NON CONFIDENTIAL FINAL OUTCOMES REPORT

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1. ABSTRACT

A flue gas catalytic membrane tri-reforming process (F3R™) has been developed (Figure 1). This process is directed towards a system for the conversion of CO_2 present in combustion flue gas to chemical products of economic value. The technology is envisaged as a bolt-on device able to rehabilitate CO_2 from the emission gases of facilities such as power plants, oil sand upgrader plants and other factories. The CO_2 is rehabilitated into synthesis gas (CO and H_2) for onward processing towards useful substances such as ammonia, fuels and methanol. Previously there has been little work exploring the possibility of using carbon rehabilitation with feedstocks such as low-cost methane. This test unit has provided a proof of concept that the tri-reforming reaction can work and has thereby extended membrane design technology towards integration into a whole process system for value-added carbon-based products from flue gas.

Ultimately, the F3R™ process may be adaptable to process heavier hydrocarbons (e.g naphtha, pyrolized biomass) using a combination of cracking, reforming, and water-gas shift chemistry in compact integrated systems suitable for dispersed air CO_2 capture, fuel cell power generation systems and stranded gas monetization.

To put the importance of our F3R™ technology into perspective, if the off gases from all oil sands upgraders in Alberta were to be successfully utilised using this process, the CO_2 emissions to the atmosphere would be reduced by 1 million tonnes in total each year. This reduction is equal to taking 210,000 cars off the road every year and is equal to the total yearly energy needs of 50,000 homes.

In addition, Alberta's oil and natural gas industry is emitting a minimum of 25 to 50 percent more methane than current estimates indicate. A clear pattern of energy waste is occurring across Canada – a problem worth a minimum of $530 million dollars (CAD) of natural gas a year, or enough natural gas to heat nearly every home in Alberta. Moreover, our F3R™ Process Technology can potentially replace all the current steam methane reformers in Alberta with huge GHG savings. The F3R™Process will therefore help in maintaining or improving provincial GDPs across Canada while also reducing emissions and will retain and, in some instances, reshape industries so they fit into a low-emissions economy and foster job creation in new giant chemical complexes. The worldwide search for such chemical complexes, the small pool of them identified in Alberta and Canada's continued reliance on resource extraction will help cushion the challenges that Canada will face as it tries to decouple its emissions and economy by 2030.

