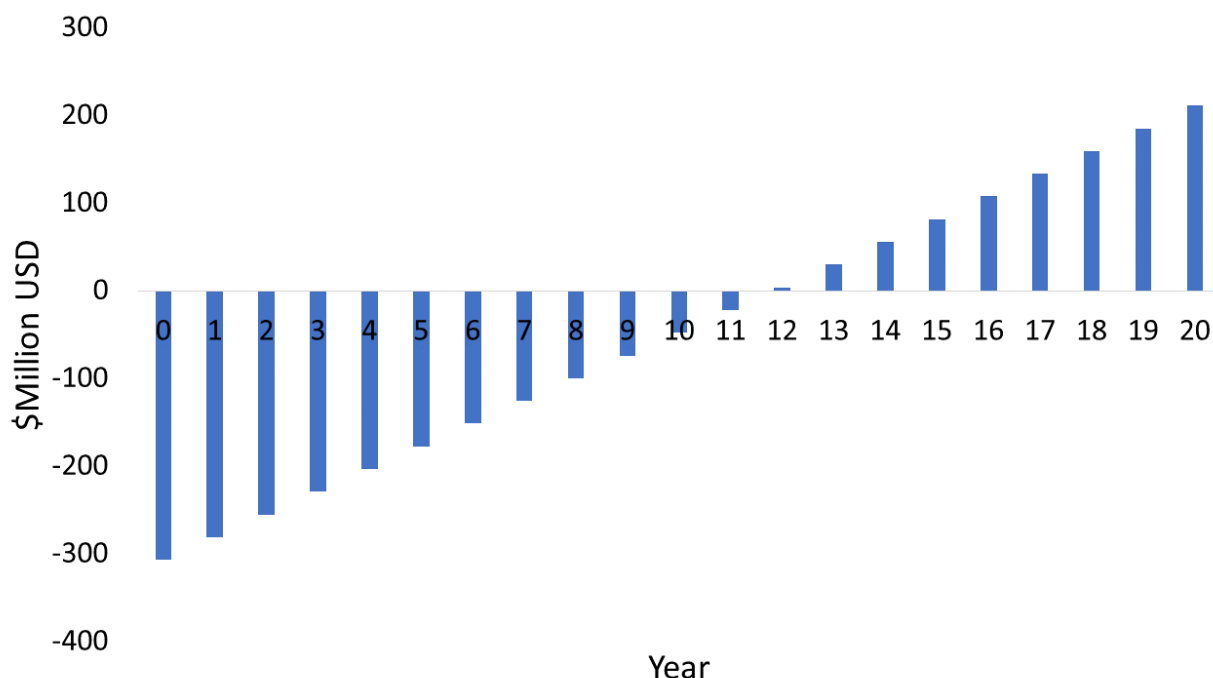


Figure 5.11. Continuous cash flow diagram assuming a 20-year plant and equipment lifetime. Building a new plant would require a large capital investment and the plant would not begin to see profits until year 12. This model also assumes solvent regeneration and re-use is at 99% and that the cost of processing the gas is even with that of amine gas treating.

After 12 years, the plant would begin to profit. Based on the analysis, over a 20-year plant lifetime, the gas processing cost would be \$3.7/GJ, just under the \$4/GJ needed to be competitive with amine gas treating and other methods. However, the present model makes several assumptions, including: solvent regeneration and re-use is at 99%, solvent prices do not increase, cost estimates in Table 5.8 and relationship between cost of different items (i.e. labor = 6x capital costs) are accurate, that natural gas pipelines prices do not increase, that process gas prices do not decrease, that the absorption operation of the plant is running at full capacity all but 5% of each year, and neglects operating costs. A sensitivity analysis showing the relationship between solvent recovery and the cost of processing the gas is shown in Figure 5.12. Based on the calculations presented, solvent regeneration and re-use would have to exceed 98% to ensure the costs remain low enough for the overall expense of treating the gas to be comparable with amine gas treating. Increased solvent recovery significantly decreases the cost of treating the gas.

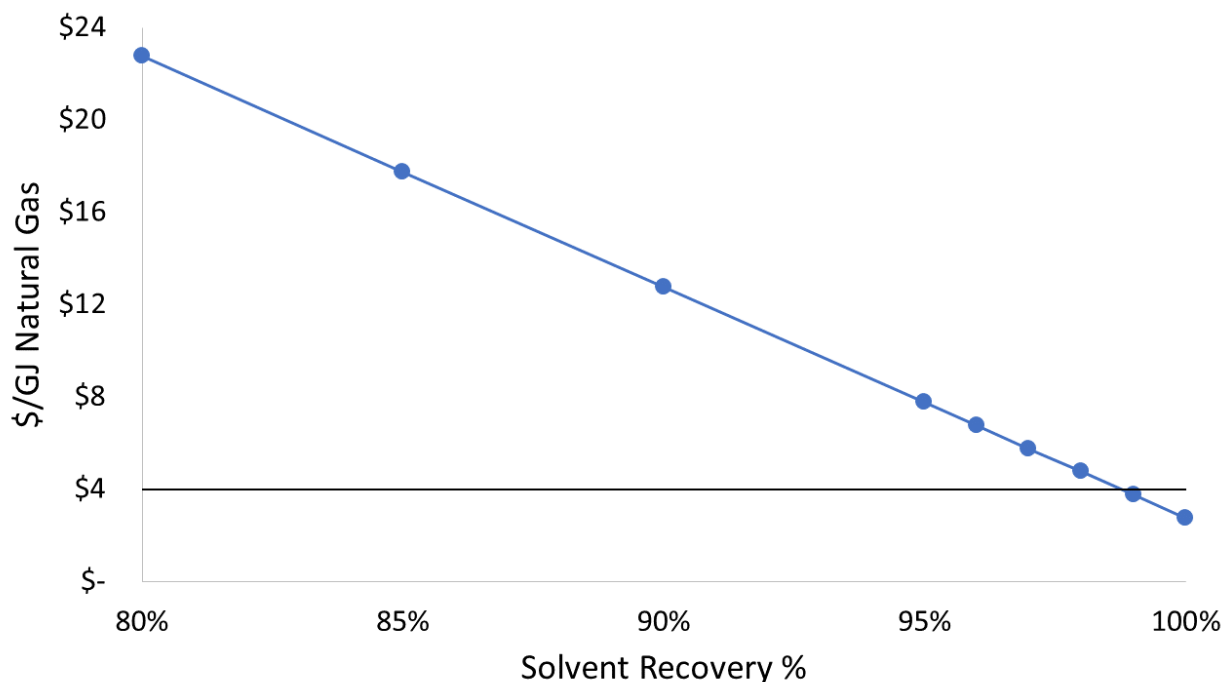


Figure 5.12. Sensitivity analysis of the relationship between solvent regeneration and recovery and the cost of processing gas. The cost of amine gas sweetening methods is approximately \$4/GJ natural gas. To be competitive, the process designed and presented here would need to achieve greater than 98% solvent regeneration and re-use.

As of yet, a definitive method for stripping the H_2S from the soybean oil and bio-solvents and regenerating the bio-oils to be used again is unknown. However, there are a number of methods for recovering H_2S gas in aqueous solutions and oils, well-described in the literature.^{114,127–129} Most methods fall into one of three categories: chemical precipitation, chemical oxidation, or biological oxidation.^{114,127–129} The key to process viability would be to develop a method that maximizes the percent of the bio-solvent that can be regenerated and re-used. An alternative to the lofty goal of 98% solvent regeneration and recovery is to find other avenues in which costs can be reduced. While the price of sweetening is well established in Table 5.8, the cost of other equipment is more loosely correlated and estimated, and a full process simulation including other equipment needs may give better insight into the overall process cost and the solvent regeneration percent that must be obtained.

