

THESIS

NATURAL GAS CONDITIONING WITH A HEAVY HYDROCARBON PERMEABLE POLYMER MEMBRANE

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## ABSTRACT

### NATURAL GAS CONDITIONING WITH A HEAVY HYDROCARBON PERMEABLE POLYMER MEMBRANE

Compressor engines located at shale gas sites run on untreated natural gas collected directly from the well since this is the most feasible energy source in many remote locations. This untreated natural gas can contain high levels of C3+ hydrocarbons which reduce the methane number of the fuel, thereby reducing the maximum load output of the engine. Here membrane separation technology is being investigated to remove heavy hydrocarbons from the natural gas stream used to run these compressor engines. A rubbery polymer membrane is being used in a plate and frame type configuration which separates gases based on solubility, with more soluble gases like heptane, hexane, pentane, etc being able to pass through the membrane material but less soluble gases like methane and ethane unable to flow through. By removing heavy hydrocarbons and increasing methane number these engines are able to run closer to their designed full load output. The scope of this project was to setup a small scale bench test system where natural gas containing high concentrations of heavy hydrocarbons was passed through the membrane and composition data was collected on both permeate and retentate streams leaving the membrane module. From this data, separation efficiencies of each gas species were found to characterize the separation effectiveness and make predictions of real world applications.

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## TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iii
LIST OF FIGURES.....	vii
LIST OF TABLES.....	vi
LIST OF SYMBOLS .....	ix
1. Introduction .....	1
1.1. Background and Motivation .....	1
1.1.1. Natural Gas Composition .....	5
1.1.2. Methane Number and Knock.....	5
1.1.3. Targeted Natural Gas Compositions .....	6
1.1.4. Current Methods of Natural Gas Separation .....	8
1.1.5. Membrane Separation .....	10
1.1.6. Membrane Modules .....	16
1.1.7. Compressor Engine Integration .....	19
2. Methods and Materials.....	23
2.1. Membrane Module Tested .....	23
2.2. Membrane Performance Scale Evaluation System .....	25
2.2.1. System Hardware.....	28
2.2.2. Gas Blending.....	34
2.3. Test Procedure .....	36
2.3.1. System Calibration .....	37
2.3.1.1. Gas Temperature Control and Measurement.....	37
2.3.1.2. Pressure .....	37
2.3.1.3. Mass and Volumetric Flow .....	38
2.3.1.4. Gas Chromatograph .....	38
2.4. Data Processing.....	39
2.4.1. Calculating Methane Number.....	39
2.4.2. Calculating Percent Removal of Particular Species.....	40
2.4.3. Rotameter Calibration Factor .....	41
2.4.4. Brake Horsepower Required for Compression .....	42
3. Performance Characteristics of the Membrane Separator.....	43
3.1. Gas Compositions.....	43

3.2.	Independent Variable Changes.....	45
3.2.1.	Pressure Difference Across Membrane .....	45
3.2.2.	System Operating Pressure.....	47
3.2.3.	Feed Mass Flow Rate .....	48
3.2.4.	Temperature .....	49
3.2.5.	Feed Gas Composition .....	50
3.3.	Membrane Performance Tradeoff.....	54
3.4.	Single Component Testing .....	55
3.4.1.	Selectivity .....	56
3.5.	Comparison of Single Component and Mixed Gas Selectivities .....	57
3.6.	Engine Derate Improvement.....	59
3.7.	Well Site Compressor Engine Membrane Integration Case Study.....	61
3.8.	Active Membrane Control.....	70
3.9.	Staged Membrane Configuration .....	72
4.	Conclusion.....	75
4.1.	Heavy Hydrocarbon Separation .....	75
4.2.	Selectivity of Individual Species .....	76
4.3.	Integration into Compressor Engine System .....	76
	References .....	78
	APPENDIX I .....	81

## LIST OF TABLES

Table 1: Properties of Hydrocarbons at STP [1] .....	5
Table 2: Assumed Bakken natural gas composition .....	7
Table 3: Suppliers of membrane natural gas separation modules and their construction [10] .....	18
Table 4: Gas Chromatograph Calibration Data .....	38
Table 5: Gas Compositions.....	44
Table 6: Comparing the % removal for different compositions under the same operating conditions. Feed mass flow rate of 100 SCFH and 50% retentate flow .....	53
Table 7: Compressor Stages and Pressures .....	62
Table 8: Sample data showing increase or decrease of composition mol% of each species in the retentate and permeate stream. Test conditions: Bakken blend, feed pressure = 60psi, permeate pressure = 39.8psi, temperature = room, % retentate flow = 41% .....	84
Table 9: Composition data from section 3.2.2 – System operating pressure, showing increase or decrease of the retentate stream when increasing permeate and retentate pressure at the same rate using the same pressure difference across the membrane. ....	84
Table 10: Testing Data .....	86

## LIST OF FIGURES

Figure 1: Cummins KTA19GC Natural Gas Compressor Engine at Well Site (Photo provided by Cummins, Inc) .....	2
Figure 2: A schematic of an absorber-stripper for amine CO <sub>2</sub> removal [10] .....	10
Figure 3: Membrane Stream Terminology [11] .....	11
Figure 4: Comparison of permeability of glassy and rubbery membranes [15] .....	16
Figure 5: Hollow fiber membrane module [16] .....	17
Figure 6: Spiral wound membrane module construction [7].....	18
Figure 7: Hollow fiber Loeb-Sourirajan vs composite membrane structure [10] .....	19
Figure 8: Fuel supply to wellsite compressor engine and proposed membrane separation system integration .....	21
Figure 9: HZG membrane module flow configuration .....	23
Figure 10: HZG membrane module and flow path .....	24
Figure 11: Plate and Frame Membrane Module.....	25
Figure 12: Benchtop test system schematic .....	27
Figure 13: (Left) Gas Bottles and Pressure Regulator, (Right) Heat Exchanger and Water Recirculation System.....	29
Figure 14: Alicat Scientific MC-Series Mass Flow Controller .....	30
Figure 15: National Instruments cRio for logging temperature and pressure.....	31
Figure 16: From left to right: Backpressure regulator, analog pressure gauge, pressure transducer, thermocouple, bleed valve .....	31
Figure 17: (Left) Brooks rotameters (Right) Methane detector, retentate, and permeate ports on membrane module .....	33
Figure 18: Mixed gas bottle composition compared to Bakken gas composition.....	36
Figure 19: Cummins Gas Properties Calculation Tool Example .....	40
Figure 20: Effect of pressure difference on methane number increase and % retentate flow.....	46
Figure 21: Effect of absolute pressure on separation with constant pressure difference .....	47
Figure 22: Effect of Feed Mass Flow Rate on Output Feeds and Methane Number Increase .....	49
Figure 23: MN increase with varying Feed Temperatures.....	50
Figure 24: Gas Composition effect on differential pressure required for MN increase .....	52
Figure 25: Tradeoff between flow and MN improvement.....	55
Figure 26: Selectivity of species mixed individually at Bakken concentrations.....	57
Figure 27: Selectivities of individually mixed gas compared to Bakken gas with all constituents .....	58
Figure 28: Engine derate curve and improvement for the Bakken gas composition .....	59
Figure 29: Membrane Configuration Options.....	64
Figure 30: Flow Paths with 50% and 25% Retentate Flow.....	65
Figure 31: Flow to membrane compared to total flow through compressor engine at full load.....	67
Figure 32: Tradeoff between recompression HP and HP gained by decreasing engine derate .....	69
Figure 33: Active membrane control .....	71
Figure 34: Power output of engine accounting for HP required for recompression.....	72
Figure 35: 75% Retentate Flow Staged Membrane Configuration .....	73
Figure 36: % Removal of ethane, propane, n-butane, and iso-butane in the Bakken blend at various pressure differentials across the membrane.....	81
Figure 37: Cummins engine derate curve showing MN of gases tested and the associated derate and maximum horsepower when using those gases before treatment.....	81

Figure 38: MN increase achieved using a pressure differential to maintain 25% and 50% retentate flow at 100 SCFH and 200 SCFH feed mass flow rates for the Lago, Bakken, and pipeline blend ..... 82

Figure 39: Membrane module testing setup ..... 82

Figure 40: Schematic of membrane module testing setup..... 83

Figure 41: Simplified schematic of membrane module testing setup showing critical measurement devices ..... 83

Figure 42: Showing the pressure differential required to maintain a 50% retentate flow with different compositions. Gases with more heavy hydrocarbons and a lower MN require less pressure difference because the permeance of the gas is lower ..... 85

## LIST OF SYMBOLS

MN - Methane Number  
STP - Standard Temperature and Pressure  
CSU - Colorado State University  
C1 – Methane (CH<sub>4</sub>)  
C2 – Ethane (C<sub>2</sub>H<sub>6</sub>)  
C3- Propane (C<sub>3</sub>H<sub>8</sub>)  
C4+ - hydrocarbons with more than 4 carbon atoms (iso-Butane C<sub>4</sub>H<sub>10</sub>, n-Butane C<sub>4</sub>H<sub>10</sub>, iso-Pentane C<sub>5</sub>H<sub>12</sub>, n-Pentane C<sub>5</sub>H<sub>12</sub>, Hexane C<sub>6</sub>H<sub>14</sub>, Heptane C<sub>7</sub>H<sub>16</sub>)  
CO<sub>2</sub> – Carbon Dioxide  
N<sub>2</sub> - Diatomic Nitrogen  
POMS - poly(octylmethyl siloxane)  
SCFH – Standard cubic feet per hour  
SLPM – standard liters per minute  
MMSCFD – Million standard cubic feet per day  
HZG - Helmholtz-Zentrum Geesthacht (membrane manufacturer)  
BTU – British Thermal Unit  
LHV – Lower Heating Value  
NO<sub>x</sub> – Oxides of Nitrogen  
CO- Carbon Monoxide  
VOC- Volatile Organic Compounds  
NG- Natural Gas  
 $\dot{m}_i$  - Mass Flow Rate of an individual Species  
R - Universal Gas Constant [kJ/kgK]  
u – Permeability  
j – Flux through Membrane  
y – Mole fraction  
P – Pressure  
 $\alpha$  - Selectivity  
S – Solubility  
D - Diffusivity

## **1. Introduction**

### **1.1. Background and Motivation**

Natural gas is a large and rapidly growing domestic energy source. The United States is the largest producer of natural gas in the world. Gas wells are located throughout the country, with many of them in remote locations far from natural gas pipelines. These remote wellheads rely on compressor engines to transport the gas from the well to a pipeline or processing facility. Because of their remote locations and the cost/complexity of delivering fuel to these sites the compressor engines operate on natural gas they are compressing extracted directly from the well. The composition of natural gas straight from the well is not always ideal, most of the time containing heavy hydrocarbons and/or diluents that cause problems with engine performance. The purpose of this project is to design a system to treat raw well gas with a membrane separation system to improve performance, emission levels, and maintenance intervals of these compressor engines.

Natural gas is mostly comprised of methane (Ideally at least 70%). Other gases such as carbon dioxide, nitrogen, hydrogen sulfide, ethane, propane, and C4+ hydrocarbons change the combustion characteristics of the gas when used as a fuel in reciprocating engines. It is therefore important to adjust the concentration of each gas to keep a compressor engine running properly [1]. The most important characteristics of fuel gas is the chemical energy in the gas, or lower heating value (measured in BTU's per cubic foot) and the knock resistance (measured in methane number, a similar measurement system to Octane number used in liquid fuels).



Figure 1: Cummins KTA19GC Natural Gas Compressor Engine at Well Site (Photo provided by Cummins, Inc)

Diluents like CO<sub>2</sub> and N<sub>2</sub> reduce the energy content of fuels and can decrease the maximum power and efficiency of an engine. Methane produced at landfills or digester gas (digas) commonly has high levels of CO<sub>2</sub> and contaminants like siloxanes and hydrogen sulfide that make it difficult to be used as a fuel in normal reciprocating engines. The fuel systems for landfill and digas engines must be redesigned to accommodate larger volumetric fuel flow rates to achieve rated engine power. The methane number of these fuels is usually high so compression ratio can be increased, but energy content of the gas is still low. In many cases the energy content of the gas is too low to use as fuel and the gas is either flared or vented to the atmosphere, both of which do not utilize energy in the gas and contribute to greenhouse gas pollution.

Often, shale gas contains high levels of heavy hydrocarbons that decrease the knock resistance (methane number) to a point where the gas could damage the compressor engine if not tuned properly. This low knock resistance is associated with high energy content of the fuel on a volumetric basis. More specifically, low knock resistance is directly related to lower auto ignition temperatures, characteristic of larger hydrocarbons. As the number of carbon and hydrogen atoms in each gas molecule increases the volumetric energy content increases while the self ignition temperature decreases. Methane (CH<sub>4</sub>), known as C<sub>1</sub> because of its 1 carbon atom has the lowest volumetric energy content of any of the hydrocarbons found in natural gas and also the highest methane number. While it has the lowest energy per molecule (volumetric) it has the highest energy content on a mass basis. High levels of ethane (C<sub>2</sub>), propane (C<sub>3</sub>), and C<sub>4</sub>+ hydrocarbons can decrease the methane number to the minimum methane number for the engine design and could potentially damage the engine.

There are a few methods to address poor fuel quality in compressor engines. One through engine management, such as retarding engine timing, derate engine power, or both when a low methane number fuel is used. Retarding ignition timing generally leads to decreased efficiency of the engine. Derating the maximum engine power reduces the amount of natural gas that the engine-compressor system can deliver. The non-ideal fuel can increase maintenance costs if engine management techniques are not sufficient to prevent knocking. Lowering compression ratios can also be used to utilize low methane number fuel. However, this has a negative impact on efficiency and cannot be adjusted in real time. As emission rules and regulations become more strictly enforced and small profit margins demand higher efficiency these options become less attractive.

The most commonly regulated exhaust emissions from natural gas engines are oxides of nitrogen (NO<sub>x</sub>), carbon monoxide (CO), formaldehyde (CH<sub>2</sub>O) and volatile organic compounds (VOC's). Formation of NO<sub>x</sub> is primarily due to the reaction of oxygen and nitrogen from the intake air at combustion temperatures. It exponentially related to in-cylinder temperatures. CO, CH<sub>2</sub>O, and VOC's are indications

of incomplete combustion of the fuel [2]. It is difficult to make generalizations about the effect of methane number on engine emissions because methane number is only an indication of a fuel's resistance to knock, and it does not fully characterize the fuel. For example, a blend of 75% methane and 25% ethane has the same methane number as a blend of 97.5% methane and 2.5% heptane (compositions are mol%'s, MN of approximately 67). Even though these mixtures have the same methane number, they behave differently in an engine. There are also different types of engines (lean burn, rich burn (stoichiometric), 2 stroke, 4 stroke, etc) and emission reduction devices (exhaust after treatment, exhaust gas recirculation, etc) so it is difficult to make general statements about the effect of fuel composition on emissions. In a low BMEP, lean burn, two-stroke GMVH-6 integral compressor engine, it was found that increasing the ethane content of natural gas had the effect of increasing NO<sub>x</sub> emissions of up to 175% at rated RPM, 100% torque with a 17% ethane content above baseline [3]. In this case it was found that a higher BTU fuel gas will increase NO<sub>x</sub> emissions, but this was due to the decreased equivalence ratio because the stoichiometric air/fuel ratio changed when ethane was added. When the air/fuel ratio was properly leaned with the addition of ethane, NO<sub>x</sub> emissions decreased to a normal level. In a report by Crawford, smaller (8.1-8.9L, 275-320hp) lean burn engines were tested. It was found that using low MN fuels with high levels of heavy hydrocarbons lead to the increased emissions of non-methane hydrocarbons (NMHC) and NO<sub>x</sub> [4].

One approach to addressing the variation in fuel quality is gas conditioning before the fuel gets to the engine. By various conditioning methods the quality of well gas can be increased to a point where it can be used without the need to adjust timing or derate the engine. This reduces the need for dynamic engine timing or load control. This can be done in various ways depending on the composition of the well gas, size of compressor engine, and emissions and power requirements. These methods involve gas to remove the unwanted constituents in natural gas. In the case of shale gas this is usually heavy

hydrocarbons, and in landfill or digas it is diluents. A method of using gas permeable membranes to separate particular gases out of fuel gas is the focus of this work.

### 1.1.1. Natural Gas Composition

Hydrocarbons with greater numbers of carbon and hydrogen molecules are commonly referred to as “Complex” or “Heavy” hydrocarbons. These heavy hydrocarbons have a larger lower heating value (BTU/ft<sup>3</sup>) than the lighter hydrocarbons. The lower heating value (LHV) is defined as the amount of energy (BTU/ft<sup>3</sup>) or (kJ/Mol) that can be converted to thermal energy, or heat, from the complete, ideal combustion of the fuel with the chemically correct amount of air, reactants and products at standard temperature 60 °F (15.6 °C), and the water in the combustion products in the vapor phase [1]. A list of hydrocarbons and their LHVs can be seen in Table 1.

Table 1: Properties of Hydrocarbons at STP [1]

Hydrocarbon	Symbol	LHV (BTU/ft <sup>3</sup> )	LHV (MJ/m <sup>3</sup> )	LHV (MJ/kg)	MN	Auto Ignition Temp (°C)
Hydrogen	H <sub>2</sub>	273	10.2	119.9	0.0	500
Methane	CH <sub>4</sub>	909	33.9	50.0	100.0	580
Ethane	C <sub>2</sub> H <sub>6</sub>	1619	60.3	47.5	43.7	515
Propane	C <sub>3</sub> H <sub>8</sub>	2315	86.3	46.3	34.2	455
iso-Butane	C <sub>4</sub> H <sub>10</sub>	3000	111.8	45.6	9.6	462
n-Butane	C <sub>4</sub> H <sub>10</sub>	3011	112.2	45.7	9.6	405
iso-Pentane	C <sub>5</sub> H <sub>12</sub>	3699	137.8	45.3	9.5	420
n-Pentane	C <sub>5</sub> H <sub>12</sub>	3704	138.0	45.3	9.5	260
Hexane	C <sub>6</sub> H <sub>14</sub>	4404	164.1	45.1	9.5	225
Heptane	C <sub>7</sub> H <sub>16</sub>	5100	190.0	44.9	9.5	215
Octane	C <sub>8</sub> H <sub>18</sub>	5796	216.0	44.8	9.5	220

### 1.1.2. Methane Number and Knock

Methane number of a gas is the indication of knock resistance in spark ignited engines. It is the ability of a fuel to be compressed without combusting due to a temperature increase as pressure is

increased. The scale is based off methane which has good resistance to knock and hydrogen, which has a low knock resistance. These gases have methane numbers of 100 and 0 respectively. A blend of 75% methane and 25% hydrogen would have a methane number of 75 [1]. Engines are designed for a specific methane number range. Cummins specifies a methane number of no less than 52 in their industrial natural gas engines. [5] Establishing the minimum methane number involves choosing a compression ratio, ignition timing, and air fuel ratio so that knock does not occur for fuels with methane numbers above the minimum. It is important to maintain the correct methane number in a fuel to provide efficiency and reliability.

### **1.1.3. Targeted Natural Gas Compositions**

By defining a specific gas composition, we can begin to examine different membranes to effectively treat well gas. The Bakken shale formation is a 14,700 sq. mile formation located in North Dakota and Montana. It is the largest crude oil accumulation in the United States. It was discovered in the 1950's but did not become a commercially viable source until recently with advancements in oil and natural gas technology [6]. A typical composition of well gas from the Bakken formation is presented in Table 2.

Important gases to note in this composition are methane (C1), ethane (C2), propane (C3), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), and water (H<sub>2</sub>O). Methane (heating value of 909 BTU/ft<sup>3</sup>) is the main source of energy and the most desirable gas in shale and natural gas. Ethane is the next most common gas, with a heating value of 1619 BTU/ft<sup>3</sup>. A blend of methane and ethane is required to produce a gas with a heating value of around 1050 BTU/ft<sup>3</sup>, which is the standard for pipeline quality natural gas [7]. Ethane is difficult to remove from methane because they have a similar molecular size and solubility, both of which highly influence separation factor when using membranes for separation. The next most prominent heavy hydrocarbon is propane with a mol% of about 11.

Table 2: Assumed Bakken natural gas composition

Bakken Composition		
Component	Symbol	mol%
Water	H <sub>2</sub> O	0.02
Nitrogen	N <sub>2</sub>	5.21
Carbon Dioxide	CO <sub>2</sub>	0.57
Hydrogen Sulfide	H <sub>2</sub> S	0.01
Methane	CH <sub>4</sub>	57.67
Ethane	C <sub>2</sub> H <sub>6</sub>	19.94
Propane	C <sub>3</sub> H <sub>8</sub>	11.33
iso-Butane	C <sub>4</sub> H <sub>10</sub>	0.97
n-Butane	C <sub>4</sub> H <sub>10</sub>	2.83
iso-Pentane	C <sub>5</sub> H <sub>12</sub>	0.38
n-Pentane	C <sub>5</sub> H <sub>12</sub>	0.55
Hexane	C <sub>6</sub> H <sub>14</sub>	0.22
Heptane	C <sub>7</sub> H <sub>16</sub>	0.09
Octane	C <sub>8</sub> H <sub>18</sub>	0.04
C9-C15 Hydrocarbons		0.02

The heavier, more complex hydrocarbons such as butane and pentane (C4-C9) make up only a small fraction of the total composition of the gas, but are still desirable to remove because of their strong impact on methane number. A small amount of these heavier hydrocarbons can have a large impact on methane number even though their mole fraction is very small. The effect of heavier hydrocarbons on methane number is not linear. The higher heavy hydrocarbons have a much greater effect on MN than the lighter hydrocarbons. Diluents such as N<sub>2</sub> and CO<sub>2</sub> are undesirable due to lowering the energy content of the gas as discussed in the previous section. It is usually desirable to have no more than 8% diluents in fuel gas for spark ignited engines [8]. In the case of this Bakken gas composition, the diluents only make up about 6% of the total composition, but lowering this number by removing diluents is still beneficial to increase the fuel energy content.

Hydrogen sulfide is the byproduct of breakdown of organic matter. It is what gives some unprocessed natural gas a “rotten egg” smell. Hydrogen sulfide is an acidic gas and can lead to corrosion

on engine and pipeline components; it is critical to remove hydrogen sulfide from the gas as soon as possible to decrease maintenance and unscheduled downtime. Hydrogen sulfide is also poisonous, and extreme caution has to be taken when working around it. Corrosive or acid gases are commonly referred to as “sour” gases, and removing those acidic components is referred to as “sweetening” the gas [7].

#### **1.1.4. Current Methods of Natural Gas Separation**

Currently, there are a few methods besides membrane separation to treat shale gas. These methods have their advantages and disadvantages and will be discussed in this section. There are different methods to separate diluents and heavy hydrocarbons to both increase and decrease the energy content and methane number of a fuel.

The first method of reducing heavy hydrocarbons and decreasing methane number is by cooling to gas to a point below the saturation temperature of the undesirable gases. This method reduces the amount of C4+ hydrocarbons because of their higher saturation temperature compared to methane. While the C4+ hydrocarbons condense to a liquid, which can be removed from the gas stream, methane (C1) stays in gaseous form. It is more challenging to remove propane (C2) and ethane (C3) because their saturation temperatures are lower than the more complex hydrocarbons. Besides the difficulty to remove C2 and C3 this method also has problems with hydrates forming in the fuel line. To avoid hydrate issues, a methane injection system has to be added, which adds to the complexity and cost of the system. Cooling can be accomplished by either mechanical refrigeration or by a Joule–Thomson pressure reduction. Another issue with this method is the storage and handling of liquid formations created by the process [7].