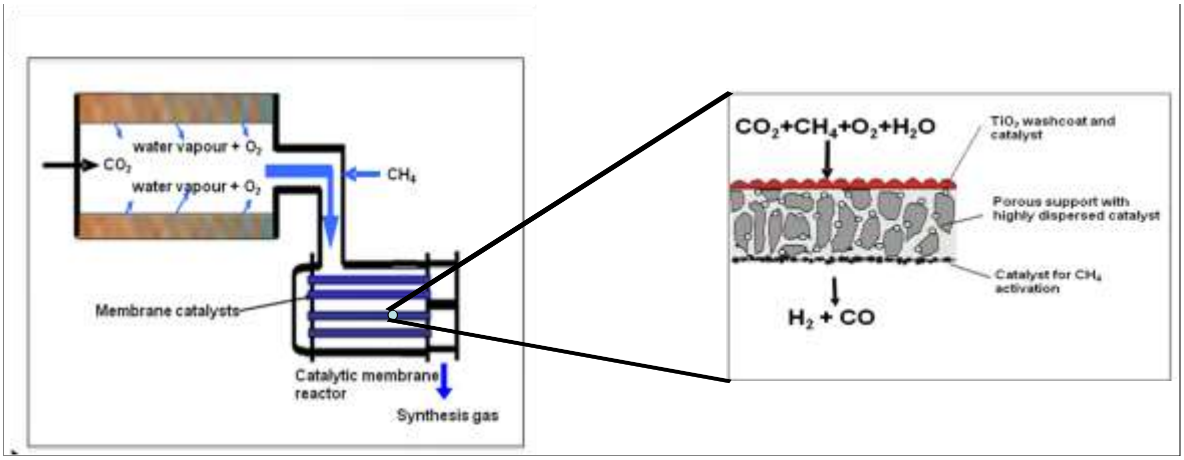


Figure 1: The Flue Gas Catalytic Membrane Reactor (F3R™) Process

2. EXECUTIVE SUMMARY

2.1 Intent of the Project/Goal

The intent of the project is to foster the technological developments that create new carbon-based, value-added products and markets that transform carbon emission into a valuable resource. The goal is to develop a catalytic membrane reactor process where the CO_2 in flue gas is rehabilitated into value-added chemical products. The reactor itself consists of gamma-alumina (g-Al_2O_3) porous ceramic supports, which provide a robust structure for creating different catalytic coatings capable of promoting chemical transformations. The reactor is fed using the flue exhaust gases consisting of carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2) together with the deliberate inclusion of CH_4. At elevated temperatures, the highly dispersed catalyst facilitates the breakdown of the CH_4 and CO_2 and then reconstitutes the resulting mixture using the O_2 already present in the flue gas to form a mixture of CO and H_2 which is diluted in the nitrogen stream. The CO and H_2 mixture called ‘’syngas’’ or ‘’synthesis gas’’ is the backbone of the heavy chemicals and petrochemicals industry and is used for the manufacture of highly useful chemical constituents such as Fischer-Tropsch fuels, hydrogen and ammonia/urea. The nitrogen stream also offers an opportunity to produce bulk nitrogen for the commercial merchant industrial gas market.

2.2 Key Results/Deliverables

Over the period 1st July 2014 – 31st August 2017, Robert Gordon University (RGU) researchers established a proof-of-concept and developed an optimized miniature scaled prototype reactor which has helped to address a number of key challenges presented in the reactor’s performance including temperature and scalability. Work has been carried out to address research and development issues associated with the scale-up of the technology. This includes the size and shape of the membrane tubes, scale-up factor considerations of membrane pore size (we have assessed pore size effects over a scale-up factor of 40,000%) and consideration of membrane tubular dimensions (we have assessed reactor dimension by a scale factor of 250%).

In this work we have generated a map of process variables that define the boundaries of optimum syngas production suitable for further conversion to value-added products. These variables include feed gas composition, flow rate, and temperature, pressure, mixing configuration and selection and dispersion of reforming catalyst. We have optimised the unit and process design to help manage the technology risk; developed repeatable and relaible techniques for manufacturing the membrane catalysts reliably and investigated experimentally the system tolerance to flue gas impurities (SO_2 and NO_2 gases).

The result is an optimum design of a scaled miniature prototype unit that has resulted in 100% conversion of CH_4 and CO_2 respectively and importantly producing a syngas composition suitable for value-added chemicals production. The technical approach delivers reactors that are mechanically strong, physically compact, and able to deal with variable flow rates.

2.3 Key Conclusions

CH_4 and CO_2 reactions have been studied under controlled temperature programs and the optimum temperature range has been discovered. The membrane support affects in a major way, the activity of the supported rhodium (Rh) catalyst for the flue gas methane reforming. Basic oxides such as magnesia (MgO) and gamma-alumina (g-Al_2O_3) have shown to promote the reaction and are also thought to catalyze the gasification of coke with steam and so help prevent deposition of carbon and are therefore the most promising supports as they both provide high surface areas and are thermo-stable. Scale-up has been confirmed for membrane pore size and tube diameter. In flue gas methane reforming, several reactions are occurring simultaneously and finding the correct ratios of reactants is not easy but it was found that oxygen (O_2) was always completely consumed as it seems to have a high affinity for active sites on the catalyst causing it to react very quickly. The membranes were stable to NO_2 and SO_2.

2.4 Recommendations For Next Steps

Funding is sought to conduct an intial 2 year industrialisation and prototype development and demonstration project. Such a programme will address the challenges of designing the system to avoid membrane degradation due to particulates and acid gases; manufacturing the membrane catalysts in large quantities; and assessing the issues associated with operating the membranes at a real power plant where there are substantial variations in operating parameters day-to-day. A subsequent 2 year “follow on” project would scale-up to demonstration plant scale (~250MW), with the first full scale power plant implementation around 2 years later (~750-1500MW). This development will deliver a competetively low energy zero CO_2-emission system in time to serve the large and completely new market in Alberta’s industrial large CO_2 emitters where there is a mandatory legislative requirement to achieve specified reductions of greenhouse gases.