5.5 Conclusion

Soybean oil and high-oleic soybean oil were used as case studies to examine viability of using bio-oils as solvents for extracting H_2S from sour natural gas, with an aim of designing an absorption operating that could process 1000 kmol/h of natural gas and remove 99.9% of H_2S from feed gas ranging from 40 – 400 ppm H_2S . Graphical methods and the Kremser method examined the absorption unit and found a trayed tower with 14 stages, a 2 m diameter and 8.5 m height, could successfully meet these goals with a soybean oil absorbent flow rate of 120 kmol/h. The cost of such an extraction column was estimated along with other capital costs, and the dependence on the economic viability of such process hinges on capability of regenerating and recycling more than 98% of the soybean oil bio-solvent to stay competitive with amine gas treating, the most popular industrial method. The viability of this process being economically favorable looks unlikely, but the estimates here show where cost-cutting measures would need to be developed for the cost of processing sour gas with bio-based oils to compete with current technologies.

5.6 Acknowledgments

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6. EXPANDING THE INVESTIGATION: BIO-OILS, TEMPERATURE EFFECTS, AND SOLVENT REGENERATION/SULFUR RECOVERY

The work presented in Chapters 4 and 5 demonstrates a clear capability of soybean oil and high-oleic soybean oil to successfully remove more than 90% of H_2S from a nitrogen gas stream at ambient conditions and at bench-scale. The economic feasibility of industrializing such a process hinges on minimizing solvent costs, achieving high solvent regenerative power, and recovering and selling sulfur as a secondary product. As such, continuing and future work on this project should focus on two aspects: investigating the difference between different seed oils (such as soybean, high-oleic soybean, canola and sunflower) and the effects of temperature on sorption capacity, and the ability to remove H_2S from the oils using a method that would allow the seed oil bio-solvents to be regenerated and recycled. Both topics are explored here with preliminary results presented.

6.1 Assessing Viability of Seed Oils in Removing H_2S from Sour Natural Gas at Varying Temperatures

6.1.1 Introduction

In silico molecular modeling combined with benchtop experiments were used to determine the impact of temperature and degree of saturation on the ability of plant-based oils and olefins to be used as bio-based extraction solvents to remove hydrogen sulfide (H_2S) from sour natural gas. Previous work demonstrated the ability of soybean oil and high-oleic soybean oil to extract hydrogen sulfide from methane and nitrogen gas at room temperature.¹⁰⁶ Plant-derived bio-solvents have potential for high-impact application in agriculture and natural gas industries. Increases in fracking has increased use of natural gas as a fuel source in the United States, whereas of 2015, 67% of daily natural gas production is from fracking.^{1,2} A major inhibitor to production of natural gas are high concentrations of hydrogen sulfide (H_2S), a corrosive natural impurity, found in shale gas reservoirs.¹ Previous *in silico* and benchtop studies demonstrated the ability to use conventional soybean oil and high-oleic soybean oil as bio-solvents to remove H_2S from methane and nitrogen gas phases at ambient temperature and pressure.¹⁰⁶

Ongoing research is focused on evaluating the feasibility of removing H₂S from natural gas using soybean and other vegetable oils and explores the impact of temperature. Soybean oil, high-oleic soybean oil, canola oil, and sunflower oil were chosen for study in addition to heptane, 1-hexene, and water. Temperatures ranging from 25 – 50 °C were chosen for investigation to expand on previous work carried out at ambient temperature.¹⁰⁶ Predictive *in silico* methods examining these compounds (H₂S, natural gas, and oil components) provide relatively fast and cost-effective methods for fundamental research into the feasibility of using vegetable oils as extraction solvents. The Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to simulate partitioning of the target molecule (H₂S) between the liquid (oil) and gas (methane or nitrogen) phases. The COSMO-RS model has been used to predict partitioning of target molecules in a variety of liquid-liquid^{29,31–35} and vapor-liquid^{36,37} systems as well as the partitioning of H₂S between gas phases and soybean oils.¹⁰⁶ The present study expands upon previous work and presents a novel use of plant-based oils as bio-solvents for sweetening gas, and has potential for scale-up to an industrial process.

6.1.2 Materials & Methods

6.1.2.1 Reagents and Equipment

Compressed gas cylinders of 40 ppm H₂S in balance nitrogen were obtained from Ideal Calibrations (Ideal Calibrations, LLC, Melvindale, MI). High-oleic soybean oil was obtained from ADM (Archer Daniels Midland Company, Frankfort, IN), soybean and canola oils were purchased locally (Great Value brand, Walmart, Inc.), and sunflower oil was purchased locally (Spectrum Naturals brand, Fresh Thyme Market). Gas analysis was performed using an Altair 5X Gas Detector equipped with a low concentration H₂S sensor, rented from Ideal Calibrations (Ideal Calibrations, LLC, Melvindale, MI). Tedlar PVF 1.6L gas sampling bags (Saint-Gobain Chemware), 18-gauge needles (Becton Dickinson & Co.), and nylon barbed luer locks (Cole-Parmer), and Omnitop 50 mL Sample Tubes with silicone dip tubes (Chemglass Life Sciences, LLC) were also used.

6.1.2.2 In silico approach: COSMO-RS

The **C**onductor-like **S**creening **M**odel for **R**eal **S**olvents was used to model a bi-phasic liquid-gas system and predict the partition coefficient, K , of the target molecule: H_2S . The primary advantage of COSMO-RS is that it only requires molecular structures of the molecules and composition of the phases as inputs for simulation.^{37,75} No experimental data is required, although in this study experimental data is used to inform reiterations of the model after the initial conditions are determined. A methodology for using COSMO-RS and related software to predict partition coefficients has been outlined by Hopmann *et al.*^{33,34} and demonstrated in a variety of studies including biomolecules^{29,31,32,35} and separating H_2S from methane.^{82,106} In this study, the liquid phase was modeled as a mixture of the fatty acid components of each oil, as shown in Table 6.1. The impact of degree of saturation and number of double bonds has been previously examined in a study using soybean oil, high-oleic soybean oil, heptane and water as extraction solvents. This study expands upon previous work by looking at vegetable oils with lower and higher carbon bond to double bond ratios than those found in soybean oils, and by examining temperature effects.

Table 6.1. Fatty acid composition of seed oils.^{85,93,111}

Fatty acid	Molecular weight	Carbon bonds: double bonds	Weight %			
			SBO	HOSBO	Canola	Sunflower
palmitic	256.42	C16:0	11.0	6.0	4.9	6.2
stearic	284.48	C18:0	4.0	3.0	1.6	3.7
oleic	282.46	C18:1	22.0	85.0	33.0	25.2
linoleic	280.45	C18:2	55.0	4.0	20.4	63.1
α -linolenic	278.43	C18:3	8.0	2.0	7.9	0.2
gadoleic	310.51	C20:1	-	-	9.3	-
erucic	338.57	C22:1	-	-	23.0	-

Three-dimensional structures of the palmitic, stearic, oleic, linoleic, and α -linolenic fatty acid molecules were generated using HyperChem (release 8.0, Hypercube Inc., Gainesville, FL) and the Molecular Mechanics + (MM+) force field. HyperChem's conformational search was used to generate up to 30 of the lowest energy conformations of each molecule, constrained by: a

maximum acceptable energy criterion of 1 kcal/mol above best, molecules considered duplicates if energy was within 0.05 kcal/mol, and RMS error restricted to 0.25 Å. Gadoleic and erucic fatty acid structures were downloaded from the National Center for Biotechnology Information PubChem Database^{130,131} and used in lieu of HyperChem-generated conformations. Screening charge density of each conformation was generated using TmoleX (Version 3.4, COSMOlogic GmbH & Co. KG, Germany) and applying Becke-Perdew (B-P) functional and triple zeta valence polarized (TZVP) basis sets.^{101,102} Using COSMOthermX (Version 13, COSMOlogic GmbH & Co. KG, Germany), chemical potential and the activity coefficient were calculated. The mass fractions of acids for each oil were used as composition of the liquid phase while the upper phase was modeled as either 100% methane or 100% nitrogen.