The next method is pressure swing absorption. This method works for both separation of heavy hydrocarbons and diluents. In this process an absorptive material is used to trap the desired gas and then recover the absorbed gas later. This is done in a multistep process. First the chamber is pressurized

with feed gas. Under high pressures the target gas is attracted to the surface of the adsorptive material. The feed gas is then evacuated from the chamber, with the absorbed gas still attached to the material. When the pressure of the chamber is lowered the target gas is then released or desorbed from the material, resulting in its separation from the rest of the gas. These systems can have multiple parallel stages so that one chamber can be at high pressure and one at low pressure to create a continuous process of gas treatment. Advantages to this system are that it can separate a large amount of gas and the process is very selective in what gases are targeted. Disadvantages to pressure swing absorption systems are that they are very energy intensive and require complex control systems. Consequently, they are not ideal for remote locations where maintenance could be difficult [9].

The most common method to remove CO<sub>2</sub> from natural gas is amine scrubbing. This process is an absorber-stripper treatment which uses amines as a sorbent for CO<sub>2</sub>. Two towers are used in this process. In the first tower high pressure feed gas is passed in counter flow against the absorbent liquid. As the liquid falls to the bottom of the tower, it becomes saturated with CO<sub>2</sub>. The saturated liquid is then removed from the bottom of the high pressure tower, heated, and sent to the low pressure tower. The decrease in pressure and increase in temperature liberates the absorbed CO<sub>2</sub> from the stripping liquid. The low pressure CO<sub>2</sub> is then collected from the top of the low pressure tank and removed from the system. The stripping liquid is then cool as it is pumped from the bottom of the low pressure tower to the top of the high pressure tower. The feed gas enters at the bottom of the high pressure tower and exits at the top of the high pressure tower with much of the CO<sub>2</sub> removed. Figure 2 illustrates this process.

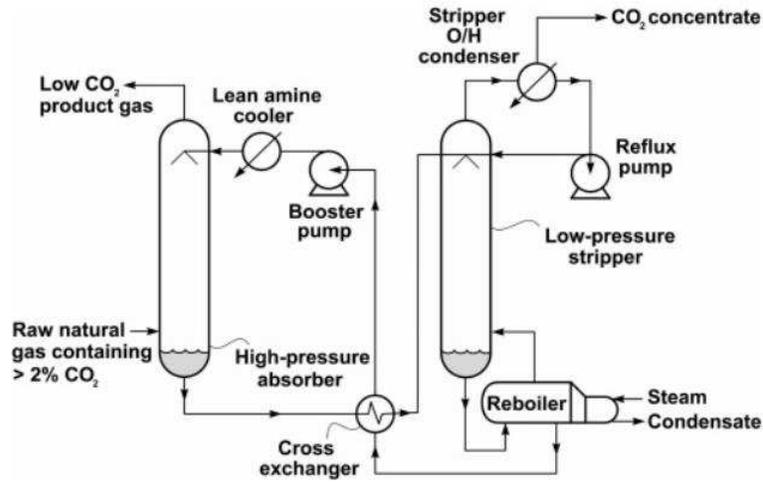


Figure 2: A schematic of an absorber-stripper for amine CO<sub>2</sub> removal [10]

The size of these systems is proportional to the mass of CO<sub>2</sub> that is being removed. These systems work very well in situations where the feed gas contains only a small amount of CO<sub>2</sub>. The disadvantages to this type of separation is the size and complexity of the systems. Constant monitoring of the system is required, as the degradation of amines leads to corrosive mixtures which can do significant damage to the system if undetected [10].

### 1.1.5. Membrane Separation

Membranes are commonly used for liquid separation. Water purification, such as reverse osmosis, is one area where membranes have been utilized to separate liquids. Gas separation by membrane works on some of the same principals as liquid separation, where certain species can diffuse through the material, but others cannot.

A membrane is a selective barrier between two different concentrations of gases. Usually these gases are at different pressures, but this is not always the case. A membrane allows certain molecules to pass through the barrier but not others. The gases that are able to pass through the membrane are called the permeate gases. The side of the membrane which these gases travel to is commonly referred

to as the permeate side and the other side is the feed side. Feed gas is passed along the surface of the membrane where some species of gas permeate through the membrane and others do not. The gas that remains on the feed side of the membrane and does not permeate through the barrier is called the retentate. The feed stream enters the membrane system and a permeate and retentate stream exit as seen in Figure 3.

In some cases the permeate stream is the desired gas, while in other cases the retentate is desired. For example, a CO<sub>2</sub> permeable membrane can be used to remove CO<sub>2</sub> from natural gas. In this case, the retentate, natural gas with CO<sub>2</sub> removed is the desirable stream. The CO<sub>2</sub> permeate stream is discarded. In the separation of nitrogen from air with a nitrogen permeable membrane, the nitrogen is the desired product. In this case the permeate (nitrogen) is desirable and the retentate (air with nitrogen removed) is discarded.<sup>2</sup>

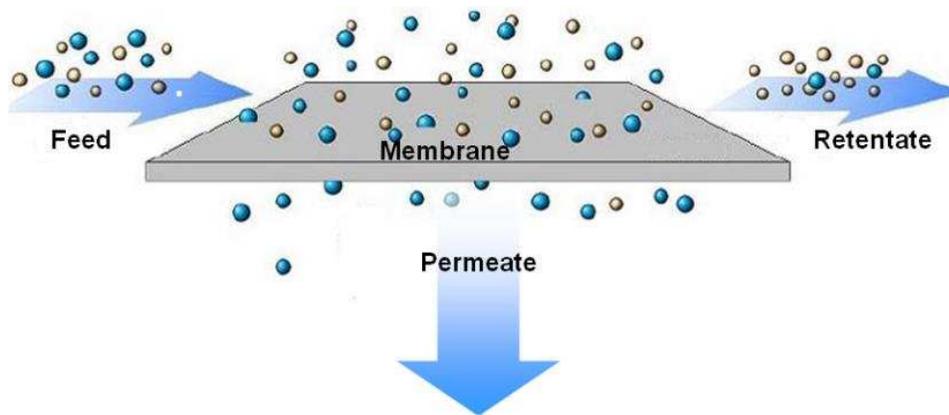


Figure 3: Membrane Stream Terminology [11]

Gas membrane separation works by a process of solution-diffusion. A gas molecule is dissolved into the polymer on the high pressure side, as it would dissolve in a liquid, then diffuses through the membrane to the low pressure side of the membrane, where the gas is desorbed. The driving factor in this process is the partial pressure difference across the membrane. As the partial pressure difference increases, so does the rate of diffusion.

Another factor that effects the rate of diffusion through a membrane is the concentration gradient on the permeate side of the membrane. At the surface of the membrane on the permeate side the concentration of species traveling through the membrane is greater than away from the surface. The concentration gradient is directly proportional to the partial pressure gradient of a certain species. In work by Lin [12], CO<sub>2</sub> is removed from natural gas and air is used to sweep the permeate side of the membrane to reduce the CO<sub>2</sub> buildup at the surface of the membrane. This increases the concentration gradient across the membrane and was shown to improve CO<sub>2</sub> permeation rate by a factor of three.

The gas flux, or rate at which gas permeates a membrane,  $j$  [kg/m<sup>2</sup>s] is defined as:

$$j = u \frac{1}{l} \Delta P = \frac{\dot{m}}{A} \quad (1)$$

where  $u$  is the permeability coefficient [kg·m/m<sup>2</sup>s·kPa],  $l$  is the thickness of the membrane [m],  $\Delta P$  is the partial pressure difference across the membrane [kPa],  $\dot{m}$  is the mass flow rate [kg/s] of the species across the membrane, and  $A$  is the membrane surface area [m<sup>2</sup>] [13].

The permeability of a gas through a membrane  $u$  is defined as:

$$u = D \times S \quad (2)$$

where  $D$  is the gas diffusivity and  $S$  is the gas solubility. The diffusivity of a gas, or how fast each molecule diffuses across the membrane, increases with decreasing gas molecule size. The solubility of a gas, which is proportional to the number of molecules that dissolve in a membrane, increases with gas condensability. In general, with a polymer membrane increasing temperature increases the permeability of a gas but lowers its selectivity, so that the permeability remains relatively constant. [14] This indicates that there is little effect on membrane separation due to temperature changes. This assumes that the operating temperature is not close to the glass transition temperature of the polymer used in the membrane and high enough that hydrocarbon dew point and condensation do not have an effect.

The ability of a membrane to separate one gas from another is called its selectivity or selectivity ratio. The membrane selectivity of gas A over gas B,  $\alpha_{A/B}$  is defined as:

$$\alpha_{A/B} = \frac{u_A}{u_B} = \frac{S_A D_A}{S_B D_B} \quad (3)$$

where  $\frac{S_A}{S_B}$  is the solubility selectivity, determined by the relative solubility of gas A and B, and  $\frac{D_A}{D_B}$  is the diffusivity selectivity, which is determined by the relative molecular size of each gas. [12]

The mass flow of a species  $\dot{m}$  [kg/s] is equal to the molar flow  $\dot{N}$  [kmol/s] multiplied by the molecular weight  $M$  [kg/kmol]

$$\dot{m} = \dot{N}M \quad (4)$$

The molar flow of a species  $\dot{N}_i$  is equal to the mole fraction  $y_i$  multiplied by the total molar flow  $\dot{N}_{tot}$

$$\dot{N}_i = y_i \dot{N}_{tot} \quad (5)$$

Therefore the mass flow of a particular species is equal to the product of the mole fraction  $y_i$ , the total molar flow  $\dot{N}_{tot}$ , and the molecular weight of the species  $M_i$

$$\dot{m}_i = y_i \dot{N}_{tot} M_i \quad (6)$$

Flux is equal to the mass flow divided by the surface area of the membrane

$$j = \frac{\dot{m}}{A} \quad (7)$$

Substituting these into the equation for permeability

$$u_i = \frac{\dot{m}_i l}{A \Delta P_i} = \frac{y_i \dot{N}_{tot} M_i l}{A \Delta P_i} \quad (8)$$

When calculating the selectivity of one gas over methane we assume that the total molar flow rate  $\dot{N}_{tot}$ , the thickness of the membrane  $l$ , and the surface area of the membrane  $A$  are the same for both gases. So these terms cancel and we are left with:

$$\alpha_{i/CH_4} = \frac{u_i}{u_{CH_4}} = \frac{y_i M_i / \Delta P_i}{y_{CH_4} M_{CH_4} / \Delta P_{CH_4}} \quad (9)$$

where  $y_i$  and  $y_{CH_4}$  are the mole fractions of the species and methane in the permeate stream (the gas that passes through the membrane).

The difference in partial pressures can be found by comparing the partial pressure of species in the permeate to the retentate using Daltons law of partial pressures where mole fractions and the total pressures are known.

$$P_i = y_i P_{total} \quad (10)$$

$$\Delta P_i = y_{i,retentate} P_{retentate} - y_{i,permeate} P_{permeate} \quad (11)$$

$$\alpha_{i/CH_4} = \frac{y_{i,permeate} M_i / (y_{i,retentate} P_{retentate} - y_{i,permeate} P_{permeate})}{y_{CH_4,permeate} M_{CH_4} / (y_{CH_4,retentate} P_{retentate} - y_{CH_4,permeate} P_{permeate})} \quad (12)$$

Using the composition for the retentate and permeate streams instead of the feed and permeate streams gives a more accurate result of partial pressure across the membrane because of the sampling techniques used. The composition of the retentate and permeate stream change as the gas flows

through the membrane module and more heavy hydrocarbons are extracted from the feed stream. Molar concentrations of heavy hydrocarbons decrease on the high pressure side as the gas passes through the membrane and increase on the low pressure side. Composition measurements were made at only the inlet and outlets of the membrane. Since composition of the permeate stream was only available at the outlet of the membrane a more accurate partial pressure difference was obtained by comparing this to the retentate stream, rather than the feed stream. The permeate and the retentate composition measurements were taken at the same point along the membrane material (the outlet). Comparing the feed and permeate compositions to obtain partial pressure difference would give a less accurate result because the feed is measured where the gas first comes into contact with the membrane material (inlet) and the permeate is measured where the gas last contacts the membrane material (outlet).

Membranes used in gas separation are made from a polymer material. Polymer membranes fall into two categories, glassy and rubbery. This distinction is made based on whether or not the polymer is above its glass transition temperature in its normal operating conditions. Membrane selectivity works differently depending on if the membrane is glassy or rubbery. Glassy membranes tend to separate gases based on molecular size, letting smaller molecules permeate more easily. This is due to the polymer chains being fixed when the polymer is below the glass transition temperature. Only molecules below a certain size are able to pass in between the polymer chains. In the case of a rubbery membrane the polymer chains are able to move which reduces the effect of molecular size of gas molecules on relative mobility. In this case the solubility term of the permeability is the dominating factor to determine permeability of a particular gas. [10]

Figure 4 classifies gases as “fast” and “slow” gases depending on if the membrane is glassy or rubbery. This references the speed at which gas permeates through the membrane. Fast gases are the first to permeate the membrane, slow gases take more time and driving force. For a CO<sub>2</sub> selective

membrane as described in Lin’s research, CO<sub>2</sub> would be a faster gas than methane. Glassy membranes favor gases with smaller molecular size. Rubbery membranes favor gases with higher solubility in polymers (hexane and propane) over less soluble gases like hydrogen and nitrogen. [5] The solubility of a gas is proportional to its boiling point. Hexane has a high boiling point (155°F) compared to methane (-258°F) and is therefore more soluble because it condenses more easily than methane.

**Glassy Membranes**

<b>Fast Gas</b>		<b>Slow Gas</b>	
Hydrogen	Nitrogen	Ethane	Hexane
H <sub>2</sub> O	CO <sub>2</sub>	Methane	Propane

**Rubbery Membranes**

<b>Fast Gas</b>		<b>Slow Gas</b>	
Hexane	Ethane	Methane	Nitrogen
H <sub>2</sub> O	Propane	CO <sub>2</sub>	Hydrogen

Figure 4: Comparison of permeability of glassy and rubbery membranes [15]

**1.1.6. Membrane Modules**

Currently there are two main type of membrane configurations used in gas separation and conditioning applications. Membranes are produced as hollow fibers and flat sheets packaged as either spiral wound or plate and frame membrane modules. Both types have advantages and disadvantages. For low pressure, low permeability applications like nitrogen separation from air the hollow fiber membrane configuration is generally used because of the large surface area of membrane compared to module size as demonstrated in Figure 5. In applications where contaminants like water, CO<sub>2</sub>and C<sub>4</sub>+ hydrocarbons are present the small feed areas in hollow fiber membranes are prone to plasticizing,

swelling, and losing efficiency. In these situations, a flat sheet membrane with a higher permeance is often better suited.

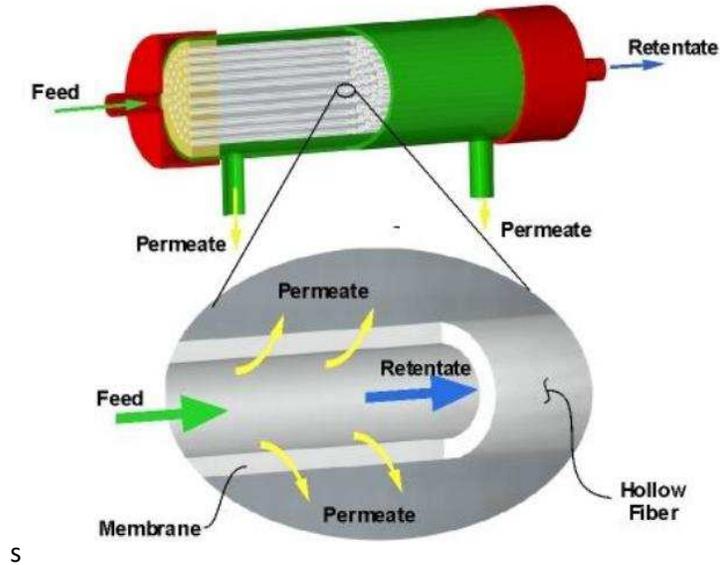


Figure 5: Hollow fiber membrane module [16]

The spiral wound flat sheet membrane configuration seen in Figure 6 performs better at high pressures (30-60 bar) and are less prone to be clogged by contaminants, oil mist, and hydrocarbon vapors. The disadvantage to these type of membrane modules is their higher cost to membrane surface area ratio [10].

While each type of membrane module has certain advantages and disadvantages there is no clear industry standard for the module configuration for natural gas processing. The distinction between spiral wound and hollow fiber membrane modules is dependent on the membrane. A sample of membrane manufactures and the module configuration they produce is presented in Table 3.

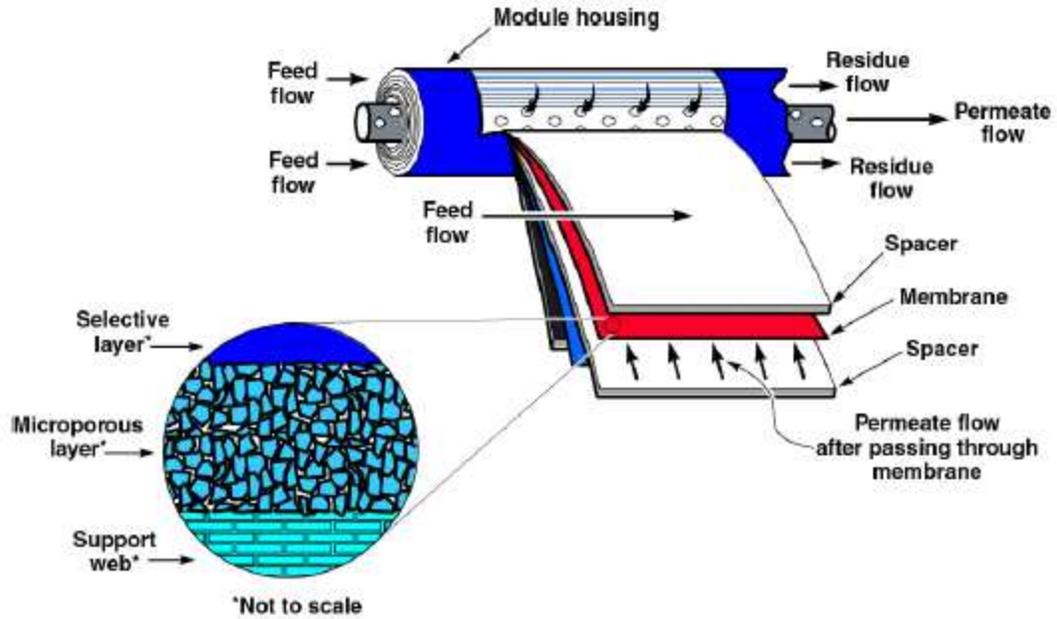


Figure 6: Spiral wound membrane module construction [7]

Table 3: Suppliers of membrane natural gas separation modules and their construction [10]

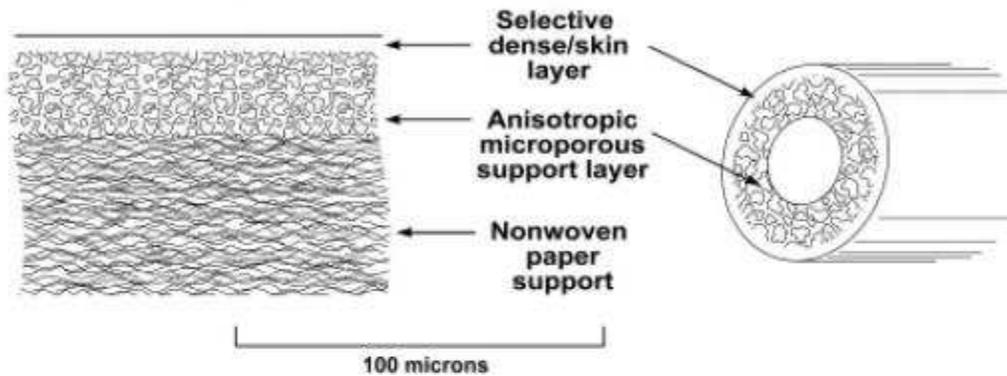
company	principal natural gas separation	membrane module type	membrane material
Medal (Air Liquide)	CO <sub>2</sub>	hollow fiber	polyimide
W.R. Grace	CO <sub>2</sub>	spiral-wound	cellulose acetate
Separex (UOP)	CO <sub>2</sub>	spiral-wound	cellulose acetate
Cynara (Natco)	CO <sub>2</sub>	hollow fiber	cellulose acetate
ABB/MTR	CO <sub>2</sub> , N <sub>2</sub> , C <sub>3+</sub> hydrocarbons	spiral-wound	perfluoro polymers silicone rubber
Permea (Air Products)	Water	hollow fiber	polysulfone

Another distinction between membrane types is Loeb-Sourirajan anisotropic membranes and the newer composite membranes. The Loeb-Sourirajan style membrane uses one material for the active membrane layer and the physical support layer. A composite membrane uses a thin permselective membrane layer (0.2-1.0  $\mu\text{m}$  thick) supported by a porous layer of a different polymer. The difference between the two is presented in Figure 7. The advantage to this is being able to optimize each layer separately to give the desired membrane separation as well as the needed mechanical strength to withstand the differential pressure across the membrane. Since membrane material is usually much

more costly than the polymers used as a support material composite membranes are usually a good choice from a cost perspective.

### a) Anisotropic Loeb-Sourirajan Membranes

Made by a precipitation process. The same polymer is used for the selective layer and the microporous support layer.



### b) Composite Membranes

Made by overcoating a preformed microporous support with a dense selective layer. The selective layer and the microporous support layer are made from different materials.

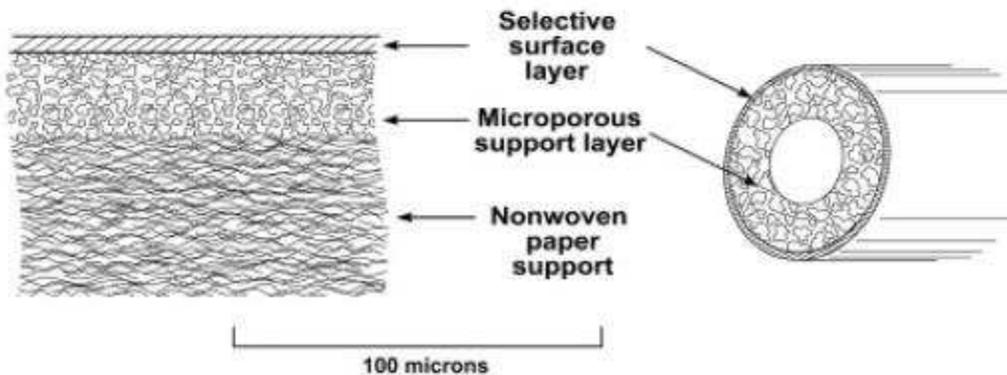


Figure 7: Hollow fiber Loeb-Sourirajan vs composite membrane structure [10]

#### 1.1.7. Compressor Engine Integration

Many shale gas wells are located in remote locations where it would be difficult to supply an engine with fuel in the form of compressed natural gas, gasoline, or diesel. These engines use the shale gas from the well as a fuel. A wellsite compressor engine is supplied with natural gas from the larger supply

of gas that is being compressed. The gas used to run the engine is approximately 5% of the total amount of gas being compressed. A pressure regulator is used to reduce this to a few psi before it enters the engine. Since the pressure required for the engine is quite low it can be supplied from the gas upstream the compressor. This configuration is shown in the upper diagram of Figure 8.