Figure 2: REMOVED COMMERCIAL IN CONFIDENCE

3. BACKGROUND OF THE PROBLEM WITH GLOBAL WARMING

3.1 The Problem with Global Warming

The 1°C (1.8°F) warming of the earth fueled by manmade greenhouse gas emissions has already caused sea levels to rise by nearly a foot, Arctic/Antarctic sea ice to vanish at a quickening pace; very extreme weather events such as droughts, rising temperatures, floods, hurricanes, tornados, monsoons and heat waves/wildfires are now more frequent and severe. If warming attains 1.5°C (2.3°F), coral ecosystems and low-lying small island states could even disappear completely. Crossing the 2°C (3.6°F) threshold would put humanity outside the "safe" envelop of warming prescribed by scientists and policymakers. Carbon dioxide (CO_2), noted for its high greenhouse effect, is produced as a by-product in the manufacture of ammonia, iron and steel respectively; during steam methane reforming, fossil power generation and as waste by-product in the processing of chemicals and synthetic/unconventional fuels. Natural gas (CH_4) itself, in some cases contains sizeable concentrations of CO_2. Most of the CO_2 produced in the above processes is simply dumped into the air where it accumulates and over time causes global warming. In May 2017, monthly global carbon dioxide peaked at 409.65 parts per million.

3.1.1 Carbon Dioxide Emissions

The current drive towards the development of new, energy-efficient and eco-friendly catalytic processes which are capable of utilizing exhaust gases containing CO_2 as the raw material for chemical complexes has been identified as one of the greatest challenges facing the environment. These exhaust stream sources are available in power plants and chemical production complexes. Alberta is home to the largest oil sands industry and can therefore utilize the CO_2 as well as upgrader off-gases as the raw materials in new complexes which can be integrated into its existing infrastructure using the Advanced Inorganic Membranes (AIM) for CO_2 Conversion to Synthesis Gas.

Currently approximately 81% of the global primary energy production is through the use of fossil fuels. This widespread consumption of fossil fuels in the current global energy mix is considered as being the major source of anthropogenic emissions of CO_2. Infarct, the global energy sector is held responsible for about 84% of worldwide CO_2 emissions and about 64% of all global greenhouse gas (GHG) emissions. In addition, many industrial and environmental issues have to be addressed to secure the long-term stability of the industry. The upgrading of heavy petroleum feedstocks, which are very bulky and hydrogen lean molecules, generally entails the injection of huge amounts of hydrogen gas during upgrading. Typically, the hydrogen is produced through methane steam reformation reactions which need the use of large amounts steam. The tri-reforming process which is capable of utilizing flue gas directly has recently received attention for its ability to consume greenhouse gases like methane and CO_2 to generate synthesis gas (syngas) with a higher

H_2: CO ratio that is desired for Fischer-Tropsch synthesis (FTS). Flue gas methane reforming therefore involves a synergetic combination of CO_2 reforming, steam reforming, and partial oxidation of methane in a single reactor.

An Annual Greenhouse Gas Index (AGGI) has been defined as the ratio of the total direct radiative forcing due to long-lived greenhouse gases for any year for which adequate global measurements exist to that which was present in 1990. 1990 was chosen because it is the baseline year for the Kyoto Protocol. This index, shown with the direct radiative forcing values in Table 1, is a measure of the interannual changes in conditions that affect carbon dioxide emission and uptake, methane and nitrous oxide sources and sinks, the decline in the atmospheric abundance of ozone-depleting chemicals related to the Montreal Protocol, and the increase in their substitutes (HCFCs and HFCs). Most of this increase is related to CO_2. For 2016, the AGGI was **1.40** (representing an increase in total direct radiative forcing of 40% since 1990). Natural gas (CH_4) itself, in some cases contains sizeable concentrations of CO_2.