The partition coefficient (K_{mod}) was calculated from the activity coefficients (γ_i) of H₂S in the upper (U) and lower (L) phases at infinite (i) dilution, as shown in Equation 6.1. The activity coefficients are multiplied by the weighted sum of the molar volumes of each phase.

$$K_{mod}^{UL} = \frac{\gamma_i^L}{\gamma_i^U} \times \frac{\sum x_i^L v_{0j}}{\sum x_i^U v_{0j}} \quad (6.1)$$

The activity coefficient of H₂S at temperatures from 10 – 100 °C were predicted for the liquid phase, and from 10 – 100 °C at 1 atm for the gas phase.

6.1.2.3 Equilibrium Extraction Studies, Isotherm and Saturation Studies, and Analysis of H₂S Gas

Studies and methods similar to those described in Sections 4.3.3, 4.3.4, and 4.3.5 were planned. Extraction solvents under investigation included soybean oil (SBO), high-oleic soybean oil (HOSBO), canola oil, sunflower oil, heptane, 1-hexene, and water. SBO, HOSBO, heptane, and water were previously investigated at ambient conditions.¹⁰⁶ 1-hexene was chosen as an olefin for comparison to hexane and to better understand the impact of alkene chains and double bonds. Canola and sunflower oil were chosen to further investigate the impact of different fatty acid compositions and total double bond availability on oils' performance as extraction solvents.

Temperatures to be studied in addition to ambient conditions (~25 °C) were chosen based on the model results and prior work, as shown in Figure 6.1.

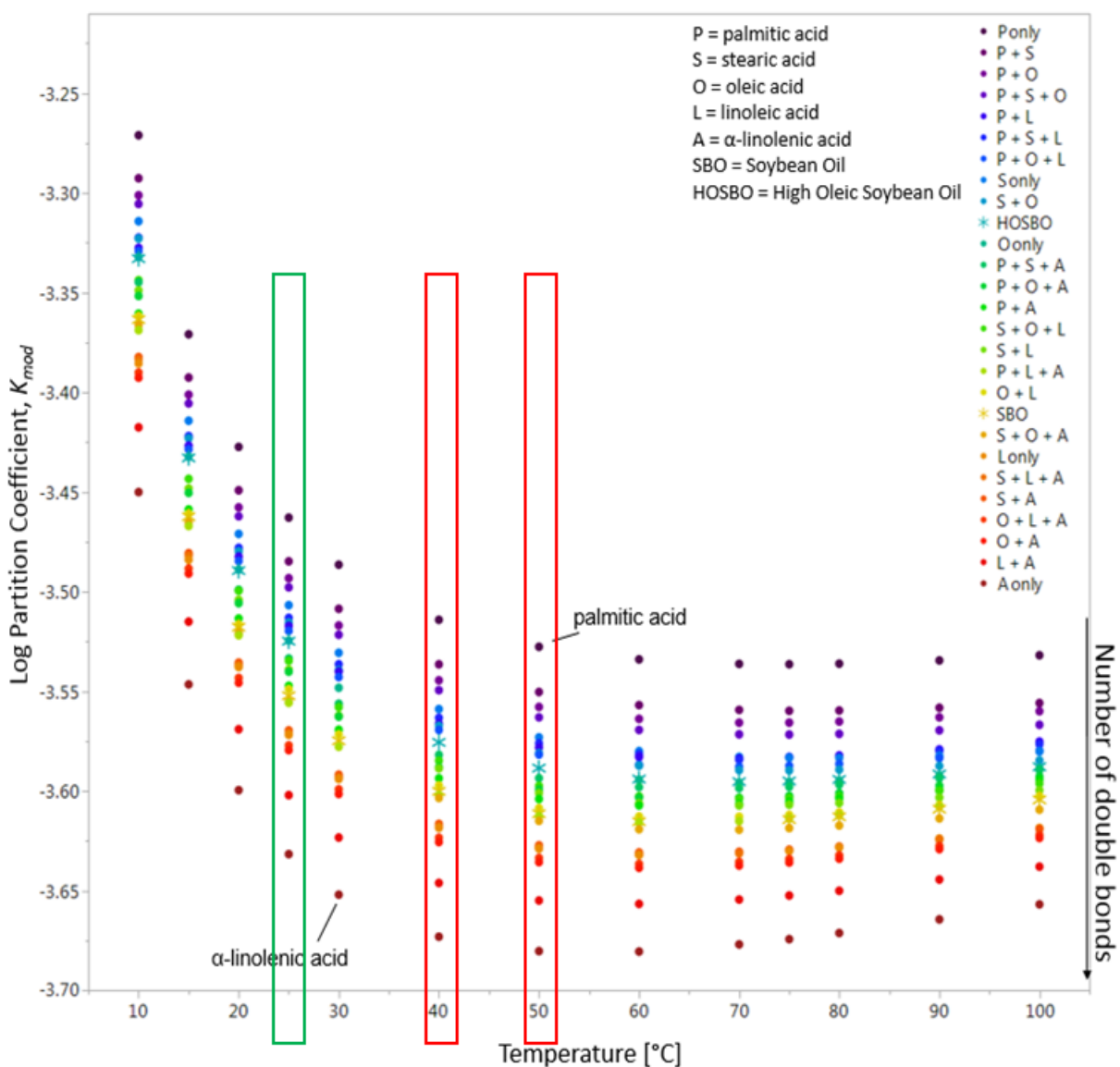


Figure 6.1. Predicted partitioning of H_2S in a bi-phasic system consisting of methane gas and fatty acids. (Reprinted with permission from Brace, E. C.; Engelberth, A. S. Assessing Viability of Soybean Oils to Remove Hydrogen Sulfide from Natural Gas. *ACS Sustain. Chem. Eng.* **2020**, *In Press*.¹⁰⁶ Copyright 2020 American Chemical Society.) The green box indicates 25 °C, where prior experiments were carried out for SBO and HOSBO; continuing and future work will include experiments for all oils at 25, 40, and 50 °C in order to investigate temperature effects and compared to predicted temperature effects.

Based on the predictive models, the partitioning of H_2S between methane and fatty acids is expected to be most favorable between 25 – 50 °C.

6.1.3 Results & Discussion

6.1.3.1 Theoretical Determination of the Partition Coefficient

The theoretical partition coefficient (K_{mod}) of H_2S in a bi-phasic system comprised of methane (gas phase) and soybean oil, high-oleic soybean oil, canola oil, or sunflower oil was calculated using the COSMO-RS theoretical method. The oil phase composition was based on the mass fraction of the five fatty acids (Table 6.1). The temperature of the simulations varied from 10 to 100 °C and pressure was atmospheric. Figure 6.2 displays the predicted results.