The membrane module takes advantage of the large pressure difference across the compressor for the driving force of membrane separation. The membrane separator schematic (lower diagram) in Figure 8 shows how the membrane can be integrated into the current compressor engine system. The membrane module feed stream is taken from the high pressure side of the compressor. The retentate stream feeds the engine with gas after heavy hydrocarbons are separated into the permeate stream. The permeate stream, containing the undesirable gas is reintroduced into the main gas stream at a lower pressure, upstream of the compressor. By allowing the heavy hydrocarbons to pass through the membrane material the MN increases and therefore the maximum load of the engine driving the compressor increases. The heavy hydrocarbons that permeate through the membrane are reintroduced into the main gas stream on the low pressure side of the compressor. The amount of gas that circulates through the permeate stream and back into the main gas stream depends on the pressure difference across the membrane, the heavy hydrocarbon content of the feed gas, and the size of the membrane material. There is an energy cost associated with recompressing the gas that flows back into the gas line. To minimize this cost it is desirable to minimize the permeate flow. The fuel flow rate to the engine at a given load is fixed. To supply the engine with high quality gas (high MN) the quantity of heavy hydrocarbons removed also must be large. This means that the feed needs to be large enough to keep the engine supplied with fuel when a significant portion of the gas is removed to increase MN. The % retentate flow indicates the fraction of gas that exits the retentate stream. The gas that does not exit as

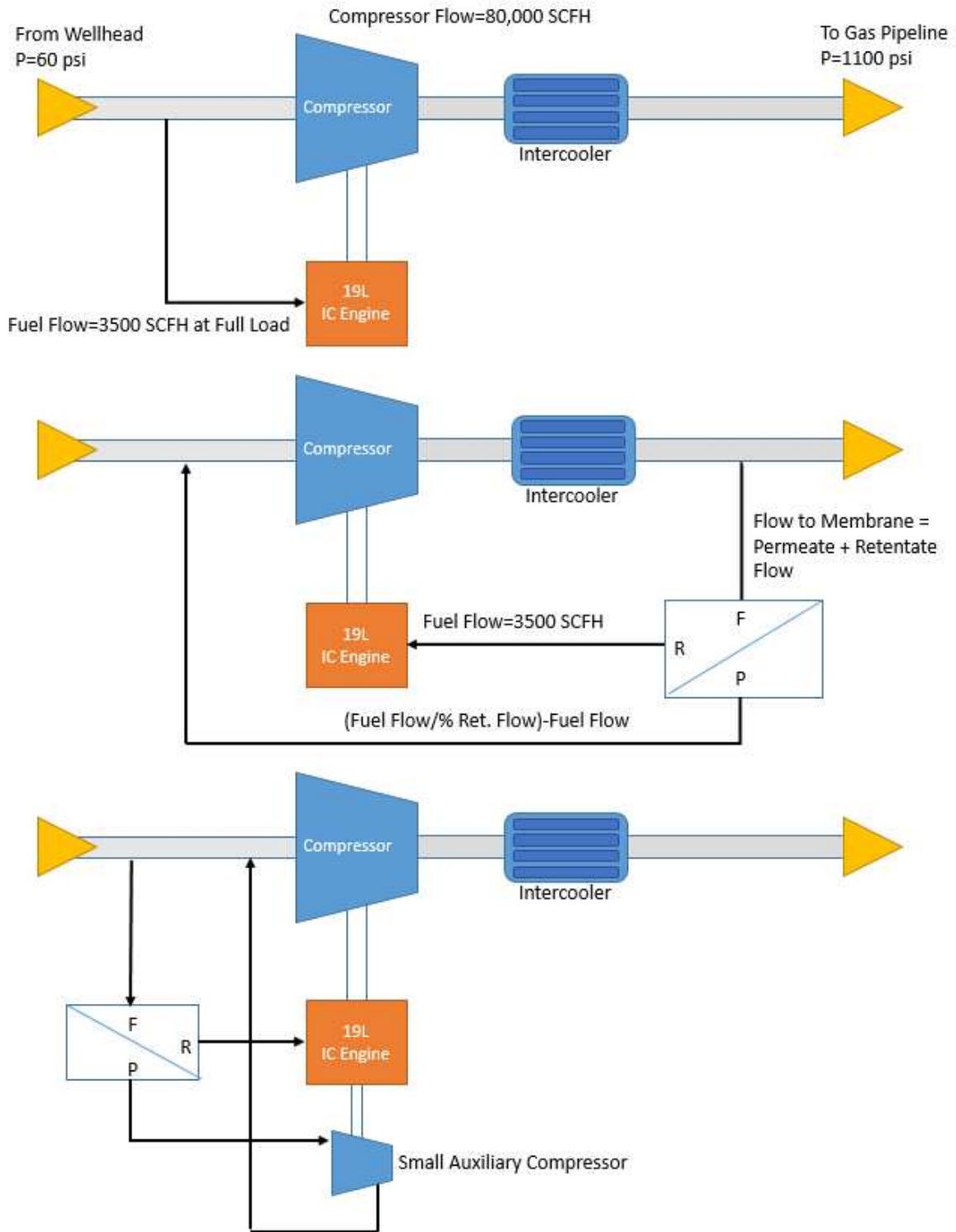


Figure 8: Fuel supply to wellsite compressor engine and proposed membrane separation system integration

the retentate exits as the permeate stream and needs to be recompressed. In low % retentate flow conditions a large portion of the gas is permeate and flows from the high pressure side of the compressor to the low pressure side through the membrane. This bypassing effect requires energy to recompress the gas. Too much flow back to the low pressure side of the compressor will negate the power gains from the higher MN. It is therefore important to keep the % retentate flow at a reasonable value to maximize the efficiency increase of the entire system.

## 2. Methods and Materials

### 2.1. Membrane Module Tested

The membrane module supplied by HZG is a plate and frame design using a flat sheet rubbery polymer membrane. It is designed to have a higher separation efficiency for heavy hydrocarbons. The membrane module tested is designed for a 200 SCFH flow rate of natural gas. A flow path of the natural gas through the membrane module and across the membrane material is shown in Figure 9 and Figure 10.

### Model

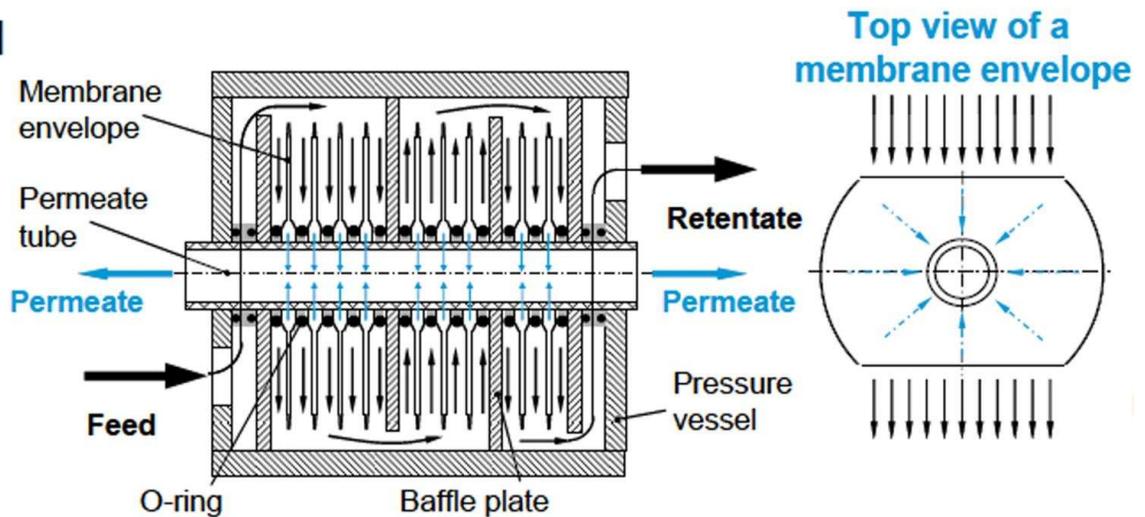


Figure 9: HZG membrane module flow configuration

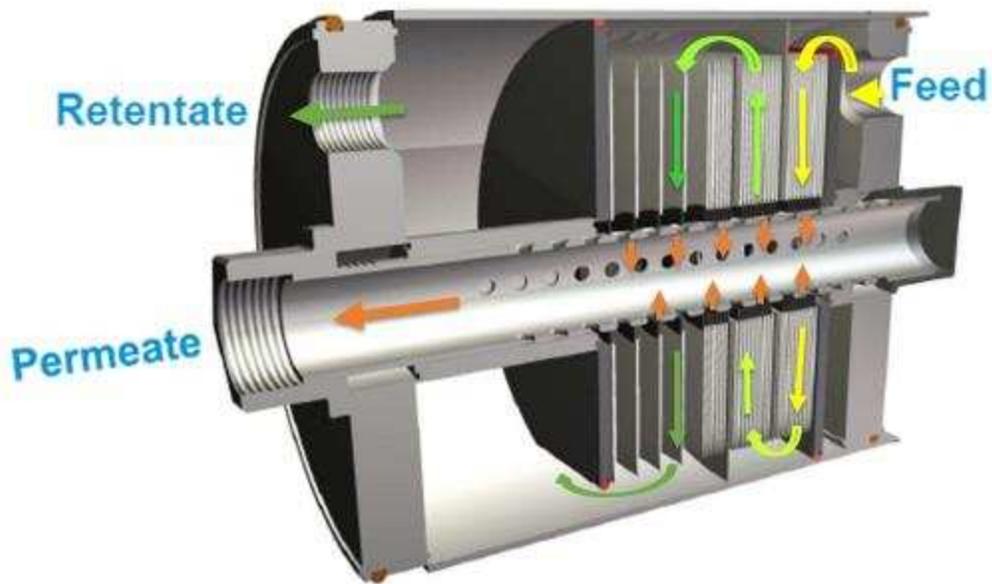


Figure 10: HZG membrane module and flow path

The membrane module is composed of layers of membrane envelopes where two pieces of flat membrane material are bonded along their outside edge and open at the inside hole. Stacking these envelopes with o-rings around the inside hole creates an accordion like structure where the membrane material separates the outer space of the membrane module from the inner permeate flow channel. The membrane module has baffle plates which force the feed to flow in a zig-zag pattern across the membrane envelopes. This maximizes the time the gas is in contact with the membrane and increases the permeation of gas through the selective layer. Any gas that passes through the membrane has an unobstructed path out of the membrane module through the permeate tube located at the center of the module. In the figure both side of the permeate tube are open. In actual testing only the permeate port on the retentate side of the module was used.

The membrane is a composite material with a poly(octylmethyl siloxane) (POMS) selective layer, poly(acrylonitrile) porous support layer, and a polyester non-woven support. The membrane surface

area is 0.8 m<sup>2</sup> encased in a stainless steel housing seen in Figure 11. The maximum operating temperature of the membrane module is 50°C and the maximum operating pressure of the module is 100 bar. The membrane manufacturer is Helmholtz-Zentrum Geesthacht (HZG).



Figure 11: Plate and Frame Membrane Module

## 2.2. Membrane Performance Scale Evaluation System

The 200 SCFH flow rate used a specification when ordering the membrane module was obtained by scaling the gas flow for a 19L engine to 1/20<sup>th</sup> of its max flow. A Cummins QSK19 engine uses approximately 4000 SCFH of natural gas at 1800 rpm under full load. A scale membrane module was used to decrease gas usage and allow for longer tests with the same amount of gas storage. The module has one inlet, or feed, and two outlets, the permeate and retentate flows. The raw untreated gas enters

the feed port, passes over the membrane material and leaves through the retentate port. The gas that passes through the membrane exits through the permeate port. In the final iteration of the system where it is implemented with the engine the retentate stream will be used to fuel the engine and the permeate stream will either be sent through the compressor with the rest of the natural gas on its way to a natural gas pipeline, or fed into a reformer where the heavy hydrocarbons are broken down and blended with the gas upstream of the compressor. In the small scale bench test, both streams were vented to the atmosphere.

Figure 12 shows a schematic of the membrane module testing system. The upper left corner of the schematic shows the mixed gas bottle, where the gas is mixed to a specific composition. Following the flow of gas, the next piece of hardware in the system is the pressure regulator where the gas from the bottle (1200-600 psi) is regulated to approximately 100 psi. The gas then flows through a heat exchanger, where water is used to heat or cool the gas to a desired temperature. The mass flow rate of the gas is controlled with an Alicat MC-series 250 SLPM mass flow controller. The gas then flows into the feed port of the membrane module and exits the membrane through the retentate and permeate ports of the module. Before the feed and after the retentate and permeate ports temperature is measured with Omega thermocouples. Pressure is measured in these locations with Omega 0-100 psi pressure transducers. Gas compositions can be measured at these three points by opening needle valves which allow a small portion of the gas to flow from the main stream to a manifold where the gas can either be sent to a Varian CP-4900 gas chromatograph or an Omega HX71 humidity sensor. Swagelok 0-100 psi backpressure regulators are used to keep the permeate and retentate streams at a set pressure. After the backpressure regulators both gas streams flow through Omega rotameters to measure the volumetric flow from each stream. The outlets of the rotameters are at atmospheric pressure and vent to the atmosphere. The pressure transducers, thermocouples, and analog output of the Alicat mass flow controller are connected to a National Instruments cRio data acquisition system where analog voltages

are scaled and converted to temperatures, pressures, and flows. A three way manually actuated ball valve is located before the feed of the membrane which allows the membrane to be bypassed and all gas flows through the retentate measurement portion of the system. A check valve is used so gas cannot flow back into the membrane and out the permeate port.

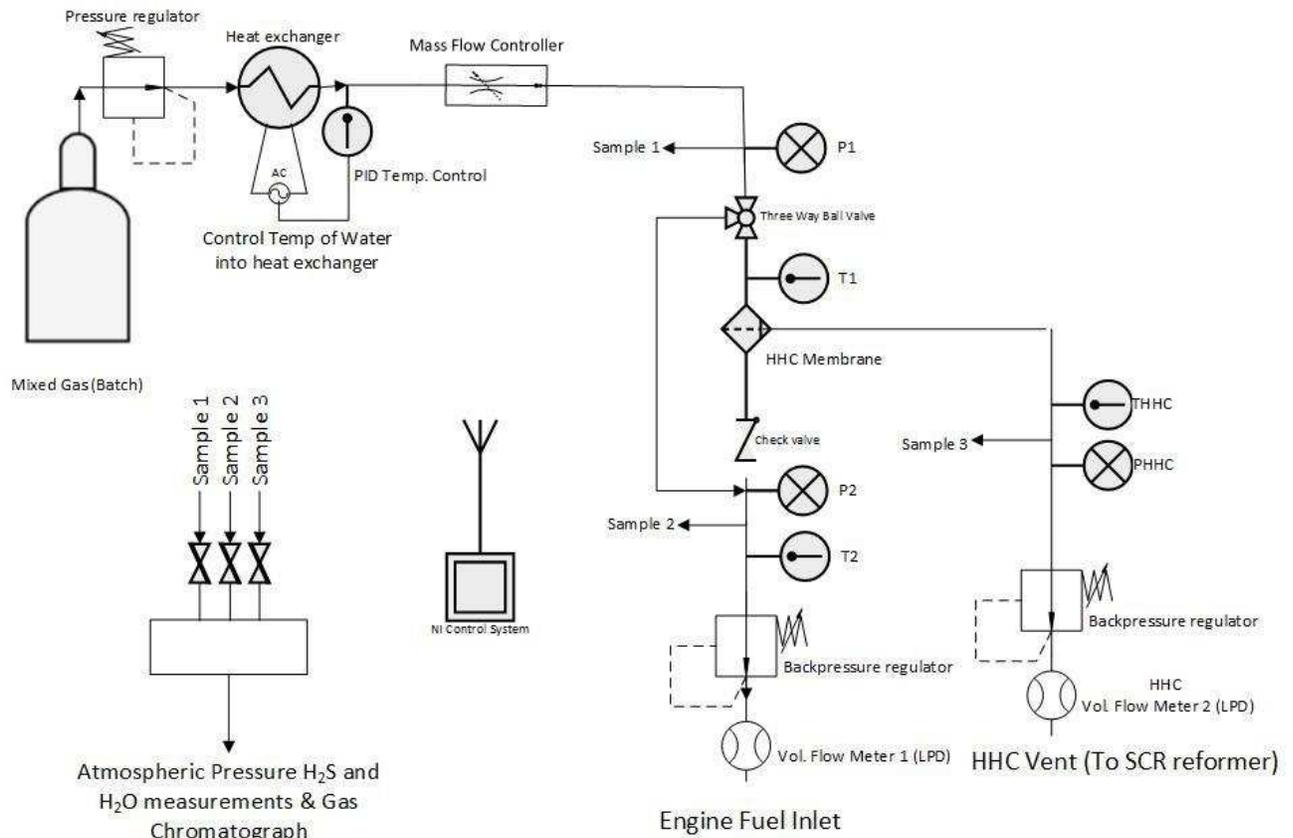


Figure 12: Benchtop test system schematic

Safety is a concern when dealing with flammable gases like methane and toxic gases like H<sub>2</sub>S. All equipment used in the test system is rated to handle natural gas at temperatures and pressures higher than that seen in testing. Since the H<sub>2</sub>S used in later tests is a corrosive it will be separated from the

main stream as long as possible. Components that come in contact with H<sub>2</sub>S or the natural gas H<sub>2</sub>S blend will be made from stainless steel or other corrosion resistant materials.

### **2.2.1. System Hardware**

In this system gas is blended in Dot 3AA-2400 gas bottles to a specified composition using the laws of partial pressures. These bottles are 2990 in<sup>3</sup> (49L) in volume and have a max working pressure of 2400 psi. These are typically filled to 600-1200 psi and stored outdoors. This pressure is regulated to approximately 80 psi using an Airgas Y11215D350 single diaphragm 0-100 psi natural gas pressure regulator. The gas flows to the building through a Teflon flexible tube into a Bell & Gossett BP400-20LP plate style heat exchanger (Figure 13). This controls the temperature of the gas entering the membrane. The other side of the heat exchanger is a closed loop water recirculation system that consists of a pump, insulated tank, and heater that is thermostatically controlled.

After the gas is heated it flows through an Alicat MC-series 250 SLPM mass flow controller (Figure 14) which measures the mass flow and controls a proportional solenoid valve to provide precise closed loop control of the flow. Because calculating mass flow is dependent on the composition of the gas a mass flow controller with user programmable compositions was selected. This makes changing gases while keeping an accurate mass flow rate possible.



Figure 13: (Left) Gas Bottles and Pressure Regulator, (Right) Heat Exchanger and Water Recirculation System



Figure 14: Alicat Scientific MC-Series Mass Flow Controller

Temperature, pressure, and composition are measured at the feed, permeate, and retentate stream (all ports entering and exiting the membrane). Omega TJ36-CASS-116U-6 K-type thermocouples are used to measure the temperature of the gas stream seen in Figure 16. They are sealed with a 1/16" Swagelok Tee fitting. To properly measure temperature of the flow the end of the thermocouple probe was placed in the middle of the gas stream. Pressure was measured using 0-5V 0-100psi Omega PX309-100G5V pressure transducers (Figure 16). These were installed in the system with Swagelok Tee fittings. Analog voltages from the thermocouples and pressure transducers were read with a National Instruments (NI) cRio-9066 chassis with a NI 9211 4ch thermocouple card and a NI 9201 analog input card (Figure 15). A custom Labview VI was used to scale these voltages into the appropriate temperature and pressure readings which were displayed on a laptop and recorded for each test.

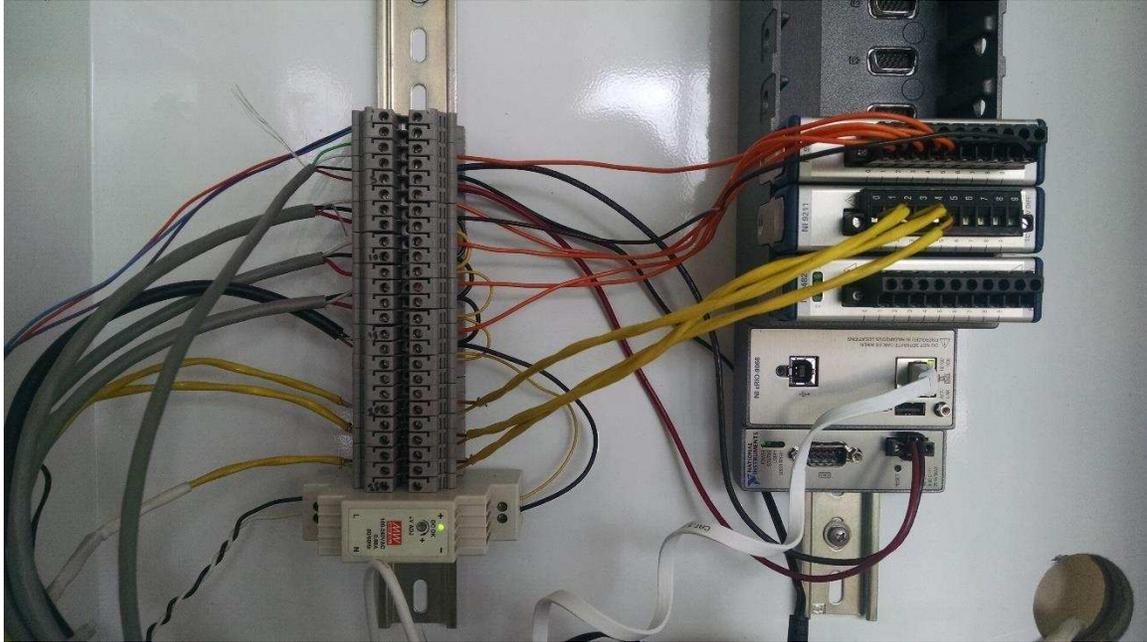


Figure 15: National Instruments cRio for logging temperature and pressure



Figure 16: From left to right: Backpressure regulator, analog pressure gauge, pressure transducer, thermocouple, bleed valve

Composition measurements were made with a Varian CP-4900 gas chromatograph. Packed columns are used to separate gas species which are detected using a thermal conductivity detector. This analyzer uses a split-sample technique where gas is measured through two columns simultaneously which provides faster results (around 2 minutes) [17]. The gas chromatograph is located one floor above the bench test hardware connected by approximately 60ft of 1/16" sample line. To sample at each of the three critical location on the membrane test system needle valves were installed to bleed off a small amount of gas to not change the flow characteristics of the system. The outlets of all three of the bleed valves fed into a 4-way manifold and flowed upstairs to the gas chromatograph.

To increase the separation of the membrane a pressure drop across the membrane is needed. To accomplish this backpressure regulators (Figure 16) were installed on the permeate and retentate streams. This way by having a large backpressure on the retentate stream and a small backpressure on the permeate stream the pressure difference across the membrane material could be large. The backpressure regulators can also be used to simulate different outlet conditions like a reformer requiring a certain inlet pressure on the outlet of the permeate stream.

Directly downstream of the backpressure regulators, Brooks 20-200 SCFH air rotameters were installed to measure flow rate (Figure 17). These are both vented to atmospheric pressure. The rotameters are used to measure volumetric flow and provide data on the flow path through the membrane at different pressure differences. Mass flow can be calculated by knowing the composition, temperature and pressure of the gas flowing through the rotameters. After the gas leaves the rotameters it flows back outside where it is vented to the atmosphere.

For leak detection a methane detector was used (McMaster part # 6631T43) (Figure 17). The threshold detection limit is 10,000 ppm of 20% of the Lower Explosive Limit (LEL) for methane. Figure 17 also shows the retentate and permeate ports of the membrane module. The retentate port has a check

valve so that when the membrane module is bypassed gas does not back flow through the membrane module and leave the permeate stream. The bypass can be seen on the right side of the Swagelok Tee fitting.



Figure 17: (Left) Brooks rotameters (Right) methane detector, retentate, and permeate ports on membrane module

The initial design of the system includes H<sub>2</sub>S and H<sub>2</sub>O injection systems. Since these systems are not available as off the shelf components and their use is primarily for durability testing they were not high

priority in the initial construction of the system. The system was designed to accommodate these features at a later time, and to focus on the separation aspects of the membrane tests.