Table 1: Global Radiative Forcing, CO_2-Equivalent Mixing Ratio, and the AGGI (2010-2016)

Global Radiative Forcing (W m^{-2})								CO_2-equivalent (ppm) (Total)	AGGI	
Year	**CO_2**	**CH_4**	**N_2O**	**CFC12**	**CFC11**	**15-Minor**	**Total**		**1990 = 1**	**% Change**
2010	1.791	0.491	0.175	0.170	0.060	0.106	2.792	468	1.29	1.7
2011	1.817	0.492	0.178	0.169	0.059	0.109	2.824	471	1.305	1.5
2012	1.845	0.494	0.181	0.168	0.059	0.111	2.858	474	1.32	1.5
2013	1.882	0.496	0.183	0.167	0.058	0.114	2.900	478	1.34	2.0
2014	1.908	0.499	0.187	0.166	0.058	0.116	2.934	481	1.356	1.6
2015	1.938	0.504	0.190	0.165	0.058	0.118	2.973	485	1.374	1.8
2016	1.985	0.507	0.193	0.164	0.057	0.121	3.027	489	1.399	2.5

Source: Adapted from THE NOAA ANNUAL GREENHOUSE GAS INDEX (AGGI), Updated Spring 2017

3.2 Characterization of Flue Gas

3.2.1 Characterization of Volumetric Composition of Flue Gas

A characterization of volumetric composition of flue gas from power plant and numerous industrial processes is presented in Table 2. With respect to the difference between recovering CO_2 from flue gas versus concentrated CO_2 sources (fermentation sources, anhydrous ammonia off gas, ethylene oxide off gas, titanium dioxide product, and some natural wells) – this is essentially a *day versus night* difference in terms of economic magnitude. When considering the other concentrated CO_2 sources such as ethylene oxide, the raw gas is concentrated, however, contains numerous minor constituents in the raw gas, as would be in some natural wells, which can require much more processing equipment, and often special front end plant metallurgy – as with ethylene oxide; and in the case of natural wells, and other concentrated sources. Outside of most ethanol sources, catalytic oxidation is then a further requirement, plus often much more process equipment.

The CO_2 found in coal fired power plant off gas is among the dirtiest forms of CO_2, even with many of the improvements in the plants; still this will yield sulfur and nitrogen compounds

(SO_x and NO_x); among other rather nasty compounds and elements such as H_2S, COS, NH_3, H_2SO_4, condensed water and Mercaptans; all dumped into the atmosphere. Flue gas discharged during the production of energy such as electric power, and gas discharged from industrial processes such as the manufacture of iron and steel, and cement. CO_2 in gas discharged from power stations amounts to 12-15% for coal-fired power generation and 3-8% for LNG-fired power generation. In iron and steel plants, CO_2 in gas from blast furnaces and sintering furnaces amounts to 22-25%.

When compared to gas treated in the petroleum, natural gas and ammonia plants, flue gas from fossil-fired power plants has unique characteristics. These characteristics are primary variables to be considered for process development. The primary characteristics are low pressure, presence of oxygen, presence of pollutants (NO_x, SO_x, and particulates), high temperature and huge gas flow rates.

Table 2: Characterisation of Volumetric Composition of Flue Gas from Power Plant and Industrial Processes