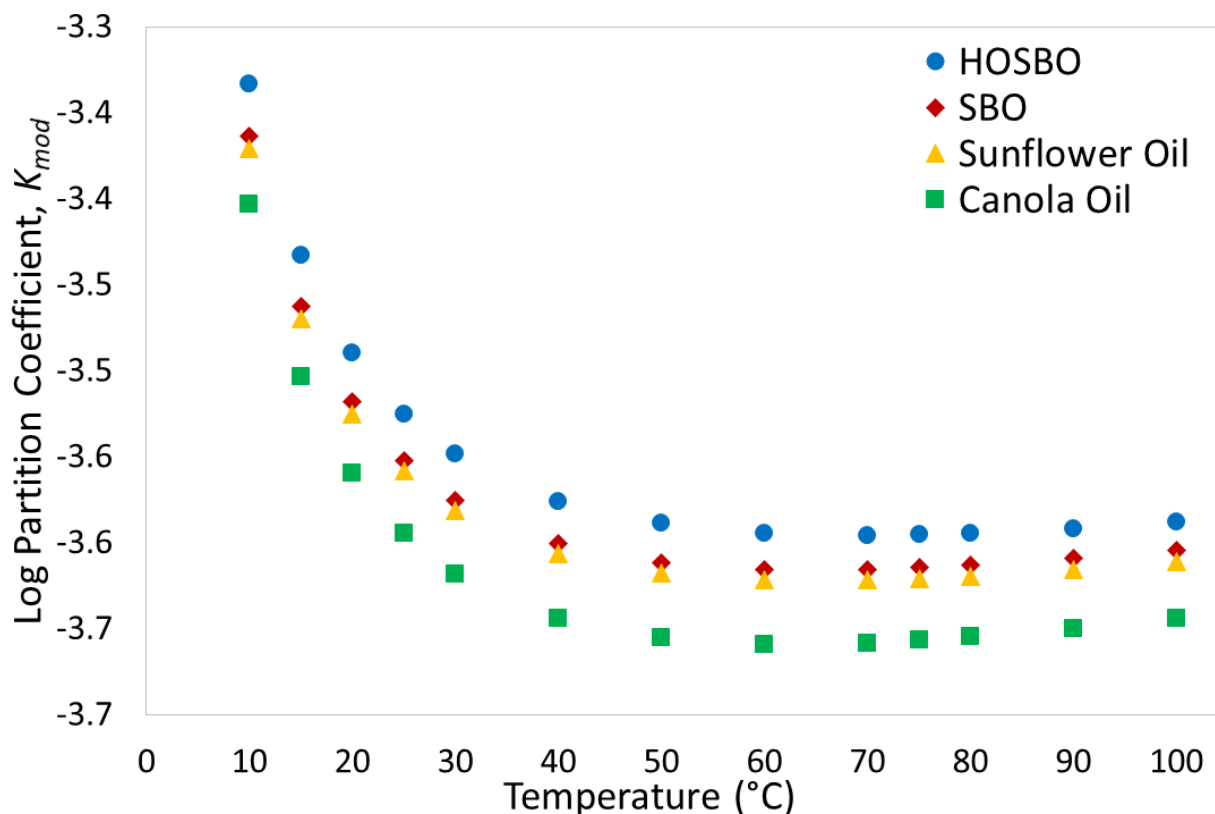


Figure 6.2. Predicted partition coefficients (K_{mod}) of H_2S between methane (gas) and different seed oils. Canola oil and sunflower oil, which have higher ratios of unsaturated:saturated fatty acids than soybean oil and high-oleic soybean oil, are predicted to have the most favorable partitioning of H_2S .

The predicted results indicate that canola oil would have the lowest $\log K$ values for H_2S and could be expected to perform best at removing H_2S from methane gas. Sunflower oil and canola oil perform better than soybean and high-oleic soybean oil is expected, given previous indication that increasing amounts of unsaturated fatty acids lead to lower $\log K$ values.¹⁰⁶ Considering the mass fractions of saturated and unsaturated fatty acids in each oil and the ratio of unsaturated:saturated

fatty acids as shown in Table 6.2, the results from Figure 6.1 support previous work¹⁰⁶ showing that increasing amounts of unsaturated fatty acids lead to lower $\log K$ values and more favorable partitioning.

Table 6.2. Saturated vs unsaturated fatty acid mass fractions in seed oils (based on compositions in Table 6.1). Unsaturated fatty acids offer interaction sites for H₂S.

Mass fractions	SBO	HOSBO	Canola Oil	Sunflower Oil
Saturated fatty acids	0.15	0.090	0.065	0.099
Unsaturated fatty acids	0.85	0.91	0.935	0.901
Ratio: unsaturated/saturated	5.7	10.1	14.4	9.1

Because H₂S gas in nitrogen rather than methane is to be used experimentally, it is important to examine how partitioning may differ in a nitrogen system vs. a methane system. Predicted results are shown in Figure 6.3.

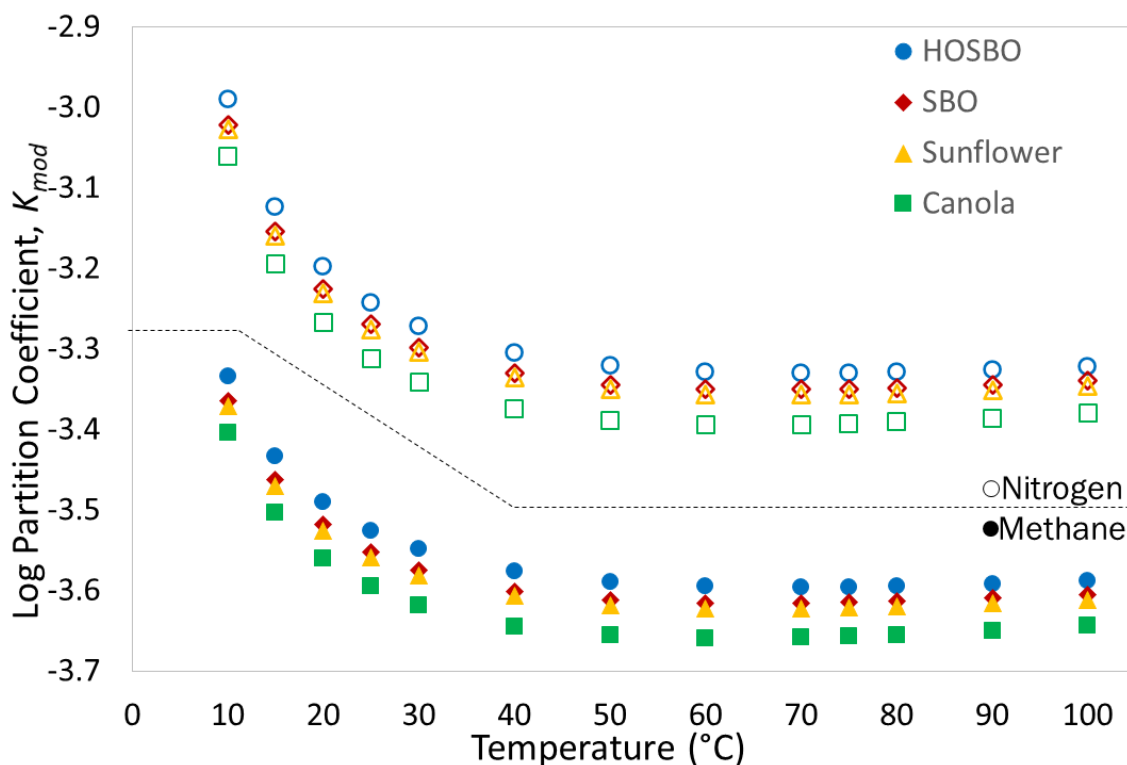


Figure 6.3. Comparison of predicted partition coefficient (K_{mod}) values for H₂S in systems containing either nitrogen or methane gas and soybean, high-oleic soybean, canola or sunflower oil. The root mean square deviation for each oil is ~ 0.28 , indicating the difference in gases causes the same effect regardless of oil and can be adjusted for.

The comparison between the methane and nitrogen models have a root mean square deviation of ~ 0.28 across all oils, indicating that the difference between the nitrogen and methane values are approximately the same regardless of temperature and oil and therefore can be corrected for. This validates that using nitrogen for safety reasons is a reasonable avenue forward.

6.1.3.2 Experimental Determination of the Partition Coefficient

Previously collected data for SBO and HOSBO at ambient conditions showed that equilibrium of the nitrogen gas, H_2S , and soy oil systems were reached quickly, with $> 90\%$ of the H_2S removed from the gas phase within 15 minutes and no statistically significant difference in partition coefficient (K) values with residence times from 15 – 60 minutes.¹⁰⁶ New investigation has determined the partition coefficient for H_2S in canola and sunflower oils at residence times from 0 – 60 minutes at ambient conditions, as well as all four seed oils at 40°C , as shown in Figure 6.4.