### 2.2.2. Gas Blending

To obtain the correct gas composition a batch gas blending process was used where gas was mixed in a high pressure cylinder and fed into the membrane. This was an alternative to metering each gas from its own individual bottle and mixing all gas streams before entering the membrane. This method was not used because of the cost and complexity of the mixing system. With the single bottle system only one pressure regulator and mass flow controller was required, as opposed to using a mass flow controller for each individual constituent bottle. Another consideration was the mixing of liquid fuels such as butane, pentane, hexane, and heptane. In a multiple bottle configuration these liquid fuels would have needed to be vaporized and injected into the gas stream. Air blast nozzles and ultrasonic injectors were investigated, but it was determined that a batch gas mixing process would be more feasible. The drawback to this system is shorter test times because of the smaller volume of gas using a single bottle. Certain tests at high flow rates and low feed bottle pressures required mixing multiple bottles and connecting them together upstream of the pressure regulator to increase the stored gas volume.

The gases were mixed using the law of partial pressures to give the correct mol% of each constituent. Dalton's Law was used to obtain the correct partial pressure for each constituent in the mixture.

$$P_i = P_{\text{total}}y_i \quad (13)$$

Where  $P_i$  is the partial pressure of the constituent,  $P_{\text{total}}$  is the desired bottle pressure, and  $y_i$  is the mole fraction of the particular constituent.

The total pressure of the bottle was determined based on the composition. The partial pressure of each constituent had to be lower than its vapor pressure so that condensation inside of the bottle would not occur. This is more of a problem with the heavier hydrocarbons like hexane and heptane.

For the liquid fuels this partial pressure was converted to a mass using the ideal gas law.

$$PV = mRT \quad (14)$$

$$m_i = \frac{P_i V}{RT} \quad (15)$$

Where  $P_i$  is the partial pressure of the constituent,  $V$  is the total volume of the cylinder,  $R$  is the gas constant [kJ/kgK] and  $T$  is the bottle temperature.

The gas cylinder was first evacuated to approximately 0.1 psia to remove any remaining gases and to help the addition of liquid fuels. The liquid fuels were mixed together and added to the gas bottle using a large sealed syringe. Then the gases were added starting with the lowest bottle pressure which was usually propane, but sometime changed as the bottles were used. Time was given between adding liquid fuels and each gaseous fuel for the mixture to equalize temperature and pressure.

Before the gas was fed into the membrane the mixed cylinders were physically rolled to fully mix the gases inside of the cylinder.

Gas blending accuracy was checked by measuring the composition of each bottle before each test. A sample of four bottles compared to the desired composition is presented in Figure 18.

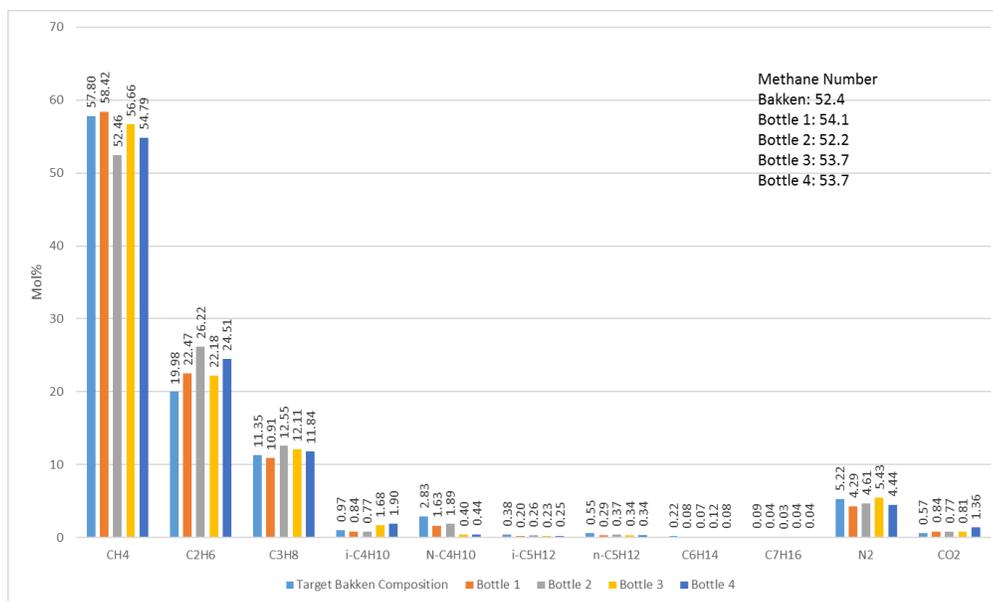


Figure 18: Mixed gas bottle composition compared to Bakken gas composition.

### 2.3. Test Procedure

Before every test the gas chromatograph was calibrated with a C1-C6, CO<sub>2</sub>, N<sub>2</sub> calibration gas. Then this cal gas was run through the GC as an unknown to confirm the calibration was successful. The GC was then set to record 50 samples, which gave about an hour and a half of sample time. If needed this number could be increased or decreased depending on the duration of the test.

On the benchtop system the mass flow rate, backpressure regulators, and water temperature were set to the desired values for a particular test. By controlling these backpressures the % retentate flow could be set. Readings from the sensors were recorded from the cRio, mass flow controller, and rotameters. These measurements were temperature, pressure, and flow of the feed, retentate, and permeate.

Composition measurements were taken from the feed, retentate, permeate streams by opening the needle valves that fed into the GC. First the composition of the bottle was checked by measuring the feed stream, then both retentate and permeate were measured. A final sample was taken from the feed

stream to insure there was no drift in the GC readings or composition change in the bottle as it was depleted. Each stream was sampled for 5-10 minutes to collect multiple samples for each stream. If the composition of the samples from the same stream varied significantly more samples were taken until the composition measurement stabilized.

### **2.3.1. System Calibration**

#### **2.3.1.1. Gas Temperature Control and Measurement**

The water heater, pump, and heat exchanger were tested to verify that the input gas temperature could be controlled. This test involved electrically heating the water to various constant temperatures then flowing gas through the system. Before flowing gas all thermocouples read the same room temperature. When gas started to flow through the system the temperature at the feed slowly increased followed by the downstream thermocouples. The permeate stream took the longest to come up to temperature because of the small amount of flow through the membrane at the low differential pressure used for the temperature test. Eventually the system reached steady state, where all of the measured temperatures became relatively constant. From this data a temperature difference between the water temperature and the feed temperature was found, so that a starting point for setting water temperature given a desired feed temperature was established.

#### **2.3.1.2. Pressure**

Pressure transducers were calibrated using calibration factors provided in the supplied data sheet and verified with the factory calibrated pressure reading in the mass flow controller. The slope and intercept was modified in LabView to correlate a given voltage output of the transducer to a pressure value.

### 2.3.1.3. Mass and Volumetric Flow

The system contains 3 flow meters. A calibrated mass flow meter upstream of the membrane module and two rotameters to measure volumetric flow rate of the permeate and retentate streams. When the membrane is bypassed all of the gas flows through the retentate flow meter. With no other path for the gas to the flow, measurements should be the same at the feed and retentate streams. By knowing the natural gas temperature, pressure, and composition a conversion was made between mass and volumetric flow. Verifying the flow was the same at the calibrated mass flow controller and rotameter verified the reading of volumetric flow.

### 2.3.1.4. Gas Chromatograph

To ensure that the composition measurements made were accurate the gas chromatograph in the engines lab had to be calibrated for the method we were using. These results are presented in Table 4. This process involved running a certified calibration gas (Actual mol%) through the GC and calibrating the mol% outputs to match the known quantities in the gas. Then the calibration gas was run as an unknown gas (Sample 1 and Sample 2) to verify that the calibration was accurate. Errors in the two samples taken of the calibration gas were between 0 and 2.2%.

Table 4: Gas Chromatograph Calibration Data

	Actual Mol%	Sample 1	Sample 2	Sample Avg	Error %
Nitrogen	1.07	1.071	1.069	1.07	2.1E-14
Methane	84.885	84.485	84.594	84.5395	0.40868
CO2	2.03	2.033	2.026	2.0295	0.02464
Ethane	9	8.96	8.928	8.944	0.62612
Propane	2.01	2.015	2.01	2.0125	0.12422
Isobutane	0.201	0.202	0.203	0.2025	0.74074
n-Butane	0.202	0.201	0.204	0.2025	0.24691
Isopentane	0.2	0.203	0.203	0.203	1.47783
n-Pentane	0.2	0.202	0.207	0.2045	2.20049
Hexane	0.202	0.203	0.202	0.2025	0.24691

## **2.4. Data Processing**

### **2.4.1. Calculating Methane Number**

Methane number was primarily calculated using a gas properties calculator provided by Cummins Westport. This tool, available to the public online, calculates MN and LHV (BTU/lbm) from the composition of the fuel [18]. The calculator also indicates if the fuel is recommended to be used in specific engines. A screenshot of this tool from the Cummins Westport website can be seen in Figure 19. The Cummins Westport tool uses a numerical, regression analysis based method utilizing an extensive set of experimental test data. The exact calculation method is proprietary, but it provides a better estimation at predicting MN of high hydrocarbon content gas blends than the SAE and ISO linear models.

Other methods were used to compute the methane number including the MWM model and the AVL gas properties calculation tool. All of these methods were relatively consistent with gas blends that consisted of mostly methane, ethane, and propane. The calculated methane number of each of these tools tended to diverge with gas blends containing higher concentrations of heavy hydrocarbons. When a mixture had high levels of heavy hydrocarbons the Cummins calculator tended to predict a higher methane number. The MWM method would predict the lowest MN. Usually the AVL calculator predicted a number in between these values. The Cummins Westport calculator was used to process all of the composition data for further analysis.

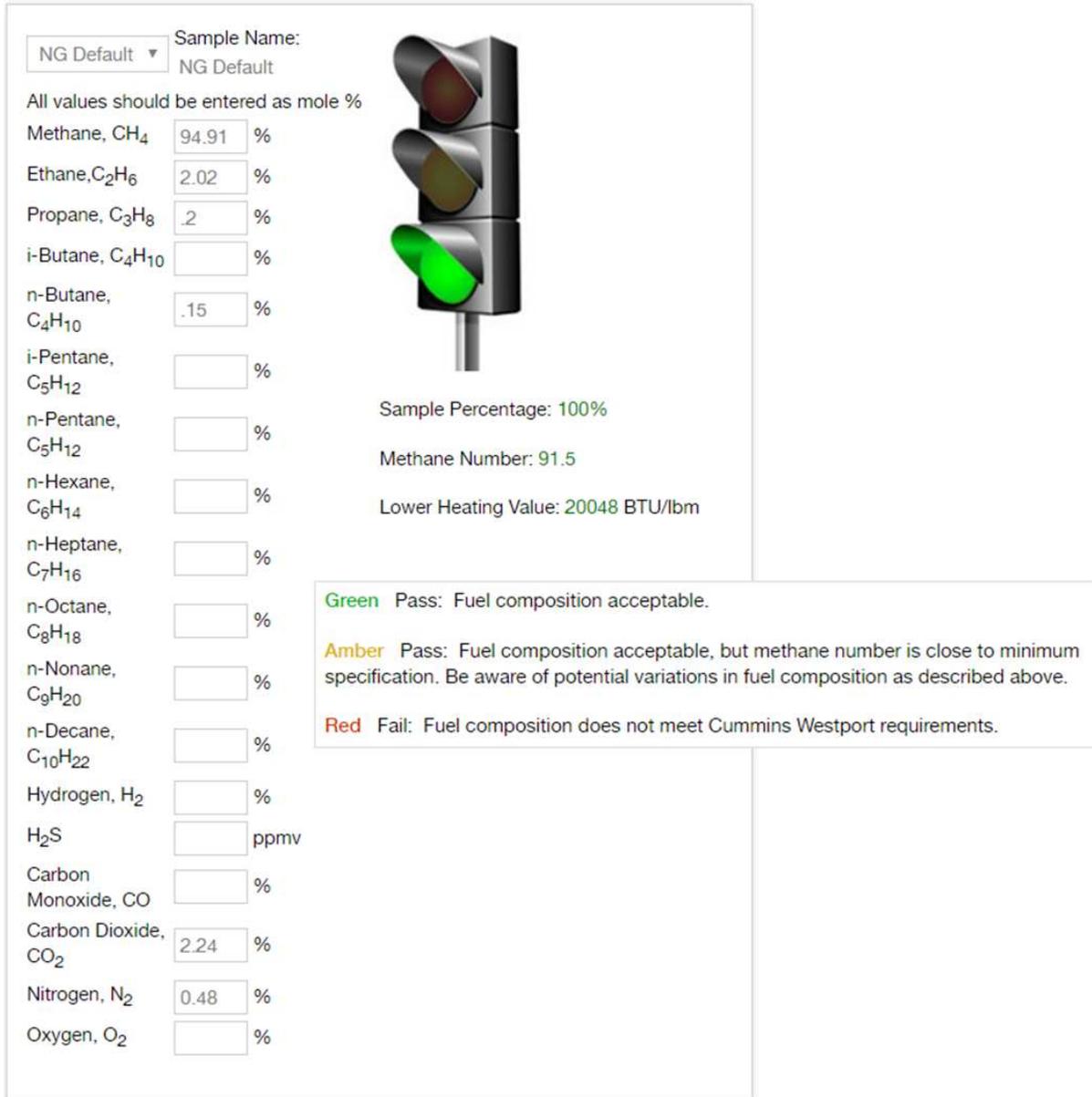


Figure 19: Cummins Gas Properties Calculation Tool Example

### 2.4.2. Calculating Percent Removal of Particular Species

To successfully treat natural gas, particular species need to be removed or reduced, while retaining methane to increase methane number. The nature of the membrane is that with enough pressure any gas will permeate through the barrier. This can be seen by flowing just one gas through the membrane.

Even with pure methane or nitrogen, which are the least permeable gas species, the flow rate of the permeate stream is significant with enough of a differential pressure.

For a more effective separation with less losses to the permeate stream the difference in % removal between the desired and unwanted gases should be large. Methane and ethane should have a lower % removal than the C3+ hydrocarbons so that the composition of the retentate stream has a larger mol% methane and ethane. A rubbery membrane separates based on condensability of the gas, which leads to heavier hydrocarbons, with lower saturation temperatures, having a higher % removal.

Under steady state conditions due to conservation of mass, the feed mass flow rate for a given species is equal to the sum of the retentate and permeate mass flow rates.

$$\dot{m}_{i,feed} = \dot{m}_{i,retentate} + \dot{m}_{i,permeate} \quad (16)$$

% removal is defined as the change in mass flow rate of a species between the feed and retentate stream of the membrane. If all of a particular gas species is removed the % removal is 100%, if the mass flow rate goes unchanged the % removal is 0%.

$$\% \text{ Removal} = \frac{\dot{m}_{i,permeate}}{\dot{m}_{i,feed}} * 100 = \frac{\dot{m}_{i,feed} - \dot{m}_{i,retentate}}{\dot{m}_{i,feed}} * 100 \quad (17)$$

### 2.4.3. Rotameter Calibration Factor

The rotameters used in the benchtop test setup to measure the permeate and retentate flow are calibrated for use with air. Because natural gas is a different density than air a calibration factor was used to obtain an accurate volumetric flow. A rotameter calibration factor takes into account temperature, outlet pressure, and density of the gas when it differs from air at standard temperature and pressure (STP). The rotameter calibration from Omega, the supplier of the rotameters is:

$$\text{SCFM}_{\text{reading}} = \text{SCFM}_{\text{true}} \sqrt{\frac{M}{28.9} \frac{T}{520} \frac{14.7}{P}} \quad (18)$$

Where SCFM stands for standard cubic feet per minute, M is the molecular weight of the gas in g/mol, T is the temperature in Rankine, and P is the pressure in psi. These values correspond to the common imperial STP units. Since the temperature of the gas was always close to room temperature and the outlet of both rotameters were at the same pressure (atmospheric) these terms were neglected and just the molecular weight was used to account for the variation in rotameter readings.

$$\text{SCFM}_{\text{reading}} = \text{SCFM}_{\text{true}} \sqrt{\frac{M}{28.9}} \quad (19)$$

Values of molecular weight ranged from 16.7 to 30.5 g/mol for the natural gas tested in the membrane. The difference in composition between the retentate and permeate streams was different enough to warrant the use of two separate calibration factors whenever measuring flow was critical.

#### 2.4.4. Brake Horsepower Required for Compression

To calculate the horsepower required to compress a certain mass flow of natural gas from one pressure to another a method from the Gas Processors Suppliers Association Engineering Data Book was used. This equation provides a reasonable estimate for calculating compressor horsepower of a large slow speed compressor (300-450 rpm), compressing a gas with a specific gravity of 0.65, and having stage compression ratios of above 2.5. These horsepower calculations estimate powers reasonable close to data from a three-stage compressor system explored in chapter 4.

$$\text{Brake Horsepower} = (22) \left( \frac{\text{ratio}}{\text{stage}} \right) (\# \text{ of stages}) (\text{MMSCFD}) (F) \quad (20)$$

Where MMSCFD is million standard cubic feet per day of natural gas, F=1.0 for single-stage compressors, 1.08 for two-stage compressors, and 1.10 for three-stage compressors [19].

### **3. Performance Characteristics of the Membrane Separator**

Tests were conducted to characterize the performance of the membrane in separating heavy hydrocarbons from a natural gas stream to increase methane number.

#### **3.1. Gas Compositions**

Three natural gas compositions were tested through the membrane. These blends were designated as “Pipeline”, “Bakken”, and “Lago”. The pipeline gas was unmixed gas taken straight from the natural gas supply to the building. This is the most ideal blend of natural gas with the highest methane number of around 78. The natural gas supply to the building is at 10-20 psi, so compression was required to meet the pressure requirements of our setup. This was carried out by using a FuelMaker Model C3 to fill the 3AA-2400 gas cylinders to around 900 psi. These bottles were then used to run the benchtop system at the required pressure. The building natural gas varied slightly in ethane content depending on the time of year, but for the most part remained around the same composition. To eliminate any error caused by this slight variation a composition sample of each bottle was taken prior to testing.

The Bakken blend is a low MN composition found in the Bakken shale formation located in northern Montana, North Dakota and Canada. This composition has a methane number of 53 and contains large percentages of ethane, propane and heavier hydrocarbons. This is an important gas composition because of the large number of compressor engines located in that particular shale gas formation.

The Lago gas composition is a blend based off data collected from the Lago Agrio oil field located in Ecuador. This composition has the lowest methane number tested of 45. This blend was modified from the original data to allow higher bottle pressures to increase testing time. The original composition had very high levels of Heptane and Hexane, which limited final bottle pressure. This is because the partial

pressure of these constituents would be higher than their vapor pressure, meaning that that particular constituent would condense in the bottle. This would cause the gas composition coming out of the bottle to change as the pressure decreased through testing as the condensed liquid would evaporate. This change would skew the results of the test as we did not have the ability to measure the composition of two streams of the membrane at the same time. If the feed composition changed while we were measuring the permeate or retentate streams it would not be captured by the gas chromatograph. It was therefore necessary to modify the blend to include more propane, butane, and pentane, which have a higher vapor pressure than hexane and heptane to increase bottle pressures and test times.

Table 5: Gas Compositions

Blend	"Pipeline"	"Bakken"	"Lago"	Methane Number	Auto Ignition Temp (°C)
	Composition (mol%)				
Methane CH <sub>4</sub>	85.10	57.67	50.75	100.0	580
Ethane C <sub>2</sub> H <sub>6</sub>	10.10	19.94	17.18	43.7	515
Propane C <sub>3</sub> H <sub>8</sub>	1.93	11.33	24.12	34.2	455
iso-Butane C <sub>4</sub> H <sub>10</sub>	0.14	0.97	3.93	9.6	462
n-Butane C <sub>4</sub> H <sub>10</sub>	0.14	2.83	1.02	9.6	405
iso-Pentane C <sub>5</sub> H <sub>12</sub>	0.00	0.38	0.56	9.5	420
n-Pentane C <sub>5</sub> H <sub>12</sub>	0.00	0.55	0.49	9.5	260
Hexane C <sub>6</sub> H <sub>14</sub>	0.00	0.22	0.05	9.5	225
Heptane C <sub>7</sub> H <sub>16</sub>	0.00	0.09	0.00	9.5	215
Nitrogen N <sub>2</sub>	0.31	5.21	0.28	NA	NA
Carbon Dioxide CO <sub>2</sub>	2.28	0.57	0.00	NA	NA
Hydrogen Sulfide H <sub>2</sub> S	0.00	0.01	0.00	NA	NA
Blend MN	76.5	52.4	45.5		

### **3.2. Independent Variable Changes**

Evaluating the operating characteristics of the membrane was challenging because changing one variable in the system usually had an effect on more than one measurement. For example, increasing back pressure of the feed stream changes not only the separation characteristics but also the retentate/permeate flow ratio.

To evaluate the individual effects of parameter changes a set of nominal parameters for pressure, flow, composition, and temperature were chosen. In some cases the nominal parameters were modified to better suit the test goals.

#### **3.2.1. Pressure Difference Across Membrane**

Pressure is the driving force of separation in the membrane module. Pressure difference is defined as pressure difference across the membrane. There is no physical restriction between the feed and retentate ports of the membrane module, while the feed and permeate ports are separated by the membrane polymer. The slight pressure difference between the feed and retentate is caused by the flow restriction of the gas passing along the membrane plates in a zig-zag pattern. At higher flow rates this pressure difference is larger, but still not significant. As there is only a small pressure difference in the feed and retentate flows the pressure difference is defined as the difference between retentate and permeate pressure.

With a larger pressure difference, more gas is driven through the membrane material. Since the membrane is more selective to heavy hydrocarbons those gases permeate through the membrane at a faster rate than the lighter hydrocarbons. This leads to an increase in the quality of the retentate gas. At higher pressures, more gas is removed, which increases gas quality of the retentate stream, but decreases flow since more gas is being diverted to the permeate stream. There is a tradeoff in gas quality increase and retentate flow when pressure difference is changed. The % retentate flow is

defined as the volumetric flow rate of the retentate stream compared to the total flow through the membrane. In a low pressure difference condition, where the pressures on both side of the membrane are the same and there is no driving force to push gas through the membrane the retentate flow is 100%. The feed and retentate flows are equal. This is the case when  $\Delta P=0$  in Figure 20. All of the feed gas entering the membrane exits through the retentate stream and there is no MN increase because there is no separation of gases. At very large pressure differences the backpressure regulator on the retentate stream acts as a closed valve, not allowing any gas to flow through it. All of the feed gas passes through the membrane to the permeate outlet and the % retentate flow is equal to zero. Only a small amount exits the retentate via the sample port for the GC.

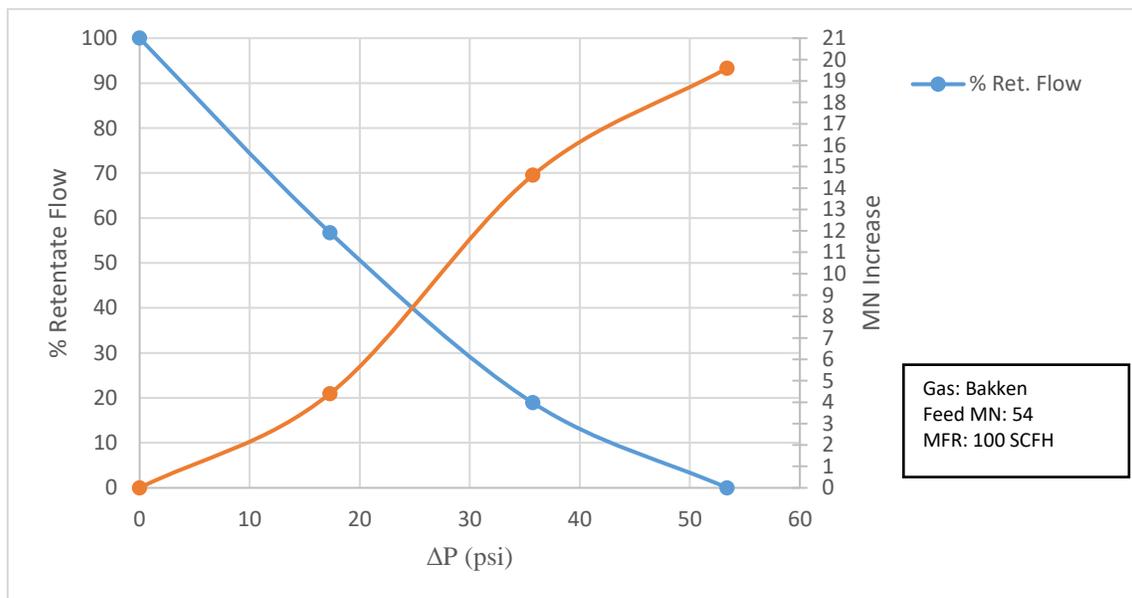


Figure 20: Effect of pressure difference on methane number increase and % retentate flow

The differential pressure required for % retentate flow to equal 0 depends on the gas composition. A more permeable gas, one which contains higher levels of heavy hydrocarbons will have a % retentate flow equal to zero at a lower differential pressure because there is less pressure required to push all of the gas through the membrane. On the other hand, when using a less permeable gas such as pure

methane, the gas is more resistant to passing through the membrane and zero % retentate flow occurs at a higher differential pressure.