Plant Type/Industrial Process Stream	N_2	H_2O	O_2	CO	CO_2	CH_4	H_2	Ar	NO_x	SO_x	H_2S
Coal (Flue gas)	74.0	8.0	3.0		14.0		0.0	1.0	0.0	0.1	
Coal (Flue gas)	71.4	10.8	4.3		12.6		0.0	0.9	0.0	0.0	
Fuel Oil (Flue gas)	73.0	13.0	3.0		11.0		0.0		trace	trace	
Natural Gas (Flue gas)	71.0	17.0	3.0		9.0		0.0		0.0	0.0	
Natural Gas (Flue gas)	70.9	17.3	2.4		8.6		0.0	0.9			
Gas Turbine (Flue gas)	75.7	7.8	13.0		3.5		0.0				
Gas Turbine (Flue gas)	75.0	6.9	13.8		3.4		0.0	0.9	0.0		
Gas Turbine (Flue gas)	74.4	8.3	12.6	0.0	3.8	0.0	0.0	0.9	0.0	0.0	0.0
Coal IGCC (Flue gas)	0.7	1.7	0.0	1.7	38.6	0.1	56.7	0.6	0.0	0.0	0.0
Urea (Steam Reformer Flue Gas)	68.0	22.0	1.0	0.0	8.0	0.0	0.0	1.0	trace	trace	
Typical Refinery (Flue Gas)	77.0	14.0	3.0	0.0	7.0	0.0	0.0				
Hydrogen Plant (SMR)	0.0	29.0	0.0	1.0	12.0	8.0	50.0	0.0	0.0	0.0	
Steel (Conventional Blast Furnace)	56.0	0.0	0.0	21.0	20.0	0.0	3.0	0.0	0.0	0.0	
Steel Plant (Corex)	12.0	1.0	0.0	44.0	24.0	2.0	17.0	0.0	0.0		
Steel Plant (CCF)	9.0	0.0	0.0	24.0	44.0	0.0	20.0	0.0			
Cement Plant (Flue Gas)	61.0	13.0	8.0		19.0						
Ammonia Production (Reformer)*	trace	5.0			95.0	trace	trace				
Ethanol (Fermentation)**		1.0			99.0						
Ethylene (Process Stream)*					100.0						
Ethylene Oxide (Process Stream)*					100.0						

*These processes also have flue gas with very high CO_2 content; **relatively clean source for food grade CO_2

3.2.2 Characterization of CO_2-Laden Flue Gas Flowrates

The off-gas from coal fired cogeneration plants yield a raw content of CO_2 probably 12 – 15% by volume as shown in Table 3. What is needed to produce a purified merchant or even a crude liquid CO_2 from flue gas is a whole additional plant, placed in front of the liquefaction / purification plant, similar to that spoken for the case of a concentrated by-product from ethanol, as shown in Table 2 above. This requirement for a whole separate plant which concentrates the CO_2, thus making liquefaction and purification possible has always made flue gas recovery economically impossible in the developed world. Some small flue gas based CO_2 plants are operating in the developing world, due to selling prices for merchant CO_2 being very expensive versus much less in the developed world.

Table 3: Characterization of Fossil-Fuel Combustion Flue Gas Flowrates from Power Generation

Characteristic	Value (Range)
Pressure	Atmospheric pressure
CO_2 concentration	12 - 15 (%, DVB*) (LNG CC: 3-8%)
N_2 concentration	86.7 – 79.5 (%, DVB*)
O_2 concentration	3.3 - 5.5 (%, DVB*)
Pollutants	Particulates, SO_2 (coal, oil), NO_x
Flue gas flow rate (N m^3/hr)	Very high • 3,400,000 (coal combustion 1,000MW) • 3,000,000 (oil combustion 1,000MW) • 2,500,000 (LNG combustion 1,000MW)

*DVB = dry volume basis

3.2.3 Characterization of CO_2 Uses in Industrial Applications

Table 4 lists the existing and emerging applications of CO_2 in liquid, solid, and gaseous states. The global market for merchant CO_2, measured by the amount of CO_2 sold in the market, which excludes in-plant CO_2 utilized by manufacturers, is estimated to be $3.2 billions/year in 2003 [Carbon Dioxide Utilization and Recovery, EGY0374, BCC Research, Dec. 2004]. Currently, CO_2 is used as refrigerant for food preservation, beverage carbonation agent, supercritical solvent, inert medium (such as fire extinguisher), pressurizing agent, chemical reactant (urea, etc.), neutralizing agent, and as gas for greenhouses. Solid CO_2 (dry ice) has a greater refrigeration effect than water ice. Dry ice is also usually much colder than water ice, and the dry ice sublimates to a gas as it absorbs heat. It should be noted that the use of CO_2 for refrigeration does not directly contribute to reduction of CO_2 emissions. There exist some chemical processes for CO_2 conversion in chemical industry, for which synthesis of urea from ammonia and CO_2 and the reduction of salicylic acid from phenol and CO_2 are representative examples. Urea is used for making various polymer materials and also for producing fertilizers. As an example of the usefulness of salicylic acid, acetyl salicylic acid is used for making Aspirin, a widely used common medicine.