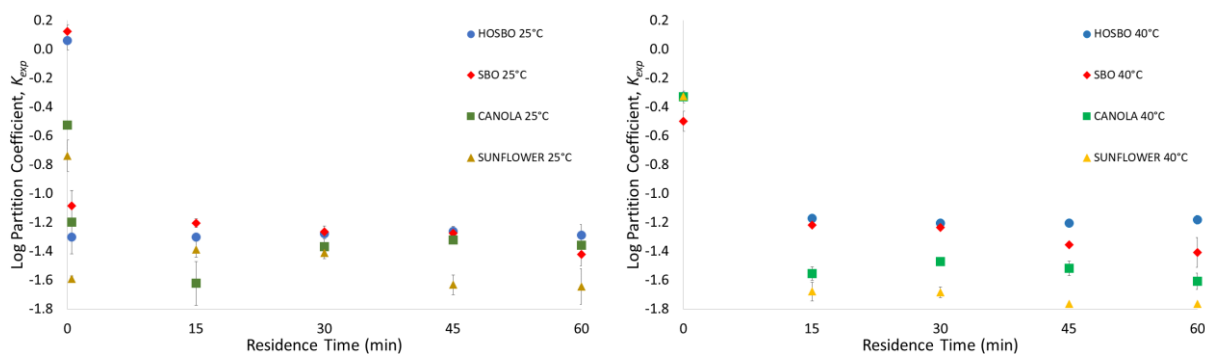


Figure 6.4. Experimentally determined partition coefficients of H_2S at 25°C (left) and 40°C (right).

The experimentally determined partition coefficients are not significantly different at residence times beyond 15 minutes nor are they significantly different between 25°C and 40°C . Further studies at temperatures higher than 40°C are recommended to fully determine if increased temperature has a measurable effect on partitioning. These results are in line with the model results which shows little change in K when temperature is increased past 25°C . The experimental and model results are compared in Figure 6.5.

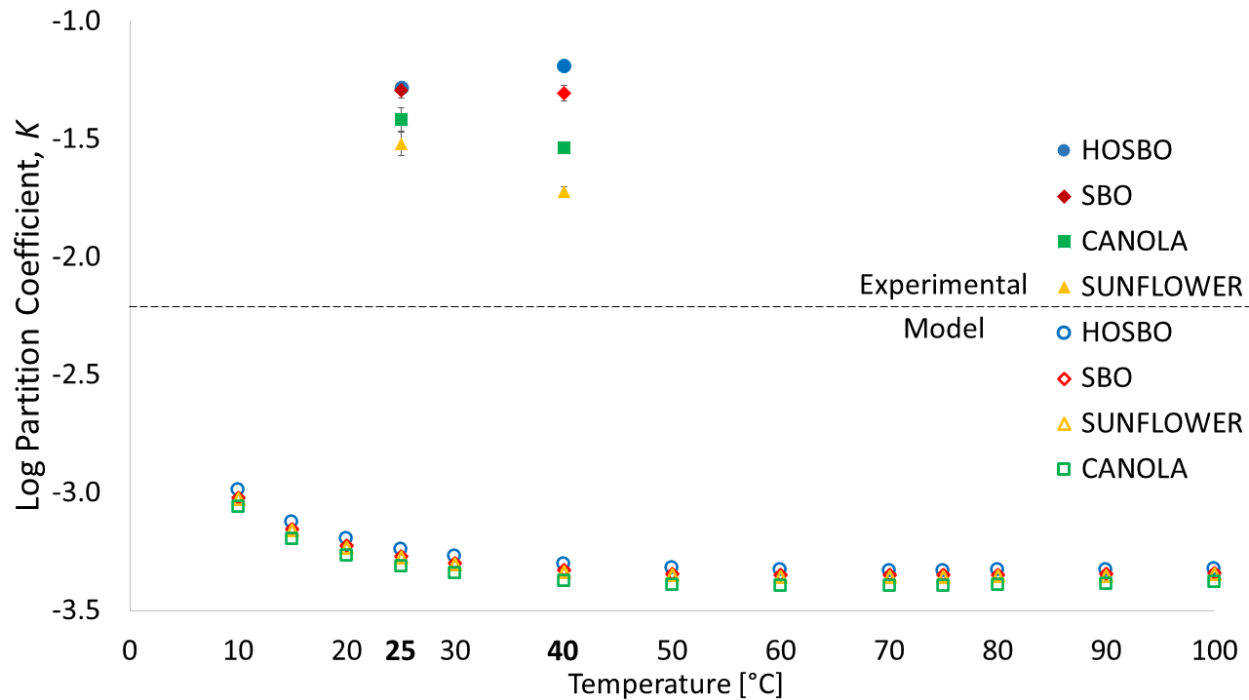


Figure 6.5. Experimental and predicted partition coefficients for H₂S in nitrogen and seed oil systems. Experimental partition coefficients at 40 °C have a wider spread than at 25 °C.

The experimental partition coefficients are not as low as predicted, but still indicate favorable partitioning of H₂S out of nitrogen and into all four seed oils. Interestingly, there seems to be wider variability between the four seed oils at 40 °C than at 25 °C. This phenomena should be further investigated through repeat studies and studies at higher temperatures, such as 50 or 60 °C.

6.1.3.3 Isotherm Models

Saturation studies and isotherm models were previously determined for SBO, HOSBO, water and heptane at 25 °C. New studies have developed isotherms for canola and sunflower oils at 25 °C as well as for all four oils at 40 °C. Experimental data was collected and fit to Langmuir and Freundlich isotherm models, as shown in Equations 6.2 and 6.3.

$$\text{Langmuir isotherm} \quad q_e = \frac{bQ_0C_e}{1 + bC_e} \quad (6.2)$$

$$\text{Freundlich isotherm} \quad q_e = K_f C_e^n \quad (6.3)$$

The Langmuir isotherm parameters are shown in Table 6.3 and the Freundlich isotherm parameters are shown in Table 6.4.

Table 6.3. Langmuir isotherm parameters.

Adsorbent	25 °C			40 °C		
	Q_0	b	R^2	Q_0	b	R^2
High-oleic soybean oil	1.16	0.843	0.952	1.10	0.677	0.958
Soybean oil	2.00	0.608	0.963	1.00	0.975	0.966
Canola oil	1.18	0.850	0.967	1.42	0.742	0.978
Sunflower oil	1.05	0.719	0.963	1.54	0.688	0.959
Water	2.38	0.537	0.970	-	-	-
Heptane	1.96	0.730	0.962	-	-	-

Table 6.4. Freundlich isotherm parameters.

Adsorbent	25 °C			40 °C		
	K_f	n	R^2	K_f	n	R^2
High-oleic soybean oil	0.504	0.515	0.888	0.426	0.558	0.909
Soybean oil	0.719	0.586	0.913	0.469	0.482	0.912
Canola oil	0.517	0.513	0.906	0.574	0.542	0.928
Sunflower oil	0.417	0.545	0.913	0.598	0.557	0.904
Water	0.793	0.610	0.928	-	-	-
Heptane	0.784	0.548	0.902	-	-	-

As was previously found, the Langmuir isotherm equation provides a better fit for the data. The experimentally determined data is plotted with the Langmuir isotherm models in Figure 6.6.

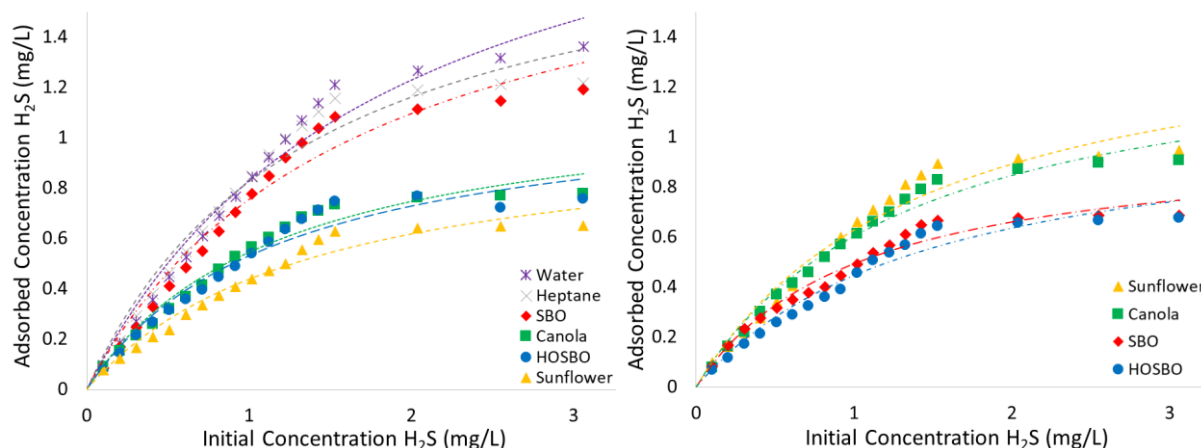


Figure 6.6. Experimentally collected data and Langmuir isotherm models for H_2S adsorption in water, heptane, soybean oil (SBO), high-oleic soybean oil (HOSBO), canola oil and sunflower oil at 25 °C (left) and 40 °C (right).