### 3.2.2. System Operating Pressure

For separation to occur a pressure difference across the membrane is required. Absolute pressures on either side of the membrane influence separation as well. It was found that higher absolute pressures decreased the performance of the membrane when the pressure difference was constant. Results from this test appear in Figure 21.

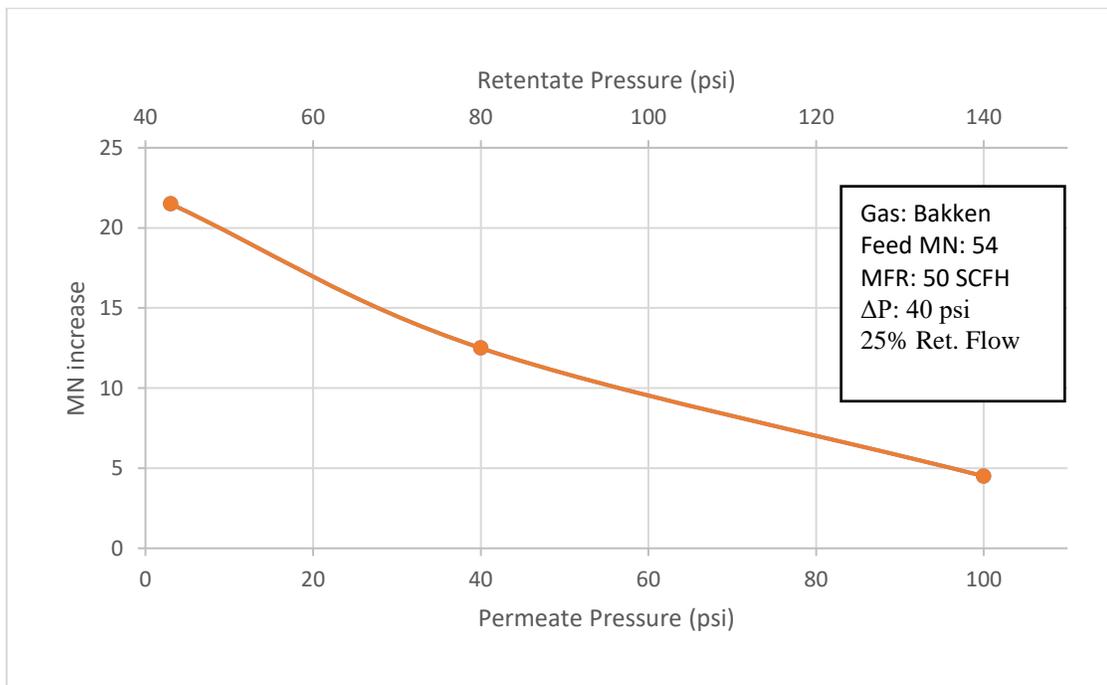


Figure 21: Effect of absolute pressure on separation with constant pressure difference

The gas in this test was the Bakken blend with a starting MN of 54. Three data points were taken, each with a pressure difference of 40 psi, 25% retentate flow, and 50 SCFH feed flow rate. Because of the lower feed mass flow rate MN increase is higher than previous tests. Absolute pressures have a significant effect on separation. The MN increase decreases by 18 points from 22 to corresponding to an

increase in permeate pressure of 100 psi at constant membrane differential pressure. The high permeate pressure causes high partial pressures of each species bringing them closer to the saturation pressure. The difference between species partial pressure and species saturation pressure is the driving force for condensation and desorption on the membrane. It is desirable to keep the permeate pressure as low as possible for a higher MN increase.

### **3.2.3. Feed Mass Flow Rate**

The feed mass flow rate was measured with a mass flow controller on the feed stream of the membrane. Volumetric flow was measured at the two outlets of the membrane, then converted to a mass flow using pressure, temperature, and composition values.

The feed mass flow rate is the rate which the gas flows through the membrane. A higher flow rate results in a lower residence time. In other words, the gas stays inside the membrane module and is exposed to the membrane for a shorter period of time. To test at higher pressures, higher feed flow rates are required to overcome the increase in permeate flow.

Figure 22 shows the permeate flow is not dependent on flow rate through the membrane. The pressure difference is driving force that allows gas to pass through the membrane, so at a constant differential pressure the flow rate of the permeate is also constant. Since the flow of gas out the permeate stream is constant, increasing mass flow rate into the membrane only increases the mass flow of the retentate stream. The consequence of this is a reduction in methane number increase. This occurs because there is only a finite amount of gas the membrane module is removing given a constant differential pressure even though the mass flow rate is increasing. At low flow rates, the membrane is able to remove a significant amount of gas, but at higher flow rates that same amount of gas is less

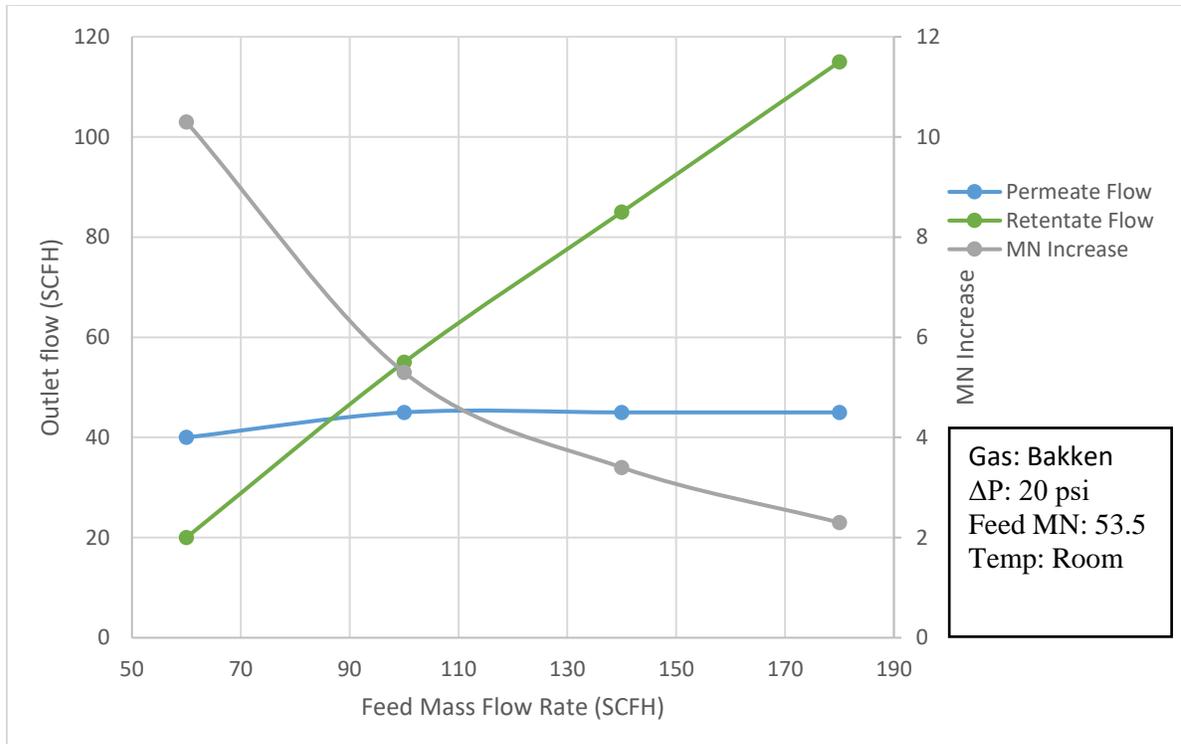


Figure 22: Effect of Feed Mass Flow Rate on Output Feeds and Methane Number Increase

significant to the total flow and the gas composition is relatively unchanged. The higher flow rates decrease the residence time in which the feed gas is exposed to the membrane. Since the diffusivity of the membrane is dependent on time this also has a negative effect on gas separation.

### 3.2.4. Temperature

Testing the membrane module at various case temperatures and feed gas temperatures showed no effect on the separation of any of the species. This was consistent with the membrane supplier HZG. There was no significant change in membrane performance caused by the change in feed gas or membrane case temperature. In general, with a polymer membrane increasing temperature increases the permeability of a gas but lowers its selectivity, so that the permeability remains relatively constant. [14] This assumes that the operating temperature is not close to the glass transition temperature of the polymer used in the membrane and high enough that hydrocarbon dew point and condensation do not

have an effect. The rest of the tests were conducted at room temperature without temperature control because temperature did not play a large role in the separation efficiency.

The experiment to test the effect of temperature on separation consisted of varying the temperature of the feed gas and composition. Feed temperatures just under the maximum operating temperature of the membrane (122°F) were achieved by using the heat exchanger and water circulation loop. The feed temperature was cooled by turning off the heater and adding ice to the water circulation loop. Data points were taken as the feed temperature of the gas dropped. With the water temperature at 32°F the lowest feed temperature achieved was around 42°F. Figure 23 shows the data from this test. Over the feed temperature range of 75°F there was only a variation in MN of about 0.3. This is not a significant change for such a wide temperature range.

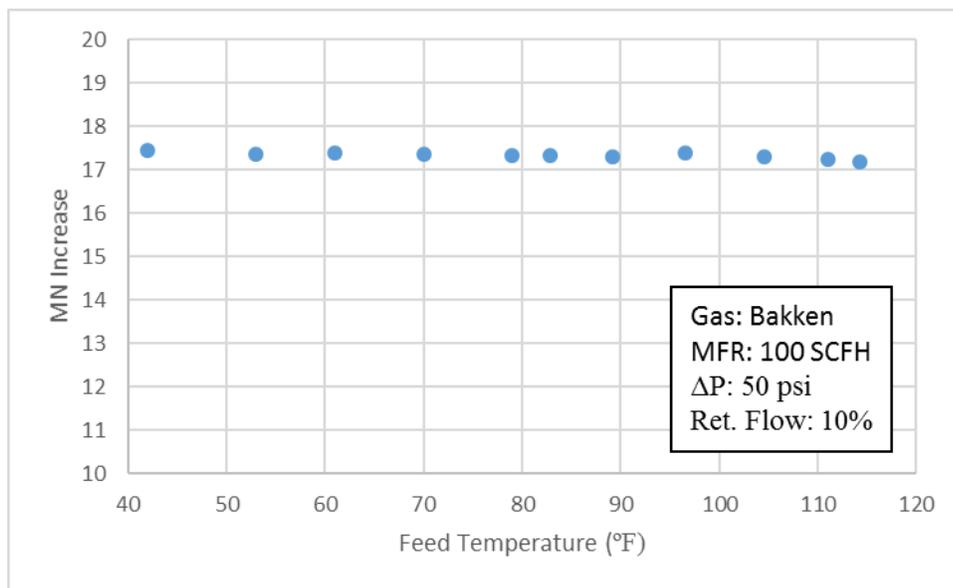


Figure 23: MN increase with varying Feed Temperatures

### 3.2.5. Feed Gas Composition

The composition of the feed gas plays a large role in the way the membrane behaves. Since constituents with lower saturation temperatures permeate through the membrane quicker than gases

like methane and ethane. The flow rate and pressure relationship changes based on gas composition. In lower MN fuels like the Lago blend the gas permeates the membrane more easily due to the large amount of heavy hydrocarbons. Since these components have less restriction to pass through the membrane material the pressure differential across the membrane is lower at a given feed flow rate than a less permeable gas. One can think of this like a traditional filter, where a more viscous fluid creates a larger pressure drop across the filter media.

This variation in flow through the membrane with different gas compositions changed the nominal parameters of the testing. When testing a wider range of gases the % retentate flow varied too much to make too much to maintain a constant pressure difference. Instead the % retentate flow was fixed at 50% and 25%. The retentate flow was equal to 50% or 25% of the total flow from the membrane. This change gave more insight into how the membrane would be used in engine applications where gas flow to the engine (retentate flow) needs to be a significant fraction of the feed flow.

In this test three different gases were used: Pipeline, Bakken, and Lago, each with an increasing amount of heavy hydrocarbons. The backpressure regulators were adjusted to maintain an equal flow between the retentate and permeate outlets, this was to simulate an engine requiring a certain flow rate of gas at full load, with natural gas supply capable of delivering 2X the engine requirement. The mass flow supplied to the membrane was set at 50 (left), 100 (middle), and 200 SCFH (right data point) for each of the gases. The methane number increase was then calculated by measuring the composition of the feed and retentate streams with the gas chromatograph and calculating methane number with the Cummins gas properties calculator. The difference in methane number between the streams is the MN increase.

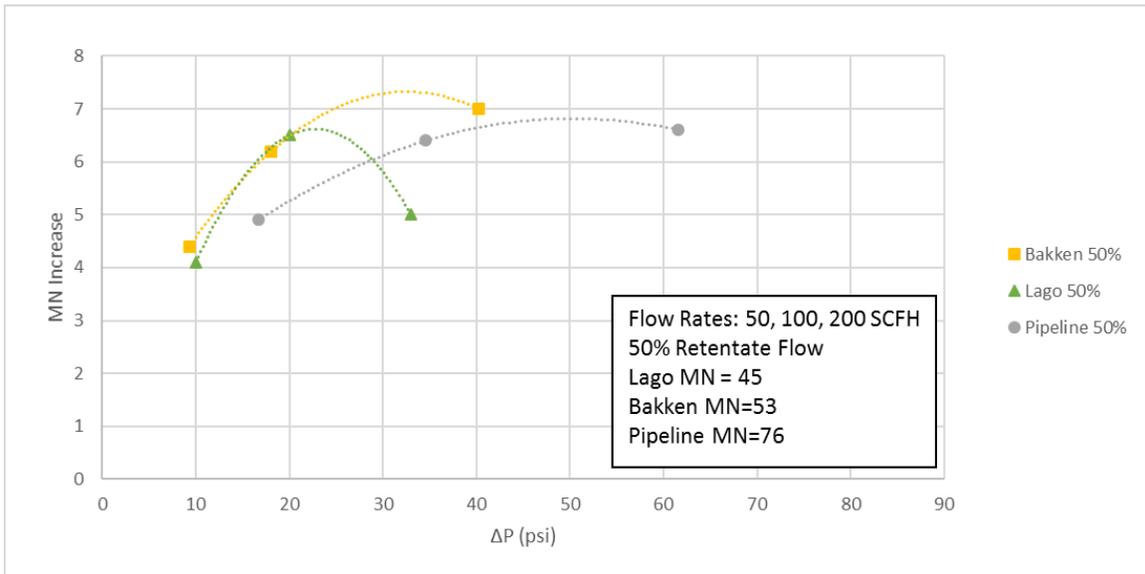
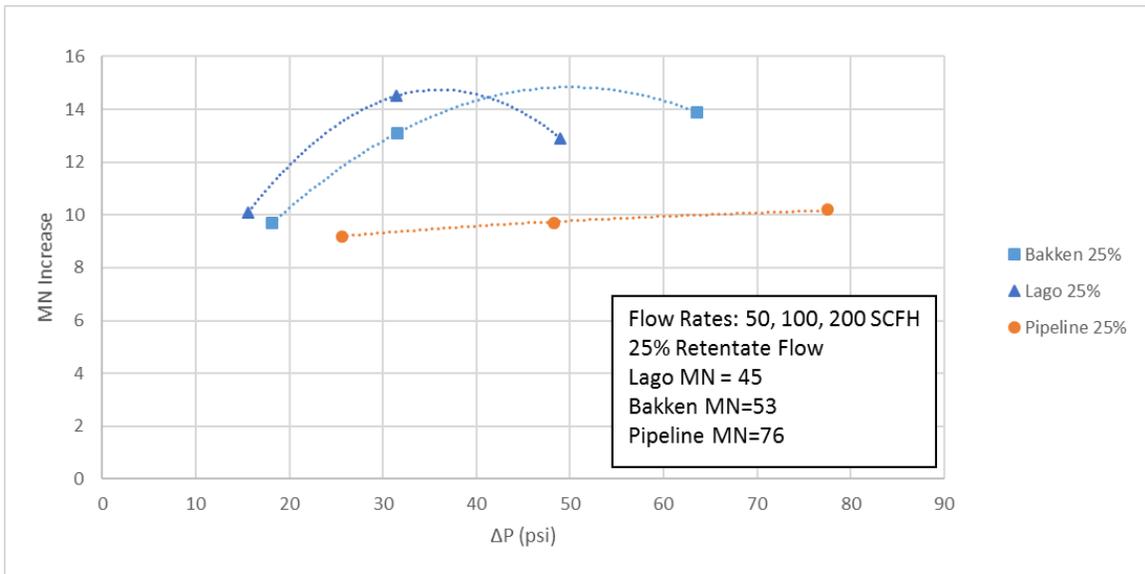


Figure 24: Gas Composition effect on differential pressure required for MN increase

What one can see from this data is the effects of permeability of the gas on separation. The pipeline gas, with the lowest concentration of heavy hydrocarbons, has the lowest total permeance. Increases are observed for both the required differential pressure and MN increase as feed mass flow rate increases.

When using a gas with a higher permeance it takes less driving force, in this case pressure, for gas to permeate through the membrane. One consequence of this is that it takes less pressure to maintain a 50% retentate flow, which can be seen in the Bakken and Lago curves on the graph, both occur at a lower differential pressure. The 200 SCFH data point for the Lago blend has a lower MN increase than the 100 SCFH test, even though it has a higher differential pressure. This is due to the shorter retention time in the membrane module and the higher total flow rate from the feed to the retentate. This is where the membrane starts to become ineffective at increasing the MN of a gas.

Table 6 compares the % removal of each species in the feed on a mass basis. Generally the more heavy hydrocarbons have a larger % removal than methane and ethane. The % removals for the butanes in the pipeline gas. These gases are almost completely removed from the retentate stream. The C4+ hydrocarbons have similar % removals for the Bakken and Lago blend. The % removal of methane decreases from the pipeline to the Lago blend. This is due to the lower pressure differential required to maintain the 50% retentate flow for the lower MN gases.

Table 6: Comparing the % removal for different compositions under the same operating conditions. Feed mass flow rate of 100 SCFH and 50% retentate flow

	Pipeline			Bakken			Lago		
	Feed Mol%	Retentate Mol%	% Removal	Feed Mol%	Retentate Mol%	% Removal	Feed Mol%	Retentate Mol%	% Removal
<b>CH4</b>	85.10	91.24	46.39	56.66	64.86	42.76	52.38	66.73	36.31
<b>C2H6</b>	10.10	6.16	69.51	22.18	16.90	61.89	15.93	13.00	59.21
<b>C3H8</b>	1.93	0.82	78.85	12.11	7.59	68.66	23.20	14.94	67.80
<b>i-C4H10</b>	0.14	0.05	81.22	1.68	0.99	70.45	3.95	2.36	70.12
<b>N-C4H10</b>	0.14	0.04	84.79	0.40	0.20	74.61	1.09	0.56	74.05
<b>i-C5H12</b>	0.00	0.00	NA	0.23	0.11	74.88	0.72	0.36	74.89
<b>n-C5H12</b>	0.00	0.00	NA	0.34	0.17	75.73	0.65	0.32	75.31
<b>C6H14</b>	0.00	0.00	NA	0.12	0.06	73.69	0.07	0.04	72.38
<b>C7H16</b>	0.00	0.00	NA	0.04	0.03	65.29	0.00	0.00	NA
<b>N2</b>	0.31	0.40	35.39	5.43	8.48	21.93	0.32	0.33	48.03
<b>CO2</b>	2.28	1.29	71.67	0.81	0.59	63.18	1.70	1.36	59.97

When dealing with high mass flow rates of heavy hydrocarbons membrane swelling and saturation can affect performance. When the membrane becomes saturated with absorbed heavy hydrocarbons it swells and does not allow any more gas to permeate. The flow rate of the permeate becomes constant

even though the differential pressure is increasing. This is the case with the 200 SCFH Lago gas blend data point. Beyond 100 SCFH and 20 psi differential pressure the membrane becomes saturated and the permeate flow does not increase. This leads to a decrease in MN increase because the amount of heavy hydrocarbons removed from the retentate stream remained constant, but the flow through the membrane module increased, so a smaller fraction of the heavy hydrocarbons were removed.

### **3.3. Membrane Performance Tradeoff**

When pressure difference is increased across the membrane, more gas is pushed through the membrane material. This means there is a smaller % retentate flow because more of the gas goes through the membrane, out the permeate stream, and less flows out the retentate stream. The small amount of gas leftover in the retentate is at a much higher quality and contains less heavy hydrocarbons, but the flow rate is low. At lower pressure differences less gas passes through the membrane, so the % retentate flow is higher, but separation is lower. A smaller amount of separation or reduction in hydrocarbons means the MN increase is small. A tradeoff needs to be made between MN increase and % retentate flow. Figure 25 shows this tradeoff for data collected under a wide range of conditions.

A compromise needs to be made when selecting where to operate the membrane separator. A significant MN increase is desired while still maintaining enough retentate flow to satisfy the engine demand. By carefully selecting the size of the membrane module, this trade off curve can be shifted upwards. This is the case of the equal retentate and permeate flow tests performed at 50% retentate flow seen in Figure 25. In these tests, the feed flow rate was increased, which allowed for the increase in pressure difference which led to better separation and a higher MN increase. This could also be achieved by using a membrane module with a smaller membrane surface area. If the membrane surface

area is too small, there will be insufficient flow through the membrane. While the pressure difference will be high, the MN increase will be small.

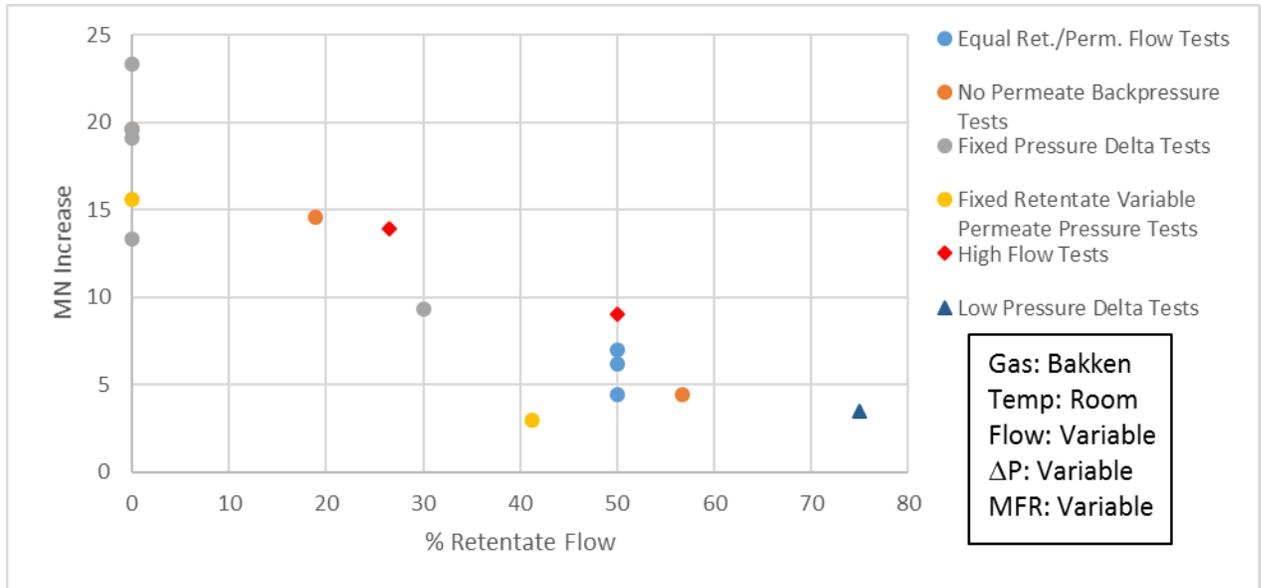


Figure 25: Tradeoff between flow and MN improvement

With only one size membrane surface area available only general conclusions can be made about the correct membrane area for a desired configuration. For example, if membrane area is too large, it only requires a small pressure difference to have % retentate flow go to 0%, because the large surface area allows all of the feed gas to pass through the membrane and exit the permeate stream. This is even more of a problem with very heavy hydrocarbon rich natural gas, which more easily permeates the membrane. To achieve adequate separation a large pressure difference is required, but to have a large pressure difference the membrane material needs to be small enough so that not all of the gas can permeate through it.