Table 4: Current Status of CO_2 Uses in Various Industrial Applications*

Sectors	Industrial Applications
Chemicals	# CO_2 is used in chemical synthesis and for controlling reactor temperatures. # CO_2 is employed to neutralize alkaline effluents. # CO_2 is used as a blowing agent for polyurethane and polystyrene foam production and for blow molding manufacturing of plastic bottles, and containers. # CO_2 is used under supercritical conditions for purifying or dying polymer, animal or vegetable fibers.
Pharmaceuticals	# CO_2 is used for making chemicals such as salicylic acid and Aspirin; for use as an inert gas, and for supercritical fluid extraction. # CO_2 is used for product transportation at low temperature (-78.8°C or -108.8°F) and also acidification (pH) of wastewater
Foodstuffs	# Liquid CO_2 can be used as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the storage and distribution of foodstuffs. # Packaging of foodstuffs to increase the shelf life of many food products due to its inerting properties and its growth inhibiting effect of CO_2 on micro-organisms. # Stunning of pigs and poultry in slaughterhouses instead of using electrical stunning
Beverage	# Carbonation of beverages such as soft drinks, mineral water or beer # Supercritical CO_2 is used to remove caffeine from coffee beans by extraction. # CO_2 is used as shielding gas for preserving drink quality, and propellant gas for emptying tanks of drinks # CO_2 is also used in drinking water treatment in modern water works together with lime or chalk
Healthcare	# CO_2 produces close-to-physiologic atmospheres for the operation of artificial organs. # CO_2 is used as a component in a mixture of oxygen or air as respiratory stimulant to promote deep breathing. # It is also used for the surgical dilation by intra-abdominal insufflations.
Environment	# Small amount of liquid CO_2 can be used in recycling of waters from Acid Mine Drainage. # Waste water treatment and waste liquid treatment by injection of CO_2 for the pH of liquid effluents. CO_2 is an excellent alternative to sulfuric acid for pH balance control.
Pulp and paper	# CO_2 enables sharp tuning of the pH of recycled mechanical or chemical pulps after an alkaline bleaching. # CO_2 can be used in the Tall Oil neutralization and for increasing the performance of paper machines. # Precipitated calcium carbonate obtained from CO_2 and CaO is used as a whitener for the paper industry
Electronics	# CO_2 is usually used as a cooling medium in environmental testing of electronic devices. # CO_2 can be used to add conductivity to ultra-pure water # CO_2 can also be used as an environmentally friendly supercritical fluid for removing photoresist from wafers
Metals industry	# CO_2 is typically used as an inert gas or for environment protection. # CO_2 is used for red fume suppression during scrap and carbon charging, for nitrogen pick-up reduction during tapping and for bottom stirring. # CO_2 is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production) in the non ferrous metallurgy. # Special grades of CO_2 are used in CO_2 lasers.
Laboratories & analysis	# Supercritical CO_2 is the mobile phase in both supercritical chromatography and supercritical fluid extraction applications.
Safety and others	# CO_2 is used as carbon dioxide snow for fire extinguishers # pH control and regulation of waste waters, swimming pools, etc.

*Carbon Dioxide Utilization and Recovery, EGY0374, BCC Research, Dec. 2004

3.2.4 GDP and Greenhouse Gas Emissions in Canada

Table 5 shows the actual change in greenhouse gas (GHG) emissions in 2005 and 2015 and the change required to meet the 2030 target for each Canadian Province. While all Canadian provinces have experienced a change in their GHG emissions and GDPs between 2005 and 2015, not all have experienced a decoupling of GDP and emissions. At one extreme, Nova Scotia and New Brunswick greatly reduced their emissions but experienced limited GDP growth, while at the other end, Alberta and Saskatchewan had significant growth in both GHG emissions and GDP. With the exception of Nova Scotia and New Brunswick, all Canadian provinces will need to reduce their GHG emissions if they are to meet their individual Intended Nationally Determined Contribution (INDC) targets. For most provinces, the size of this problem cannot be overstated. For example, **Alberta's** GHG emissions grew by 4.1 million tons/year, increasing to 233 million tons in 2005 and to 274 million tons in 2015. If Alberta is to reach its 30 percent GHG emissions reduction target by 2030, it will need to reduce her emissions by 7.4 million tons/year. In contrast, Ontario's