The isotherm data and models seem to indicate sunflower oil has a higher adsorption capacity at 40 °C while soybean oil has a lower adsorption capacity at 40 °C and adsorption capacity has minimal change at either temperature for canola or high-oleic soybean oil. Further statistical analysis of the difference may yield insight as to if temperature effect is really significant for any of the four oils.

6.1.4 Conclusions & Recommendations for Future Work

Investigation into temperature effects on high-oleic soybean oil, soybean oil, canola oil and sunflower oil as extraction solvents for removing H_2S from nitrogen or methane gases indicate that there is no significant impact on partitioning when increasing temperature from 25 to 40 °C. Additional studies between 25 and 40 °C or at higher temperatures such as 50 °C may be useful in determining if increasing temperature does significantly change the partition coefficients for H_2S in any of the four oils or if the difference between the partition coefficients widens, but from the results at 25 and 40 °C as well as the models, this seems unlikely. Additional investigation into the exact composition in the particular brands and batches of oils used may help elucidate the reasons for the slight differences in the isotherm models at 25 and 40 °C. For example, is some component of the sunflower oil breaking down when heated that allowed it to better adsorb H_2S at 40 °C than 25 °C? Overall, operating at ambient/low temperatures is less energy intensive and improves the feasibility of using soybean oils as extraction solvents.

6.2 Regeneration of Oils/Sulfur Recovery

6.2.1 Introduction

As discussed in detail in Chapter 5, the feasibility of using seed oils as bio-solvents for removing H_2S from natural gas hinges on an ability to regenerate the bio-solvents and recycle them and to recover the H_2S and convert it to elemental sulfur for sale as a chemical building block. There are two strategies which could be applied: using oxidative or precipitative methods to convert dissolved H_2S to sulfur or other sulfur species (*Section 6.2.2*) or trying to force the dissolved H_2S back into the vapor phase and sending gaseous H_2S on for treatment using the Claus process (*Section 6.2.3*).

6.2.2 Solvent Regeneration and Removal of H_2S

Many methods exist for removing H_2S from aqueous solutions and other types of oils, and are well-described in the literature.^{114,127–129} There are three primary categories of methods: chemical precipitation, chemical oxidation, and biological oxidation,^{114,127–129} as shown in Figure 6.7.

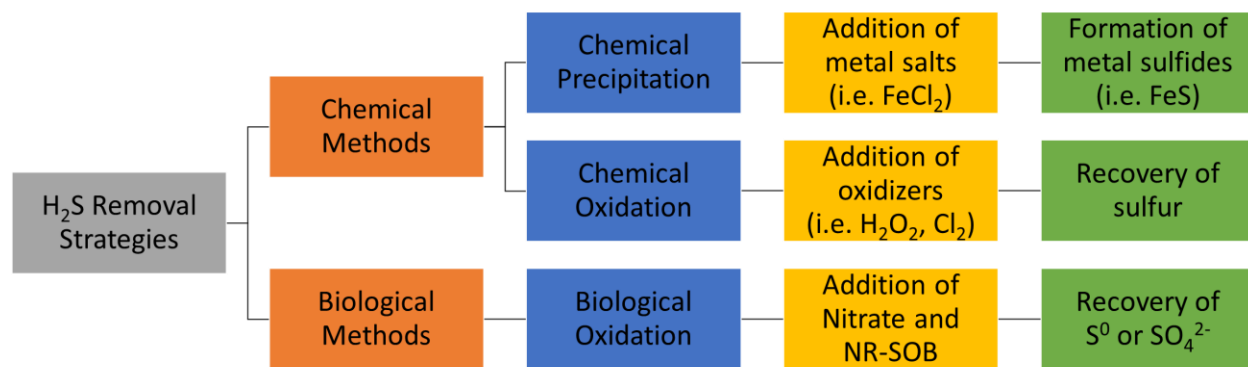


Figure 6.7. H_2S removal strategies can be classified by chemical or biological methods. Chemical methods rely on addition of agents that cause precipitation, such as metal salts which precipitate metal sulfides, or addition of oxidizing agents which oxidize H_2S to sulfur. Biological methods rely on presence or addition of nitrate and addition of nitrate reducing-sulfur oxidizing bacteria, which can lead to recovery of S^0 or SO_4^{2-} .

Each of these methods has advantages and disadvantages based on the concentration of H_2S in the solution being treated, the cost of the removal agents being added, the percent of H_2S that is successfully converted to another sulfur species.

6.2.2.1 Chemical Precipitation of H₂S

Metal (iron, copper, zinc, nickel, manganese) salts have long been used in treatment of sewage to remove H₂S^{114,132,133} and offer opportunities for precipitating metal sulfides out of other H₂S-containing solutions. Ferrous and ferric chlorides are most commonly used, forming iron sulfides in reactions like those shown in Reactions 6.4 and 6.5.¹¹⁴



There is no consensus in the literature regarding whether FeCl₂, FeCl₃, or some combination of the two is most effecting in removing H₂S, and Table 6.5 summarizes some of the findings in the literature.^{114,132,134–138}

Table 6.5. Scale and effectiveness of adding iron salts to sulfide solutions to precipitate iron sulfide. Partially adapted from Zhang et al. 2008.¹¹⁴

Chemical agents	Ratio of chemicals to S (w/w)	Scale and reactor volume	Upstream sulfide concentration (mg S/L)	Average % removal of sulfide	Cost (\$/kg S)	References
FeCl ₂ + FeCl ₃	2.5:1	Plant scale, 75,000 m ³ /day	6.4	97	8.1	Padival et al. 1995 ¹³⁶
FeCl ₃	1.5:1	Lab scale, 3.00 L	3.8	100	34.2	Nielsen et al. 2005 ¹³⁷
FeCl ₂ •4H ₂ O	6-7:1	Plant scale, 59,000 m ³ /day	> 4.0	90	25.3 – 29.5	US EPA 1992 ¹³⁸

The primary disadvantages of using iron and other metal salts to precipitate metal sulfides is the cost of the salts, the need to add more metal salts than what is stoichiometrically necessary to precipitate all dissolved sulfides,^{114,132,133,136,138} and whether or not metal sulfides are a desired product. However, chemical precipitation methods are the most promising for removing H₂S from the bio-solvents, as oxidative methods would likely oxidize components of the bio-solvents, thereby complicating or preventing solvent regeneration.

6.2.2.2 Chemical Oxidation of H₂S

A variety of well-established oxidizers have been demonstrated to oxidize dissolved sulfide, thereby converting H₂S to elemental sulfur.¹¹⁴ Hydrogen peroxide, chlorine, and potassium permanganate have all been demonstrated to convert dissolved hydrogen sulfide to elemental sulfur or sulfate molecules, which can then be separated from a solution.^{114,127,128,135,138,139} An example of such a reaction is shown in Reactions 6.4 and 6.5. Formation of potassium hydroxide (KOH) in the first reaction (6.6) will create basic conditions for the second reaction (6.7) to proceed.

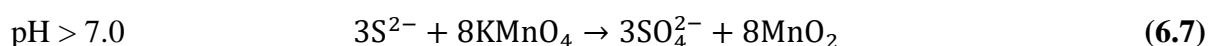
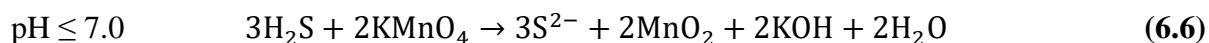


Table 6.6 lists some of the usage details and advantages and disadvantages of each oxidizing agent.