### 3.4. Single Component Testing

When gases are absorbed and diffuse through the membrane material the polymer reacts by swelling due to the presence of excess hydrocarbon molecules between the polymer chains. This slows

the diffusion process by increasing the distance the molecules have to travel through the membrane material. In work done by Schultz, this has been shown to decrease the selectivity of a single species when other species are present [20]. To test for this type of swelling and to see how the membrane would react to single constituents, tests were performed under the same operating conditions as the mixed gas tests, but with only two gases present in the mixture instead of the complete natural gas mixture. The concentrations of the target gases were the same as the Bakken blend. For example the Bakken blend is approximately 20% ethane. In the single constituent test for ethane a mixture of 20% ethane and 80% carrier gas, in this case methane, was used. Having the same concentration of the gas under observation without the interference of the other hydrocarbons in the mixture allowed comparison of the selectivities of each species individually to selectivity of that species in the mixture.

#### **3.4.1. Selectivity**

Each species was tested individually with the mole concentration found in the Bakken composition and the remaining concentration made up of methane. Using Equation 9 selectivities were calculated using the feed and permeate composition and the difference in partial pressures (Equation 11) derived from the total pressure on each side of the membrane and the molar concentration.

The results from these tests were as expected. The heavier hydrocarbons like heptane and hexane had a much higher selectivity than the lighter hydrocarbons like ethane and propane. This indicates that the heavy hydrocarbons permeate through the membrane at a faster rate than the lighter hydrocarbons. This agrees with Schultz's on POMS membranes where heavier hydrocarbons have higher selectivities. Because of this trend a POMS membrane is a good choice for increasing MN by decreasing levels of heavy hydrocarbons.

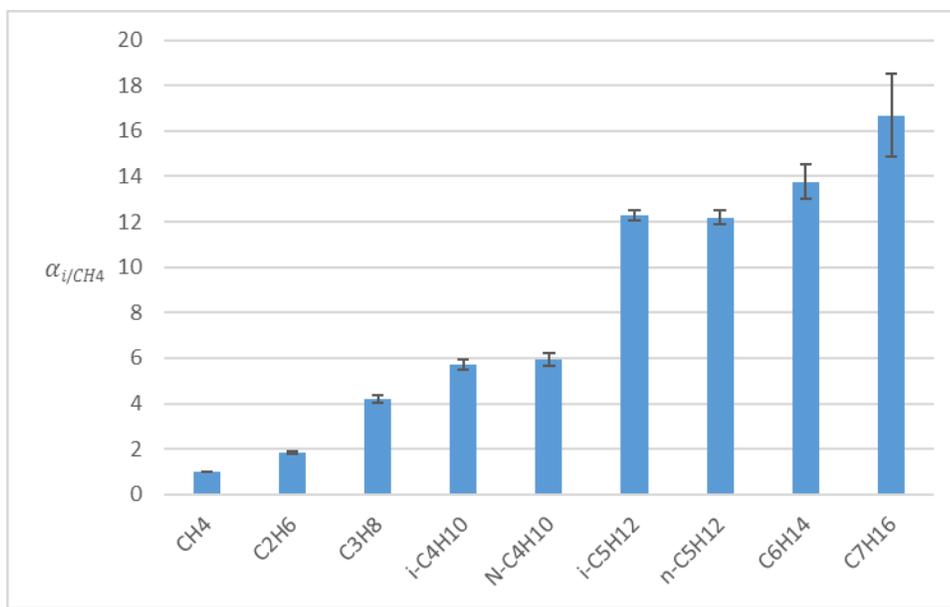


Figure 26: Selectivity of species mixed individually at Bakken concentrations

Isomers such as isobutane (i-C<sub>4</sub>H<sub>10</sub>) and isopentane (i-C<sub>5</sub>H<sub>12</sub>) having the same selectivities as their normal counterparts. This is interesting because the membrane is supposed to separate by solubility, and the boiling point of isomers differ from that of normal molecules. This could be due to permeability being a function of solubility and diffusivity. While the solubility of isomers are lower (lower boiling point) their diffusivity coefficient could be higher due to them having a more compact molecular arrangement and being able to move between the polymer chains more easily.

### 3.5. Comparison of Single Component and Mixed Gas Selectivities

By comparing the single constituent test data to selectivities calculated from running the Bakken blend as a complete mixture the effect of other hydrocarbons were seen. The other gases in the Bakken blend influence the selectivity of an individual gas a significant amount. Figure 27 shows a comparison of selectivities from single constituent and Bakken blend tests.

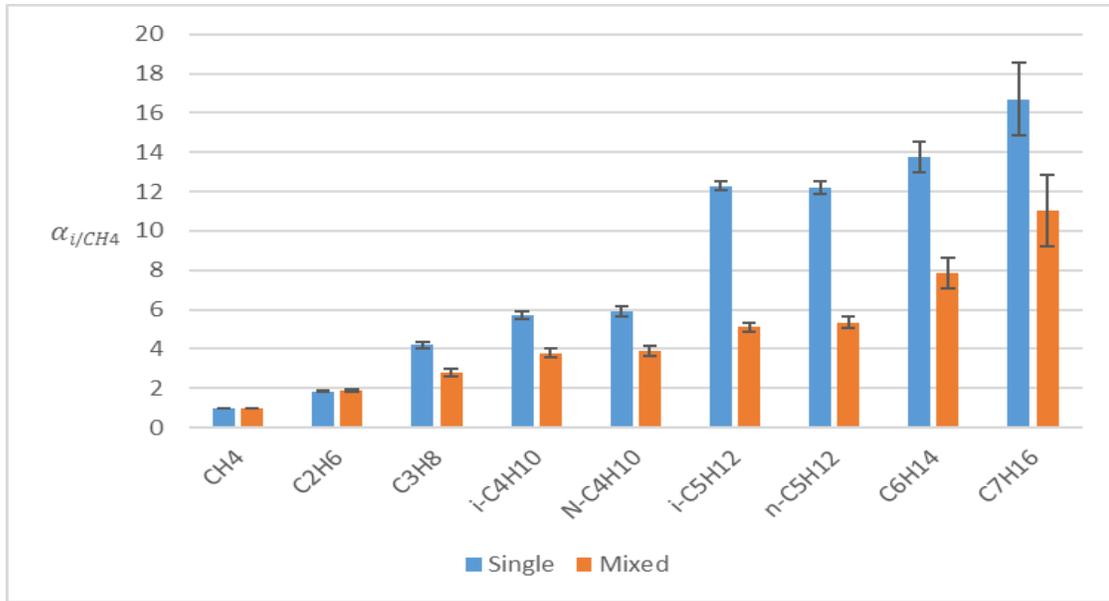


Figure 27: Selectivities of individually mixed gas compared to Bakken gas with all constituents

The selectivities for the Bakken blend were considerably lower than that of each component tested separately. This reinforces the hypothesis that the other heavy hydrocarbons diffusing through the membrane cause the polymer to swell, which lowers the permeability of the other constituents. This also reinforces the conclusion that the membrane has a limit to the amount of heavy hydrocarbons that can permeate through it, and that with very low methane number fuels the membrane becomes “saturated” and loses its effectiveness at separating heavy hydrocarbons at higher flow rates. This gives more insight into choosing the right size membrane for a desired flow and gas composition.

The concentration and partial pressure of a particular species determine the rate at which that species permeates. Effect such as swelling can cause the diffusion rate of a particular species to change. This is why a gas with multiple permeable species will have lower individual permeation rates for each species. The swelling of the membrane material and increased thickness slows diffusion through the membrane.

### 3.6. Engine Derate Improvement

The overall objective of this work is to increase the load capacity of an engine with low methane number well gas. Because recompression of the permeate stream out of the membrane module is energy intensive a large MN increase with a small % retentate flow is not desirable. A 25% or 50% retentate flow is more reasonable for when the system is integrated into a compressor engine system. An example of the engine derate improvement for a 60L Cummins natural gas engine is presented in Figure 28. A 60L engine running on Bakken composition natural gas with a MN of 53 can safely be run at 73% of its maximum load without causing damage to the engine.

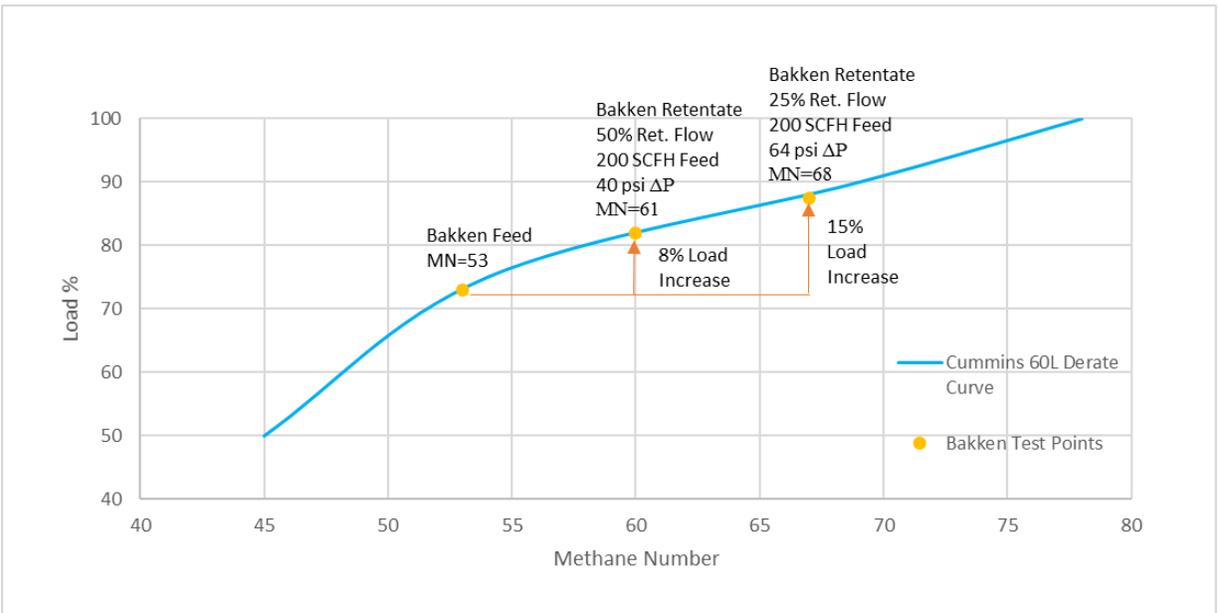


Figure 28: Engine derate curve and improvement for the Bakken gas composition

By using the membrane module with 50% retentate flow a MN increase from 53 to 61 was achieved, resulting in a load increase from 73% to 81% of maximum. Using a higher pressure differential with 25% retentate flow the engine could safely be run at 88% of maximum. However, this diverts more of the fuel gas away from the engine. The engine will require about the same flow rate of fuel for a given load regardless of the methane number. The drawback of lower % retentate flows is that the membrane

module has to be supplied with more fuel than the engine consumes. The engine must be supplied with twice the amount of gas as the engine normally requires at 50% retentate flow or four times the amount with 25% retentate flow. The permeate gas is introduced back into the system upstream of the compressor at lower pressures. Consequently, the retentate flow must be recompressed. A trade-off needs to be made between MN increase and percent retentate flow to optimize the system based on methane number of the well gas, size of the engine, flow rate through the compressor, pressures available upstream and downstream of the compressor, and desired load increase. In some cases it might be possible to use a smaller engine at a lower derate when the fuel is conditioned.

## 4. System Integration

### 4.1. Well Site Compressor Engine Membrane Integration Case Study

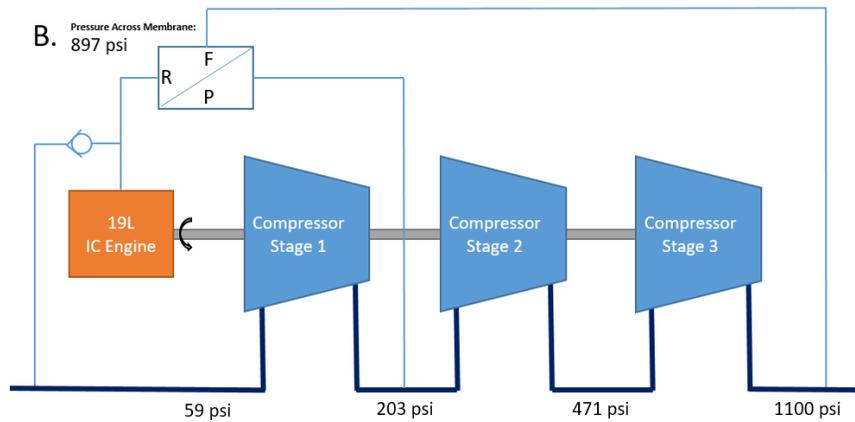
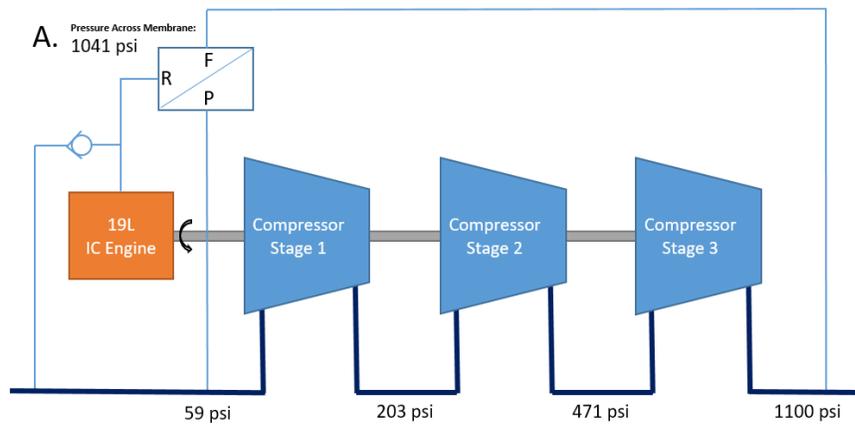
A case study of a 19L well site compressor engine was performed to show the feasibility of implementing a membrane fuel conditioning unit. In this example a three-stage reciprocating compressor driven by a 380hp Cummins KTA19GC engine was used. The engine output was 341 brake horsepower (BHP) at the given flow and pressure. Well gas was compressed at a rate of 81000 SCFH from the well pressure of 60 psi to the pipeline pressure of 1100 psi. The pressure difference across each of the three stages was 145 psi, 267 psi, and 629 psi. With a power output of 341 bhp at 1800 rpm the engine consumes 3435 SCFH of natural gas. The natural gas consumption of the engine compared to the amount of natural gas flowing through the compressor is 4%.

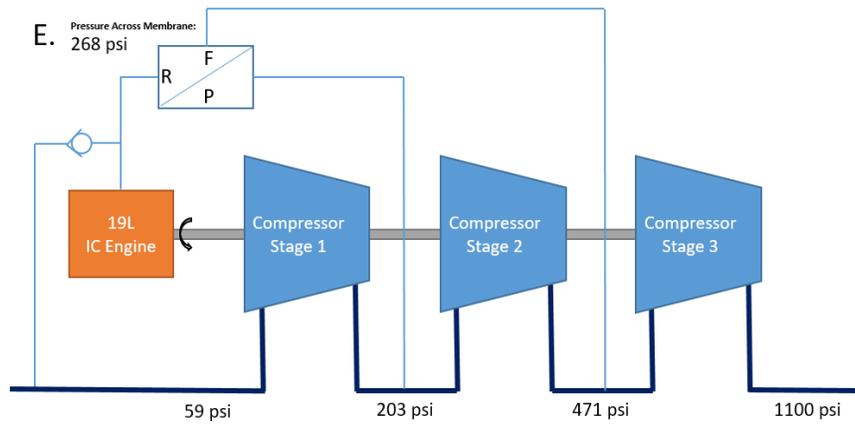
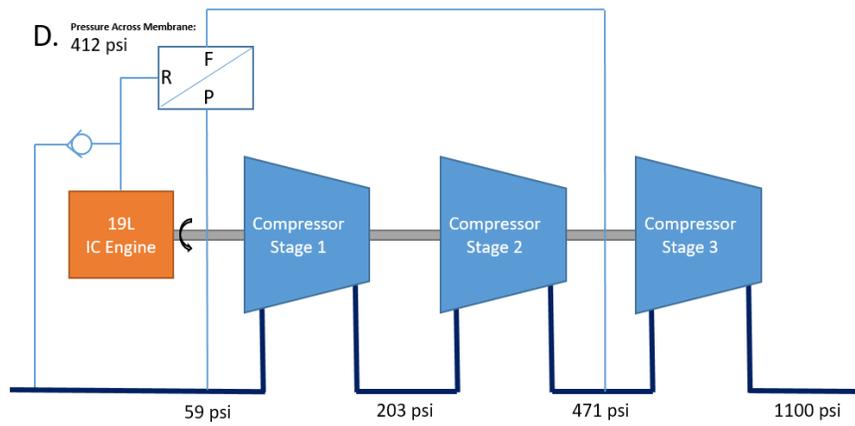
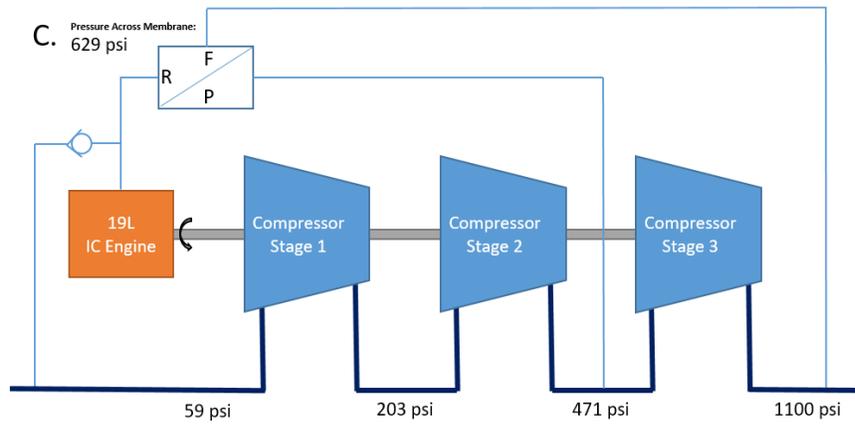
A pressure difference across the membrane is required for gas separation. With three stages of compression there are many options for picking a pressure difference across the membrane. The smallest pressure difference is between the inlet of the first compressor (well pressure) and the outlet of the first compression stage. The largest pressure difference is between the outlet of the third compressor stage and the inlet of the first stage. Other pressures can be obtained by using a combination of the different stages; this is demonstrated in Table 7 with a schematic of each configuration in Figure 29. To start the engine a source of natural gas is required. Normally this natural gas is taken from the wellhead before the first compressor stage. Because these are reciprocating type compressors, there is no flow through the compressor when it is not running, so taking gas from in between the compressor stages is not possible. To start the engine, a check valve would need to be installed between the inlet to the first compressor and the retentate stream that feeds the engine. Once

the engine starts and the compressor builds pressure, the check valve closes and the engine uses the pressurized gas from the retentate stream of the membrane module.

Table 7: Compressor Stages and Pressures

Absolute Pressures		Pressure Delta Options	
Inlet Pres	59.25 psi	A. Comp3-Inlet	1041 psi
Comp 1 Pres	203.7 psi	B. Comp3-Comp1	897 psi
Comp 2 Pres	471 psi	C. Comp3-Comp2	629 psi
Comp 3 Pres	1100 psi	D. Comp2-Inlet	412 psi
		E. Comp2-Comp1	268 psi
		F. Comp1-Inlet	144 psi





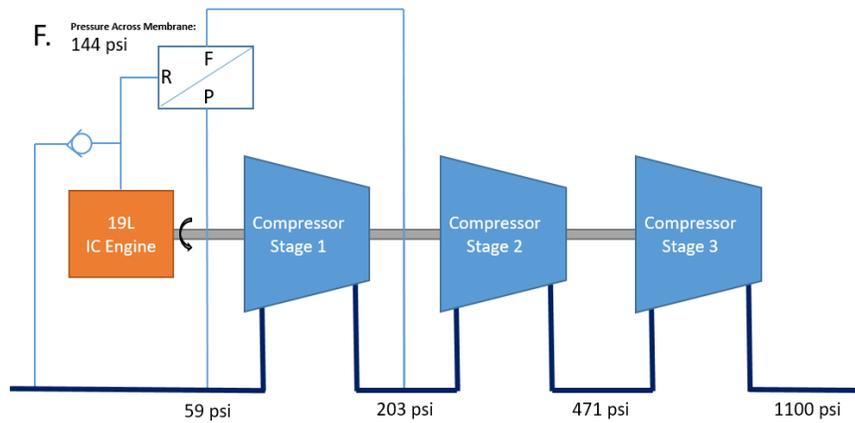


Figure 29: Membrane Configuration Options

A difference in pressure is required to move gas across the membrane and back into the compressor system. While there are many options for pressure difference across the membrane it is generally more advantageous to choose pressures that require less pressure regulation. When gas is throttled from a high pressure to a low pressure it takes energy to recompress this gas. Another consideration is the effect of absolute pressure on the membrane separation. For example, if only 200 psi of pressure difference is required it would be better to take 60 psi and 260 psi sources instead of 160 psi and 260 psi. The membrane module performs better at lower absolute pressures if the pressure difference remains the same.

The amount of gas that permeates through the membrane and returns to a lower pressure area is a concern because of the energy it takes to recompress the gas. Another approach would be to flare the permeate gas, which is also an energy loss. The flow to the engine remains relatively constant when it is operated at a constant load. When the membrane module is sized and setup to produce 50% retentate flow this means that 3250 SCFH of pressurized gas is lost through the permeate stream. This either needs to be recompressed, which requires energy from the engine, or flared where chemical energy is lost. In the more extreme case where % retentate flow is 25% (meaning 75% of the flow to the

membrane is recycled to a lower pressure) 9750 SCFH of gas requires recompression. This is approximately 12% of the total flow through the compressor and requires a significant amount of energy to recompress. Figure 30 demonstrates a simplified version of the membrane integration into the compressor engine to show the difference in flows between 25% and 50% retentate flow. The compressor stages are neglected and the routing is simplified.