Table 6.6. Use of oxidizing agents for removing H₂S from solution.^{114,135,138–140}

Oxidizing Agent	Details	Advantages	Disadvantages
H ₂ O ₂	1.3-4.0:1 H ₂ O ₂ :S (w/w) treatment ratio; can achieve 85-100% sulfide removal	<ul style="list-style-type: none"> • Inexpensive treatment (< \$11/kg S) • H₂O₂ decomposes to water and oxygen 	<ul style="list-style-type: none"> • Instability/short lifetime of H₂O₂
Cl ₂	2:1 Cl:S (w/w) treatment ratio; can be added as a gas or as a sodium hypochlorite solution	<ul style="list-style-type: none"> • Most inexpensive treatment (< \$4.7/kg S) 	<ul style="list-style-type: none"> • Highly reactive/ likely to interact with other species
KMnO ₄	Ideally fed as a 6-7% aqueous solution	<ul style="list-style-type: none"> • Highly effective strong oxidizing agent 	<ul style="list-style-type: none"> • Most expensive: ~\$25/kg S

Despite their relatively low cost and high effectiveness in removing H₂S, oxidizing agents may not be a wise choice for regenerating the bio-solvents. The oxidizing agents are likely to oxidize the bio-solvent itself, therefore complicating or preventing the solvent regeneration and re-use.

6.2.2.3 Biological Oxidation of H₂S

Biological oxidation may be more effective than chemical oxidation in regenerating the bio-solvents since sulfide reducing bacteria used as oxidizing agents would be selective for H₂S and less likely to oxidize other components of the bio-solvents. A number of studies have shown that use of nitrate reducing – sulfide oxidizing bacteria (NR-SOB) can metabolize H₂S and convert it to sulfate or sulfur.^{114,141–145} However, whether these bacteria would produce the sulfate or sulfur as an intracellular or extracellular product would complicate recovery of the sulfur species, and many additional steps and investigation would need to be taken to develop a culture system for the bacteria to live in a bio-solvent regeneration tank and oxidize H₂S into a sulfur species that could be harvested.

6.2.3 Converting gaseous H₂S to Sulfur: the Claus Process

An alternative to trying to precipitate a sulfur species from the H₂S-containing soybean oils would be to try to use a thermal method where heat is applied to force the H₂S back into the vapor phase. The H₂S-rich vapor phase could then be removed for conversion to sulfur while the ‘stripped’ bio-solvent could be recycled. This type of absorption-stripping cycle is commonly used in amine gas treating.⁴¹

The Claus Process is a widely used two stage process for converting gaseous H₂S to elemental sulfur, S.^{41,146} First developed in 1883 and significantly modified in 1936, the modified Claus process is ubiquitous in treating acid gas streams, typically an output of oil and gas refining operations.^{41,146} A thermal conversion stage consisting of two reactions is followed by a catalytic stage with one reaction. Reactions 6.8, 6.9, and 6.10 are the three reactions in the Claus process.

Thermal stage	$\text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{S}$	(6.8)
(> 1700 °F)	$\text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_2$	(6.9)
Catalytic stage	$2\text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons 2\text{H}_2\text{O} + 3\text{S}$	(6.10)
(dew point < operating temp < 700 °F)		

In the catalytic stage, there is a trade-off in that temperatures closer to the mixture dew point achieve more complete conversion to sulfur, but sulfur deposition becomes an issue. For this reason, the catalytic stage is usually multiple stages of condensers in practice.¹⁴⁶ A simple schematic is shown in Figure 6.8.

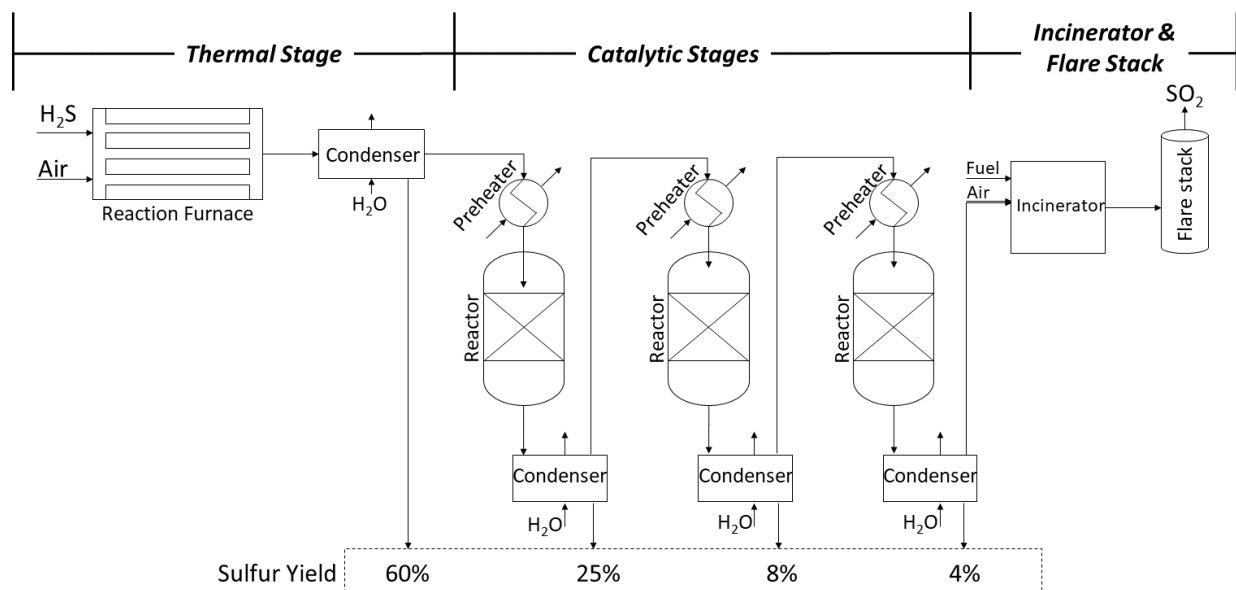


Figure 6.8. Schematic of the Claus process for recovering sulfur from H_2S gas. The thermal stage recovers most of the sulfur, and catalytic stages continue to add to the sulfur recovery and yield. 2-3 catalytic stages are common and can result in 94 – 97% yield. In straight through mode, all H_2S gas passes first through the thermal reaction furnace. In split-flow mode, H_2S with less than 50 mol% H_2S bypasses the thermal stage and heads straight to the first catalytic stage reactor.^{41,146}

There are also two operational modes for the Claus Process: split-flow and straight-through. The desired method depends on the concentration of H_2S in the feed gas, as shown in Table 6.7.

Table 6.7. Operation modes for the Claus process depend on the concentration of H_2S in the feed gas.

H_2S mol%	Recommended process
50 – 100	Straight-through
20 – 50	Split-flow

In the straight-through mode, all gas passes through the thermal stage reaction furnace. In split-flow mode, feed gas with a reduced H_2S concentration bypasses the reaction furnace and goes

straight to catalysis.¹⁴⁶ Feed gas with concentrations less than 20 mol% H₂S are not recommended for treatment with the Claus process. When H₂S concentrations are so low, oxidation of the H₂S using special catalysts is preferred.¹⁴⁶

6.2.4 Conclusions & Recommendations for Future Work

In summary, H₂S could be removed from the oils either in its gaseous form using thermal methods or converted into another sulfur species through chemical or biological precipitation or oxidation methods. Use of temperature flashing or another thermal shift to remove gaseous H₂S from the used oils would allow for capture of the H₂S, which could be then converted to sulfur with up to 96% recovery using the Claus process. The oils would then be easily regenerated and available for re-use. Another option is chemical precipitation using metal salts, which would precipitate metal sulfides. Chemical and biological oxidation are also options, but pose more complex challenges as they may oxidize the oils themselves.

7. CONCLUSIONS

Conventional soybean oil and high-oleic soybean oil, along with other seed oils, offer potential for use as natural gas sweetening agents to sorb gaseous hydrogen sulfide (H_2S).