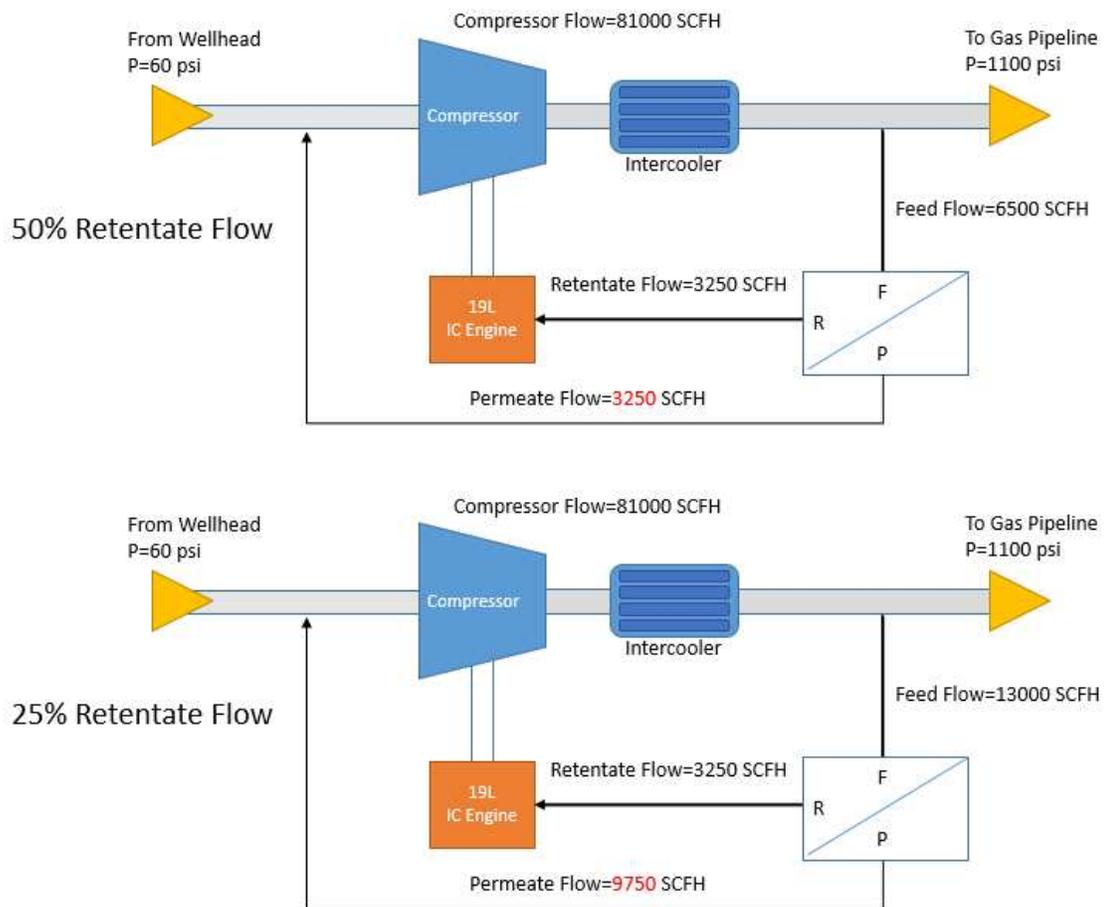


Figure 30: Flow Paths with 50% and 25% Retentate Flow

Depending on the pressure difference across the membrane and permeate flow, the energy required to recompress the permeate stream could be greater than the HP increase a higher MN gas allows. In the extreme example of having to compress 9750 SCFH of natural gas from 60 psi to 1100 psi

as shown in Figure 30 it would take approximately 46 horsepower to recompress the gas. This pressure differential is significantly higher than the pressure limitations of the benchtop membrane testing system, but extrapolating from recorded data predicts a MN increase of over 20. This would allow the engine to be run at full load without derate. This is a somewhat unrealistic case, because a pressure difference over 1000 psi is not required for adequate separation of heavy hydrocarbons. The case shows how a membrane separation system could be integrated into an existing system with minimal additional hardware.

Another approach which would give more flexibility would be to install an auxiliary compressor on the engine so that any pressure difference across the membrane could be achieved. It was shown from test performed on the Bakken blend that pressure differences as low as 60 psi could have a significant effect on MN to increase engine horsepower by eliminating the need for derate.

Figure 31 shows the amount of gas required for the membrane in comparison to the total natural gas flow through the compressor for % retentate flows from 100% (no membrane improvement) to 5%. This assumes the engine is close to full load and using 3250 SCFH of gas from the well. The feed flow rate increases exponentially with decreasing % retentate flow. At 5% retentate almost all the gas is separated to the permeate stream. To keep the engine supplied with 3250 SCFH of conditioned gas the membrane would have to be supplied with 65,000 SCFH of unconditioned, pressurized gas. This is approximately 80% of the total flow through the compressor and is not feasible due to the pipe sizing required. 20% retentate flow is approximately 20% of the total gas flow through the compressor engine system. % Retentate flows lower than this require over 20% of the total flow through the compressor. This is a significant amount of gas, compared to the total flow through the compressor.

At higher % retentate flows the flow to the engine is the significant part of the gas being taken from the well. When % retentate flow decreases more of this gas flows through the membrane and is unused

by the engine. At lower % retentate flows the permeate stream dominates the distribution of flow through the membrane. This is shown by the feed and permeate flow lines converging in Figure 31.

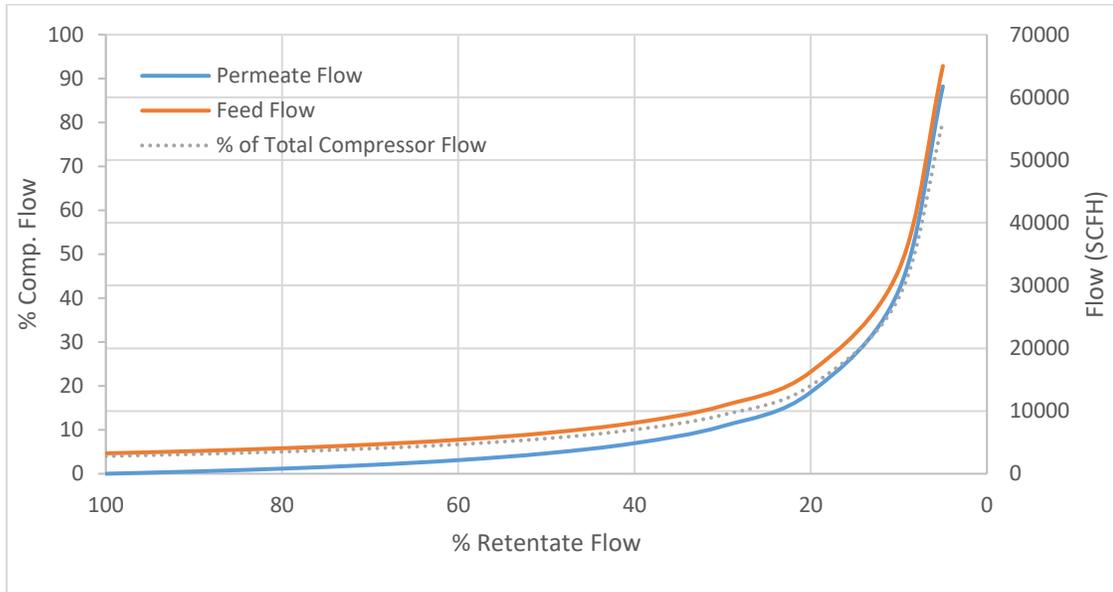


Figure 31: Flow to membrane compared to total flow through compressor engine at full load

To produce this curve the following equations were used. If the mass flow of the feed is equal to the sum of the mass flows leaving the membrane by the retentate and permeate and the % retentate flow is the ratio of the retentate mass flow to the feed mass flow it is possible to calculate the permeate and feed flow rates at any % retentate flow.

$$\dot{m}_{\text{feed}} = \dot{m}_{\text{retentate}} + \dot{m}_{\text{permeate}} \quad (21)$$

$$\% \text{ Retentate Flow} = \frac{\dot{m}_{\text{retentate}}}{\dot{m}_{\text{feed}}} \quad (22)$$

$$\dot{m}_{\text{permeate}} = \frac{\dot{m}_{\text{retentate}}}{\% \text{ Retentate Flow}} - \dot{m}_{\text{retentate}} \quad (23)$$

These calculations were performed under the assumption that engine fuel flow rate would remain constant at 3250 SCFH. During operation when the % retentate flow goes down, the MN of the fuel

would go up, allowing the engine to run at higher loads which would require more fuel. Even though this fuel flow rate difference could be hundreds of SCFH the trends remain the same.

At a constant feed flow the % retentate flow is controlled by the pressure difference across the membrane. The permeate stream would need to be recompressed to or above this pressure difference to be reintroduced into the main source of gas. In this example, a compressor running off the accessory drive of the engine could be used to recompress the permeate gas. The compressor could be specified to compress the gas to the optimal pressure, which is about 200 psi for the membrane characterized in this work, assuming a 60 psi permeate pressure. The auxiliary compressor takes power away from the engine and reduces the useable HP available to drive the main compressor. As flow through the auxiliary compressor increases with decreasing % retentate flow the power required to recompress gas increases. While it takes more power to recompress the gas it also enables more power by improving the MN of the retentate gas and reducing the derated HP. This tradeoff can be seen in Figure 32. At around 10% retentate flow the power required to compress the large permeate stream is greater than the derate improvement from increased MN. At this point it would be the same total power output as running the engine derate with untreated gas. The best power gains occur around 25% retentate flow. Where the flow to the membrane is approximately 15% of the total flow through the compressor. Data used in these calculations were from tests performed on the Bakken NG blend at 100 SCFH feed flow rate (the membrane surface area would have to be sized approximately 20 times larger for a 19L engine) with a differential pressure up to 50 psi across the membrane.

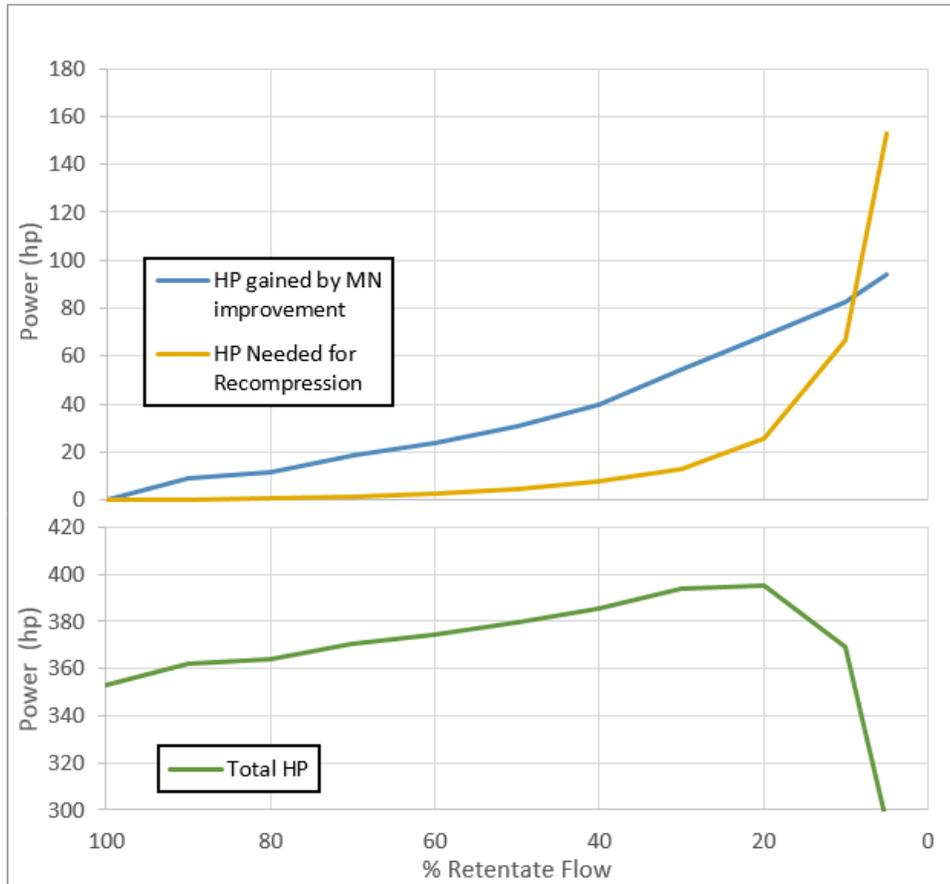


Figure 32: Tradeoff between recompression HP and HP gained by decreasing engine derate

Another option to deal with the permeate stream would be to flare the gas or feed it into a reformer. This would require no power to recompress the gas (a reformer would require energy input though). If the gas was sourced from upstream of the main compressor the total output of the compressor would not be effected; it could operate at maximum power assuming the derate could be eliminated. This option could be feasible if the cost of the untreated shale gas from the well was not significant and the increased power output could better meet natural gas demand. The drawbacks to this option are loss of well gas that could be sold and the environmental impact of flaring the gas. Factors such as the value of uncompressed, untreated well gas and emission regulations would determine if this was a feasible solution.

#### 4.2. Active Membrane Control

Engine derate because of low MN fuel only applies when the engine is operating at high loads. At lower loads auto ignition and knock are not an issue. For example, if a certain MN causes a 10% derate of an engine, the engine would still be able to operate normally up to 90% of its maximum power output. There is no need to increase MN of the gas if the load on the engine is less than the derated maximum power output of the engine. Because it takes energy to recompress the gas that permeates through the membrane it is more efficient to only activate the membrane separation module when it is needed, which is when the engine load exceeds the maximum derated load. As opposed to a passive system using only pressure regulators, an active membrane control system would allow the pressure difference across the membrane to be zero so that no gas is separated when a MN increase is not needed. As the engine attempts to increase load above the derate, the permeate pressure drops and there is a pressure difference across the membrane. This allows gas to be separated from the stream of fuel flowing into the engine to increase the MN so that knock does not occur. An example of how this system could operate is shown in Figure 33.

When an engine is running below the maximum load the membrane system is deactivated and the % retentate flow is 100%. Under these operating conditions there is no permeate flow, so no energy is lost in recompressing the gas. When the engine reaches maximum load, where normally the engine would stop producing power, the membrane system is activated. The % retentate flow decreases as more gas is separated through the membrane which increases the MN of the gas flowing to the engine. This enables the engine to run at higher loads, but also saves energy where the engine normally runs at lower loads by deactivating the membrane separation unit.

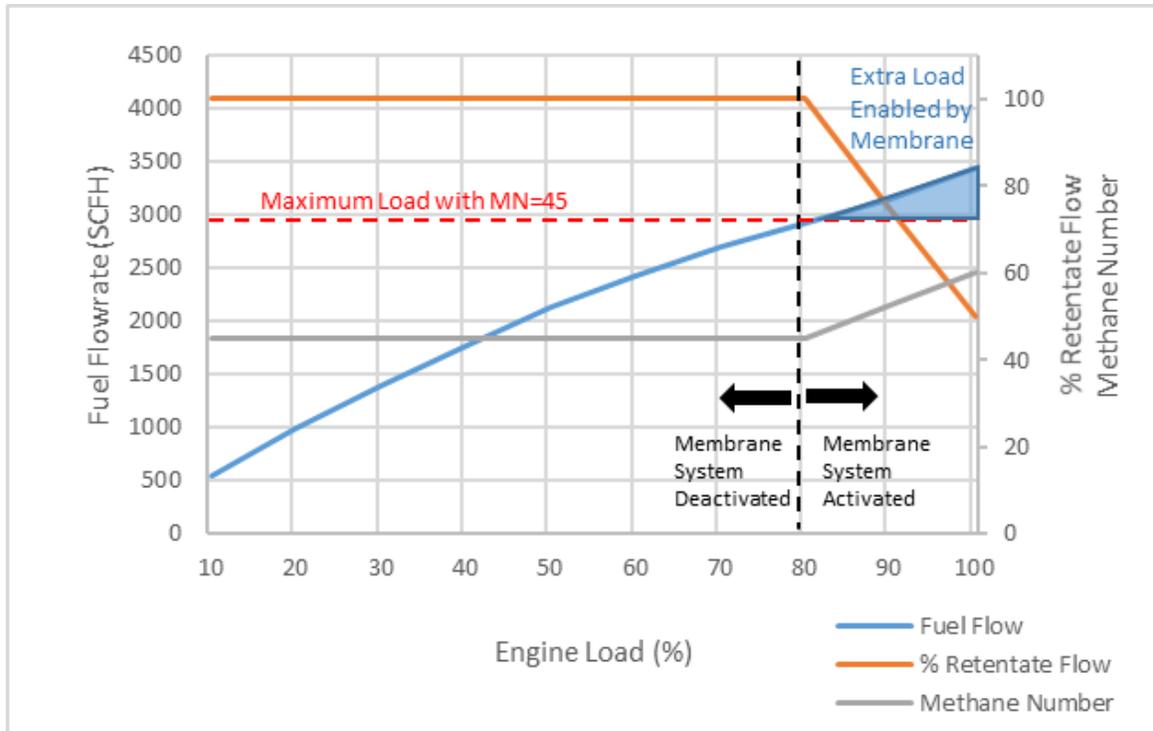


Figure 33: Active membrane control

One option to incorporate this is a electronic backpressure valve on the permeate side of the membrane that is controlled by the engine management system. This valve would be normally closed, so that there is no flow through the membrane and MN increase. When the load on the engine is increased, this valve would open and gas would be separated from the fuel stream to increase MN of the gas going into the engine. Ideally this valve would be proportional so that as engine load increase the MN would increase and the % retentate flow would decrease.

If using an auxiliary compressor to recompress the permeate stream, an electronic clutch could be installed on the compressor, so that it would be disengaged when the engine is running under derated load. When engine load exceeds the derate load the clutch would engage and pull gas from the permeate side of the membrane increasing the MN of the fuel going into the engine. This system would operate similar to an air conditioning compressor on a car or truck; the compressor is only engaged

when it is needed. Because it takes energy to recompress the gas, the power output of the engine is still not as high as it would be as using a high MN source of natural gas. This is shown in Figure 34.

Incorporation of a flare could also be part of active control. When the membrane is active the permeate flow would be flared. As described above, the membrane is activated only when needed, and the permeate flow is controlled to minimize the flowrate of flared gas. With this approach the engine-compressor set would be capable of achieving 100% of rated compression power. However, some well gas would be lost and there are potential environmental and regulatory concerns, as noted above.

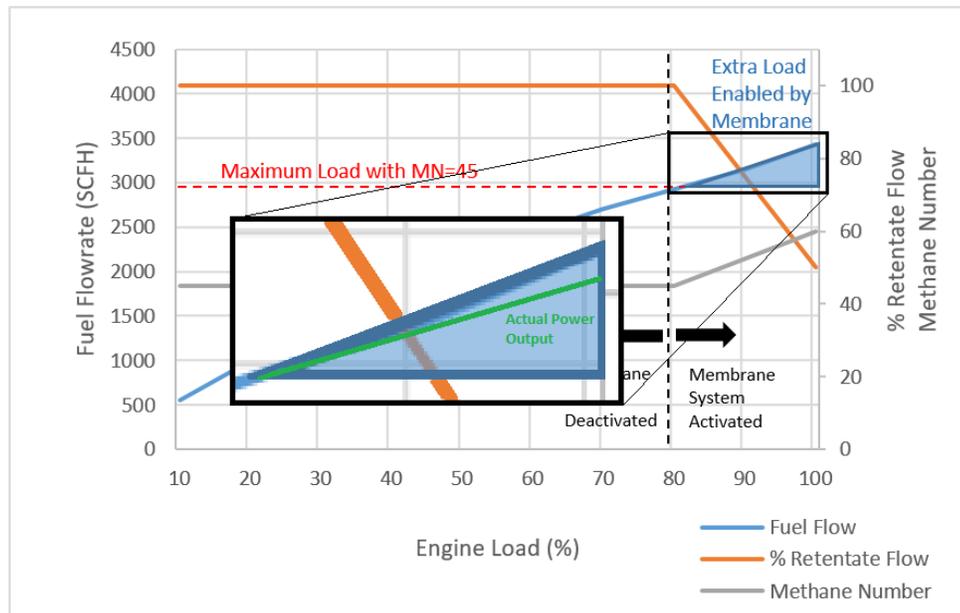


Figure 34: Power output of engine accounting for HP required for recompression

### 4.3. Staged Membrane Configuration

To increase the efficiency of the membrane separator a series of membrane modules connected in a system was investigated. The goal of this was to maintain the same % retentate flow while improving MN increase or maintaining the MN increase while gaining more retentate flow. In the proposed configuration, the permeate stream of the first membrane would be sent into the feed of a second

membrane with half the membrane surface area. This would further purify the heavy hydrocarbon permeate stream, creating more usable gas for the engine. Using a 50% retentate flow through the first membrane, the half size second membrane should perform in a similar manner to the first. By combining the retentate stream of the first membrane with the retentate stream of the second membrane the total flow from the system is 75% of the feed stream. Combining these streams gives a fuel gas with a lower MN than a 50% retentate flow from a single membrane, but with much less gas wasted through the permeate stream. This is obtained with the same pressure difference across the entire membrane system and the same mass flow rate into the first membrane, shown in Figure 35.

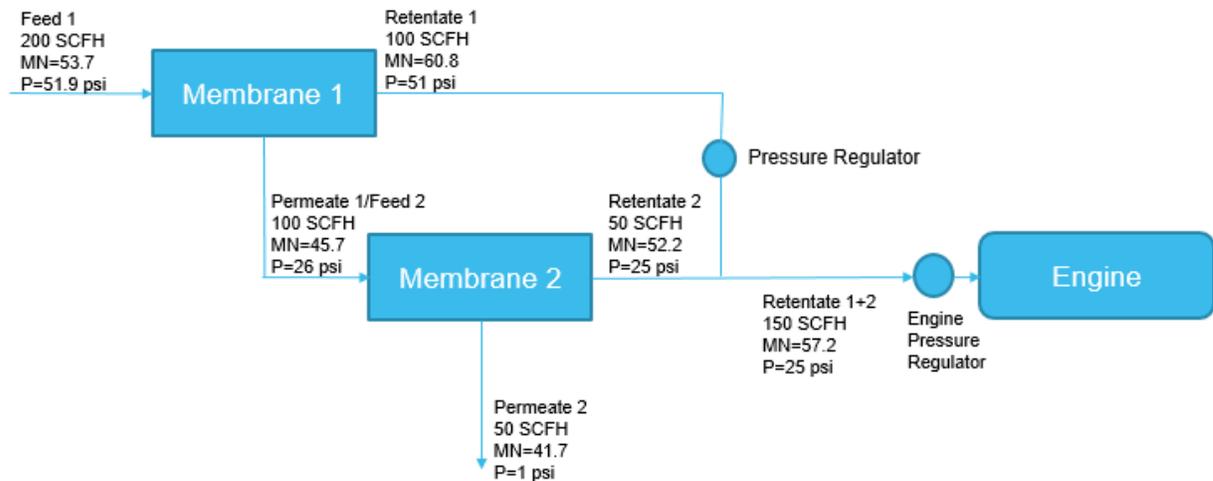


Figure 35: 75% Retentate Flow Staged Membrane Configuration

Since a second membrane was not available, separation data from multiple tests was used to make calculations for a two-stage membrane separator. A Bakken blend was tested in the first stage of the membrane, then a gas with the same composition as the permeate stream was fed through the membrane to simulate the second membrane. The retentate compositions from these two tests were combined to give a total MN improvement of the entire system.

Additional membrane stages could be added using the same basic configuration for each stage. It is anticipated that a larger overall system differential pressure would be needed as stages are added. There are many multi-stage membrane configurations that have been studied [13]. More work is required on multi-stage configurations to quantify advantages and disadvantages for this application.

## 5. Conclusion

The purpose of this work was to examine how a gas permeable membrane would perform at increasing MN by separating heavy hydrocarbons from natural gas, specifically for compressors at shale gas wells. Performance characteristics of the membrane module and trends were tested and recorded to help explain how the membrane behaved at different operating conditions. Trends were used to provide guidance on how to optimize the flow, pressure, and sizing of a membrane separator system to condition fuel for a compressor engine.