Molecular modeling using the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to develop a H_2S removal method using high-oleic soybean oil. A bi-phasic solvent system consisting of methane (representative of natural gas) and conventional soybean oil and high-oleic soybean oil was set up by first developing three-dimensional structures of the fatty acids that comprise soybean oils as well as the gas molecules. The lowest energy conformations were found using computational methods. A bi-phasic system was set-up with fatty acid ratios in the liquid phase to represent the soybean oils and methane as the gas phase representing natural gas. The partition coefficient of H_2S in both oils and methane was calculated for temperatures from 10 – 100 °C. This predictive method found H_2S in soybean oil had a slightly lower (more favorable) partition coefficient than high-oleic soybean oil, and there was no significant difference in partition coefficient value above 40 °C. An *in silico* study of different fatty acid ratios found that the partition coefficient decreased as the concentration of unsaturated fatty acids increased, indicating that unsaturated bonds in oleic, linoleic, and α -linolenic fatty acids contribute to the oils' predicted ability to sorb H_2S . Predicted partition coefficient values ranged from 0.00022 – 0.00050. Additional *in silico* studies were used to examine the difference in H_2S partitioning if nitrogen was used as the carrier gas instead of methane. These studies found that H_2S partitioning followed the same trend whether nitrogen or methane was used, and allowed for H_2S in nitrogen gas to be used experimentally as a safer alternative to methane.

Physical experiments were carried out to attempt to validate the model and demonstrate that soybean oils are capable of removing H_2S gas. Equilibrium absorption experiments carried out in headspace bottles at ambient temperatures using residence times ranging from 0 – 60 minutes found that the concentration of H_2S in the gas phase was decreased by 90% in less than five minutes of mixing and residence time. These studies also demonstrated that residence times beyond 15 minutes did not significantly increase the H_2S removal from the gas phase when using a 2:1 gas to oil ratio (with feed gas of 40ppm H_2S in nitrogen). These experimental partitioning experiments

found partition coefficient values of 0.1 for high-oleic soybean oil and 0.08 for soybean oil at 25 °C. This confirmed the model prediction that H₂S partitioning would be more favorable in soybean oil than high-oleic soybean oil, although the results are not necessarily statistically significant. Additional physical experiments carried out at ambient laboratory conditions were used to collect equilibrium isotherm data and construct isotherms for soybean oil, high-oleic soybean oil, water, and hexane. The data was fitted to Langmuir isotherm models and confirmed the results of the theoretical and experimental partitioning studies and found that soybean oil has a higher capacity for sorbing H₂S than high-oleic soybean oil does.

A techno-economic analysis was conducted to determine the feasibility of using seed oils (such as conventional soybean, high-oleic soybean, canola and sunflower) as H₂S scrubbing agents for treating sour natural gas. Using the experimentally determined partition coefficients for H₂S in soybean oil and high-oleic soybean oil, a feed gas flow rate equivalent to that used in industrially popular amine gas treating, and desired H₂S removal of 99.9%, a graphical method and the Kremser method were used to determine the necessary number of equilibrium stages and necessary column dimensions. It was determined that a 2.5 m diameter trayed column with a height of 8 meters and 14 trays could treat sour gas ranging from 40 – 400 ppm, removing > 99.9% of the H₂S within 14 stages using soybean oil or high-oleic soybean oil as the bio-solvent. The cost of the column and other capital costs were estimated. Revenues would include the sale of sweet gas and of elemental sulfur recovered from the process; a relationship showing revenues as a function of H₂S was developed. A more sour gas will lead to less purified gas but more revenue through sale of sulfur. The cost of treating a unit of natural gas using amine gas sweetening was used to set a limit on the price of treating a unit of gas using this method, and given all other costs and revenues, the need for solvent regeneration and recycle was determined. 98% of the soybean oil bio-solvent would need to be re-used and recycled in order for this process to be profitable, and a plant of this 20-year design could expect to begin to see profits in year 12 of operation. A more realistic solvent regenerative power could be allowable if other operating costs or capital costs were reduced.

7.1 Future Work

7.1.1 Temperature Effects

As addressed in Section 6.1, temperature effects and type of seed oil used are of interest for future study. Temperature effects from 25 – 50 °C may be able to foster better partitioning and removal of H₂S by seed oils. Predictive models and preliminary results show that partition coefficients for H₂S in soybean, high-oleic soybean, canola and sunflower oils increase slightly up to 40 – 50 °C and investigating if experiments observe the same effects would allow for determination of an optimal temperature for the process. Additionally, it has been demonstrated that increasing concentrations of unsaturated fatty acids allow for higher capacity of seed oils to sorb H₂S. Canola and sunflower oils both have higher amounts of oleic, linoleic, and α -linolenic acids than soybean oil and high-oleic soybean oil and based on preliminary *in silico* studies may act as better removal agents for treating sour natural gas. However, canola and sunflower oil also have very different cost and availability than soybean oils, which also needs to be considered.

7.1.2 Determination of the Mechanism of Bio-Oils Sorbing H₂S

Definitively determining the mechanism by which the soybean oils sorb H₂S may be necessary to indicate the best path forward for regeneration of the bio-oils and removal of the H₂S from the bio-oils. Although in the course of experiments thus far there was no observable indication that a chemical reaction occurred between the gas and the soybean oil, techniques such as NMR and/or FTIR spectroscopy may be useful in examining the H₂S-saturated oils to identify if a reaction has occurred and any new species have formed. This knowledge would assist in charting a course forward for removing the H₂S from the bio-oils and help eliminate some trial-and-error oil regeneration efforts.

7.1.3 Bio-Oil Solvent Regeneration

Removal of H₂S and regeneration of the bio-oil solvents is critical to the viability of this process and remains unanswered. A number of methods for either stripping off H₂S gas or converting dissolved H₂S to sulfur species from solvents or solutions are outlined in Section 6.2. If gaseous H₂S can be stripped off the bio-oil solvents (for example, through pressurization and/or

temperature crashing), the gaseous H_2S can be captured and converted to elemental sulfur (to be sold as a chemical building block) using the well-established Claus process (as outlined in Section 6.2.3). The most likely solution will be addition of a chemical precipitant or oxidizing agent to convert H_2S to sulfur or sulfate. Methods for doing so are extensively outlined in *Section 6.2.2*. Oxidizing agents, while highly effective, are likely to also oxidize the oils themselves: an unfavorable outcome. Addition of precipitating agents may be the most favorable outcome. Addition of a salt such as iron chloride may be able to precipitate the H_2S as iron sulfide, and the iron sulfide and resulting hydrochloric acid could be relatively easily separated from the oils and the oils then recycled. The economic impact of using an expensive regeneration/precipitation agent like iron chloride as well as safety hazards would need to be considered.

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VITA

Emma C. Brace is originally from Topeka, Kansas. As a first-generation college student, she earned her bachelor's degree in Biological Systems Engineering with a minor in Chemistry from Kansas State University in May 2014 and earned a master's degree in Agricultural & Biological Engineering from Purdue University in August 2016. During her time at Purdue, Emma has been an active participant in the ABE Graduate Student Association, serving as secretary, webmaster, and symposium marketing chair (twice). She served on the Leadership Team for the Women in Engineering Program's mentoring programs for graduate students and strives to make diversity and inclusion of women and minorities in STEM a priority in her life and her career. Emma received the 2019 Emily M. Wadsworth Graduate Mentoring Award from the Women in Engineering Program and the 2019 Outstanding Graduate Student Service Award in ABE from the College of Engineering, as well as the Purdue Doctoral Fellowship and a Bilsland Dissertation Fellowship. She has been the recipient of many travel grants, including from the Women in Engineering Program, Purdue Graduate Student Government, Purdue College of Engineering, Society for Industrial Microbiology, and Conference on Countercurrent Chromatography. She has presented her work at several conferences and has published three peer-reviewed publications. Emma enjoys teaching and mentoring students and is pursuing a career in academia.

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