### 5.1. Heavy Hydrocarbon Separation

The POMS membrane module was able to separate heavy hydrocarbons from a heavy hydrocarbon rich natural gas stream to increase the methane number. A higher pressure difference between the permeate and retentate side of the membrane led to a larger reduction in the amount of hydrocarbons in the retentate stream, but also a smaller flow rate of gas. A trade-off must be made between the MN increase and the amount of retentate flow that feeds the engine. A larger MN increase with the same amount of retentate flow, or more retentate flow with the same MN increase can be achieved by properly sizing the membrane material surface area based on the feed gas composition, desired flow rates, and required MN increase. More testing would have to be done with different sizes of membrane surface areas to be able to predict the correct sizing.

- A MN increase of 54 to 74 is possible with a pressure difference of 50 psi and feed mass flow rate of 100 SCFH. In this case there is very low retentate flow; not enough to supply the engine.
- A lower % retentate flow results in a higher MN increase, but the permeate flow is larger.

- A 100 psi pressure increase on both sides of the membrane reduces MN increase from 22 to 4. It is best to use the lowest possible permeate pressure.
- A higher feed mass flow rate can be used to create a larger pressure difference, which increases flow, but the lower residence time has a negative effect on separation.
- Temperatures from 40-115°F of the membrane and feed gas did not have a significant effect on separation.
- A lower MN feed gas (more heavy hydrocarbons) has a lower % retentate flow at similar pressure differences because heavier hydrocarbons pass through the membrane easier than lighter hydrocarbons.

## **5.2. Selectivity of Individual Species**

It was found that the individual selectivities of each gas was higher than the selectivity of a particular gas when it was mixed with other heavy hydrocarbons. This is most likely due to the swelling effect the other heavy hydrocarbons have on the membrane material. The swelling of the membrane increases the distance absorbed gas molecules have to travel through the membrane and lowers the diffusion rate. A lower diffusion rate leads to a lower selectivity.

- The selectivities of heavier hydrocarbons are higher than lighter hydrocarbons which creates a permeate stream with higher levels of heavy hydrocarbons and a retentate stream with reduced levels of heavy hydrocarbons.
- The presence of other hydrocarbons reduce the selectivity of a single species by saturating and swelling the membrane.

## **5.3. Integration into Compressor Engine System**

A membrane module, like the one tested, could be used on a well site compressor engine to improve the MN of gas flowing into the engine by removing heavy hydrocarbons from the natural gas

coming out of the well. A reciprocating compressor skid pressurizes gas to 500-1100 psi to move it to a processing station or larger pipeline. This high pressure gas source could be used to provide a large pressure difference across the membrane to increase the effectiveness of the membrane module further than what was tested. By using backpressure regulators and feeding the permeate stream back into the low pressure side of the compressor, a passive system could be created to improve fuel quality without complex control and monitoring.

- If flaring is not an option, the recompression of the permeate stream takes mechanical energy from the compressor engine.
- The energy required for compression increases with lower % retentate flow and higher pressure difference across the membrane.
- Because the membrane performs better with lower absolute pressures it would be better to use an auxiliary compressor instead of a pressure difference across one of the main compressor stages.
- Considering the power required to recompress gas, it is most efficient to run the membrane at 25% retentate flow. In this case the feed flow to the membrane is about 15% of the total flow through the compressor engine system.
- Active membrane control can be used to deactivate the membrane system when load is below the derated power. This significantly improves system efficiency because the membrane is not needed at lower loads.

## References

- [1] C. McFarden, "Stationary Natural Gas Engine Selection and Adjustments as a Function of Fuel Compositions," Cummins Inc, 2013.
- [2] EPA, "AP 42 Compilation of Air Pollutant Emission Factors," United States Environmental Protection Agency, Washington DC, 2009.
- [3] G. Bourn, "High BTU Gas Effects on Performance and Emissions in a Two-Stroke Integral Engine," Southwest Research Institute, San Antonio, 2006.
- [4] R. Crawford, "Effects of Gas Compositions on Emissions of Heavy-Duty Natural Gas Engines," Sierra Research, Inc, Sacramento, 2009.
- [5] C. Inc, *Engine Performance Data QSK19G-G3 FR 4704*, Columbus, Indiana: Cummins Inc, 2016.
- [6] North Dakota Oil & Gas Division, "Overview of the Petroleum Geology of the North Dakota Williston Basin," North Dakota Geological Survey, [Online]. Available: <https://www.dmr.nd.gov/ndgs/resources/>. [Accessed 2016].
- [7] S. Joshi, "Reduce Emissions for Compressor Stations in Condensate-rich Shale Gas Plays by Reducing Heavy Hydrocarbons in Fuel Gas," Gas Machinery Conference, Nashville, 2011.
- [8] C. Inc, *Generator set data sheet 1400 kW continuous*, Columbus Indiana: Cummins Inc, 2009.
- [9] M. J. Landrum, "PROCESS TO REMOVE NITROGEN AND/OR CARBON DIOXIDE FROM METHANE-CONTAINING STREAMS". United States of America Patent 7,314,503 B2, 1 January 2008.

- [10] R. W. Baker, "Natural Gas Processing with Membranes: An Overview," *Industrail & Engineering Chemistry Research Ind.*, no. 47.7, pp. 2109-2121, 2008.
- [11] N. Schmeling, "Functionalized copolyimide membranes for the separation of gaseous and liquid mixtures," *Beilstein Journal of Organic Chemistry*, vol. 1, no. 6, pp. 789-800, 2010.
- [12] H. Lin, "Membrane selective exchange process for dilute methane recovery," *Journal of Membrane Science*, vol. 1, no. 469, pp. 11-18, 2014.
- [13] J. Seader, *Separation Process Principals: Chemical and Biochemical Operations*, Hoboken, NJ: John Wiley & Sons, Inc, 2011.
- [14] A. J. Kidnay, *Fundamentals of Natural Gas Processing*, Boca Raton, FL: CRC Press, 2011.
- [15] L. Kaaeid, "New Membrane Applications in Gas Processing," Membrane Technology Research, Inc., Menlo Park, CA.
- [16] J. P. Montoya, "Membrane Gas Exchange Using Hollow Fiber Membranes to Separate Gases from Liquid and Gaseous Streams," MedArray, Ann Arbor, 2010.
- [17] "Control Room Emissions Analyzers," Colorado State University Engines and Energy Conversion Lab, Fort Collins.
- [18] [Online]. Available: <http://www.cumminswestport.com/fuel-quality-calculator>.
- [19] Gas Processors Suppliers Association, "Engineering Data Book FPS Verson Volume 1 Sections 1-15," Gas Processors Suppliers Association, Tulsa, 1998.

- [20] J. Schultz, "Membranes for separation of higher hydrocarbons from methane," *Journal of Membrane Science*, vol. 110, pp. 37-45, 1996.
- [21] T. Brinkmann, "Theoretical and Experimental Investigations of Flat Sheet Membrane Module Types for High Capacity Gas Separation Applications," *Chemie Ingenieur Technik*, vol. 85, no. 8, pp. 1210-1220, 2013.
- [22] W. J. Koros, "Terminology for Membranes and Membrane Processes," International Union of Pure and Applied Chemistry, 1996.

Appendix I

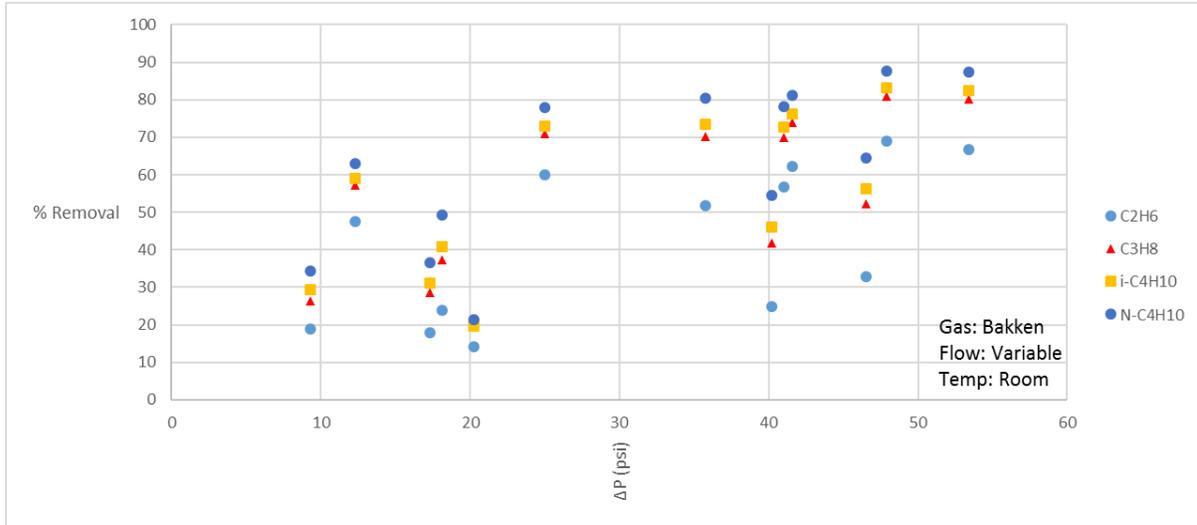


Figure 36: % Removal of ethane, propane, n-butane, and iso-butane in the Bakken blend at various pressure differentials across the membrane

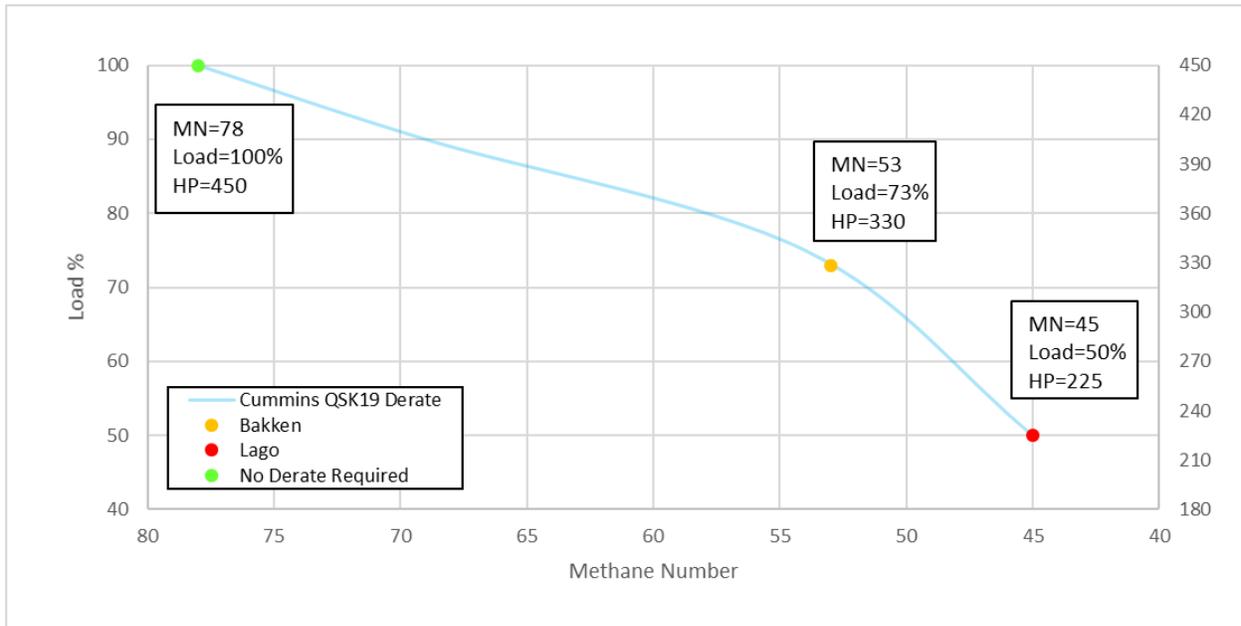


Figure 37: Cummins engine derate curve showing MN of gases tested and the associated derate and maximum horsepower when using those gases before treatment

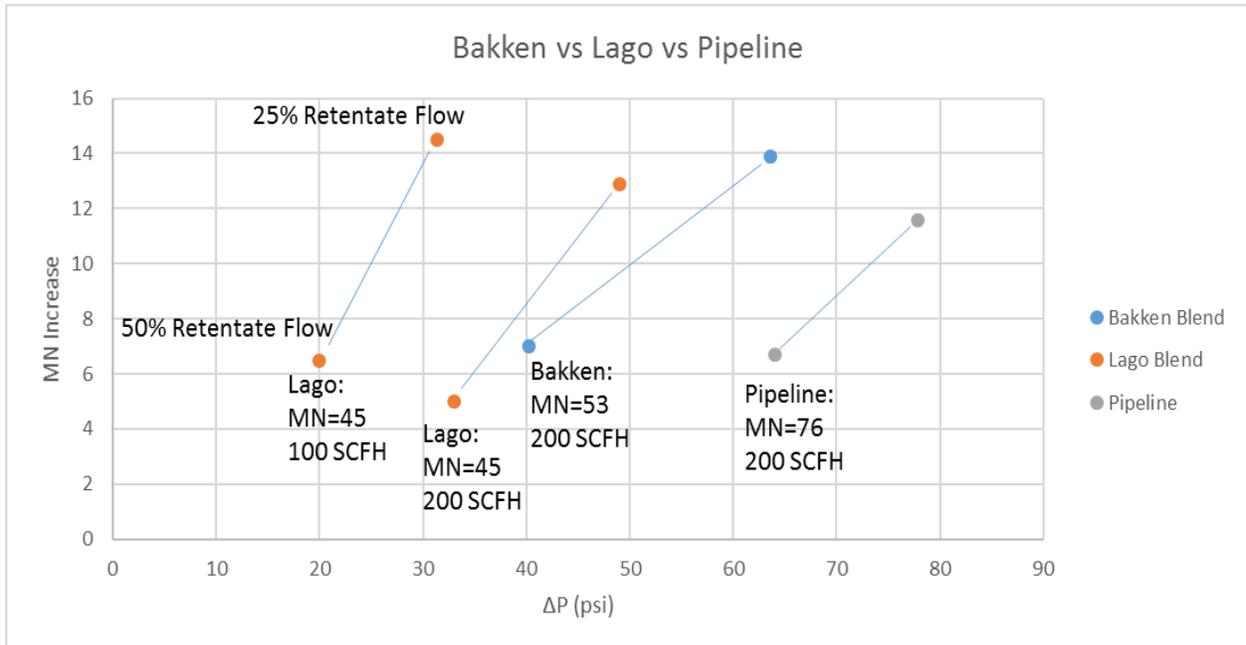


Figure 38: MN increase achieved using a pressure differential to maintain 25% and 50% retentate flow at 100 SCFH and 200 SCFH feed mass flow rates for the Lago, Bakken, and pipeline blend



Figure 39: Membrane module testing setup

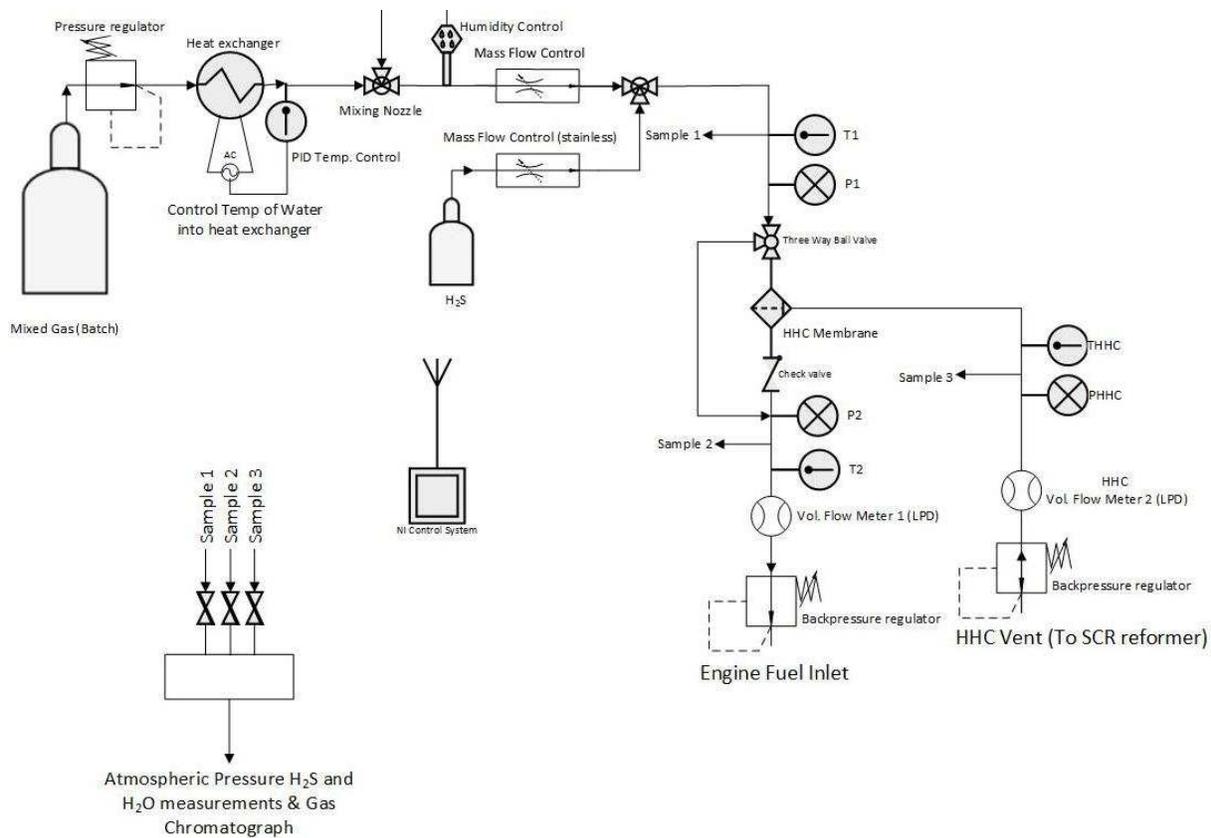


Figure 40: Schematic of membrane module testing setup

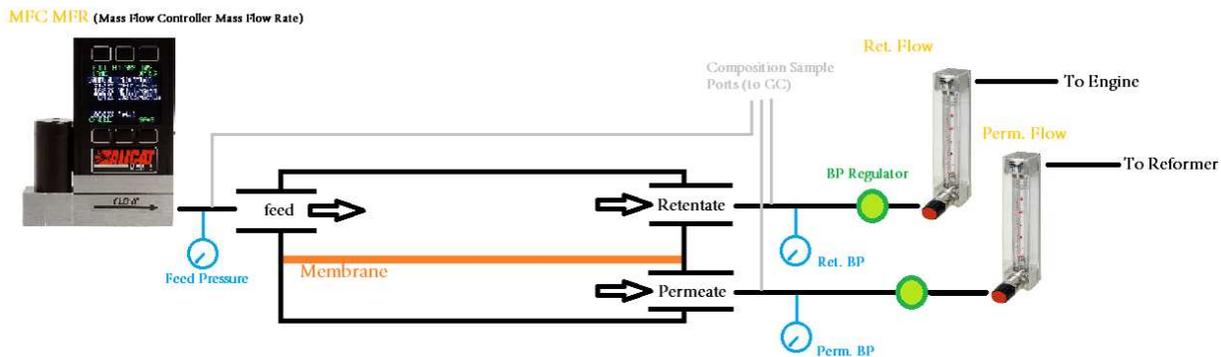


Figure 41: Simplified schematic of membrane module testing setup showing critical measurement devices

Table 8: Sample data showing increase or decrease of composition mol% of each species in the retentate and permeate stream. Test conditions: Bakken blend, feed pressure = 60psi, permeate pressure = 39.8psi, temperature = room, % retentate flow = 41%

Species	Composition (mol%)					
	Feed	Retentate	Increase/Decrease	Permeate	Increase/Decrease	
<u>CH4</u>	58.42%	62.45%	4.03%	58.11%	-0.31%	
<u>C2H6</u>	22.47%	19.26%	-3.20%	22.48%	0.01%	
<u>C3H8</u>	10.91%	8.80%	-2.11%	11.04%	0.14%	
<u>i-C4H10</u>	0.84%	0.68%	-0.17%	0.87%	0.03%	
<u>N-C4H10</u>	1.63%	1.28%	-0.35%	1.73%	0.10%	
<u>i-C5H12</u>	0.20%	0.16%	-0.04%	0.23%	0.02%	
<u>n-C5H12</u>	0.29%	0.23%	-0.06%	0.34%	0.05%	
<u>C6H14</u>	0.08%	0.06%	-0.02%	0.11%	0.03%	
<u>C7H16</u>	0.04%	0.02%	-0.02%	0.07%	0.03%	
<u>N2</u>	4.29%	6.34%	2.05%	4.18%	-0.10%	
<u>CO2</u>	0.84%	0.72%	-0.12%	0.84%	0.00%	
<b>MN</b>	<b>54.1</b>	<b>57.1</b>		<b>53.7</b>		

Table 9: Composition data from section 3.2.2 – System operating pressure, showing increase or decrease of the retentate stream when increasing permeate and retentate pressure at the same rate using the same pressure difference across the membrane.

	Feed	Increase/Decrease		
		Low Pressure	Med. Pressure	High Pressure
<u>CH4</u>	58.42%	11.18%	7.69%	3.95%
<u>C2H6</u>	21.00%	-15.21%	-9.98%	-4.41%
<u>C3H8</u>	10.58%	-9.01%	-6.10%	-2.70%
<u>i-C4H10</u>	2.01%	-1.75%	-1.21%	-0.55%
<u>N-C4H10</u>	0.63%	-0.57%	-0.40%	-0.18%
<u>i-C5H12</u>	0.24%	-0.22%	-0.16%	-0.07%
<u>n-C5H12</u>	0.32%	-0.29%	-0.21%	-0.10%
<u>C6H14</u>	0.06%	-0.06%	-0.04%	-0.02%
<u>C7H16</u>	0.04%	-0.04%	-0.04%	-0.01%
<u>N2</u>	5.85%	16.61%	10.85%	4.27%
<u>CO2</u>	0.85%	-0.63%	-0.40%	-0.16%
<b>MN</b>	<b>54.5</b>	<b>76.0</b>	<b>67.0</b>	<b>59.0</b>

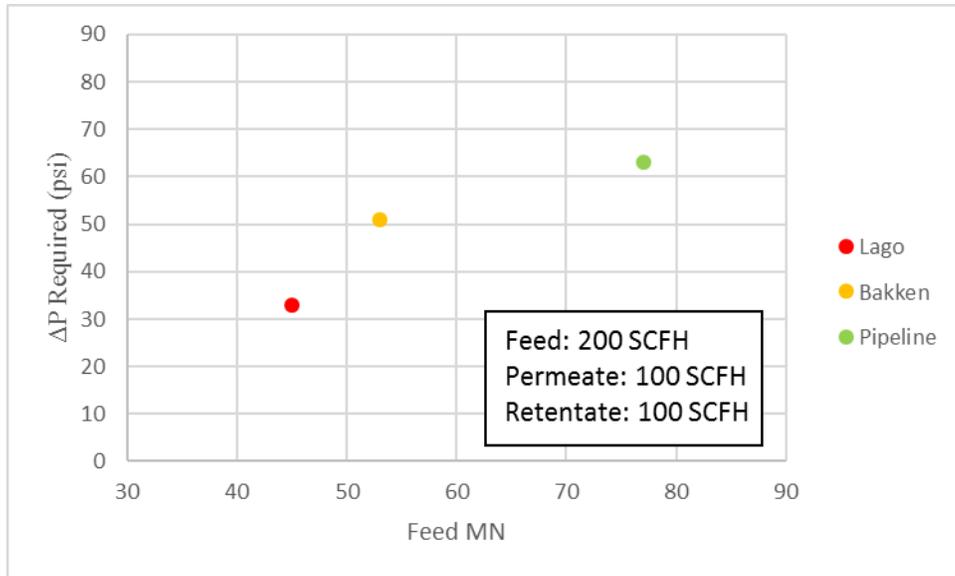


Figure 42: Showing the pressure differential required to maintain a 50% retentate flow with different compositions. Gases with more heavy hydrocarbons and a lower MN require less pressure difference because the permeance of the gas is lower