GHG emissions fell by 3.8 million tons/year between 2005 and 2015, requiring it to achieve annual reductions of 1.5 million tons/year between 2015 and 2030 (Table 5). There is no one-size-fits-all approach to GHG emissions reduction. GHG emissions can be reduced by accident such as for example, through the phase-out of coal in Ontario or by design such as through regulations in Quebec which have targeted the use of oil in industrial processes. In some instances, reductions can have economic consequences as witnessed in Nova Scotia's mill and refinery closures or create future risks such as Ontario's decision to replace coal with natural gas. The F3R™Process will help in maintaining or improving provincial GDPs across the whole of Canada while simultaneously reducing GHG emissions. Successful commercialisation of the F3R™Process will therefore help to retain and, in some instances, reshape several industries so that they can fit into a low-GHG emissions economy and in so doing, foster job creation in new giant chemical complexes. The worldwide search for such giant chemical complexes that can be adapted to incorporate the F3R™Process, the small pool of them in Canada; and Canada's continued reliance on resource extraction will help cushion the challenges Canada will face as it tries to transition to a low-carbon economy and decouple its GHG emissions and GDP by greatly reducing emissions while boosting GDP growth by 2030.

Since 2009, Alberta's economy and emissions have been strongly coupled together, with the continued expansion of the petroleum industry and support industries, including transportation, construction and real estate. The fall in the price of crude oil in 2014 had a major impact on Alberta's economy, but not to the same extent on GHG emissions, since construction projects and oil production continued into 2015. Although having the second-highest emissions growth and the fourth-largest GDP growth of any province, Saskatchewan experienced only a minor decline in its GDP in 2015 and no change in emissions. This is due in large part to the diversification of its primarily resource-based economy and industrial base, which rely heavily on emissions-intensive energy sources. Large carbon emitters in Alberta are expected to pay upwards of $1.2 billion a year in levies by 2020 under updated regulations announced on Wednesday, December 6, 2017. The Alberta government however plans a phase-in period and significant funding assistance to make it easier for industry to adapt to the new regime, while offsets and credits mean government will take in closer to $800 million. The new regulations are intended to provide incentives to industries for reducing emissions, with facilities below a set level of emissions rewarded and those above it penalized. The new rules are expected to reduce emissions by 20 million tonnes by 2020, and 50 million tonnes by 2030, about the same as the emissions from 11.5 million cars. The new structure, called the Carbon Competitiveness Incentives (CCI), came into effect on January 1, 2018 and applies to facilities like oil sands operations, cement plants and fertilizer production that produce more than 100,000 tonnes of carbon dioxide a year. Industry will only have to pay 50 per cent of the costs in 2018, moving to 75 per cent for 2019, before the full regulations take force by 2020. The regulations also set longer-term incentives for improved performance, with the amount large emitters are allowed to produce without costs reduced by one per cent a year. Overall, the large emitter regulations exempt much of the facility emissions from the carbon levy in an effort to allow them to remain competitive against jurisdictions with less stringent regulations. The government said the $1.4 billion in funding announced Wednesday, December 6, 2017 will also help industry adapt and increase efficiencies before the full costs of the new regulations take force, including $440 million specifically for steam-based oil sands operations to improve efficiencies and reduce emissions.

Table 5: Actual Change in GHG Emissions for 2005 and 2015, and the Change Required to Meet 2030 GHG Emissions Target in Canada

Province	GHG Emissions (Million Tons/Year)			Actual Change (Million Tons)	Required Change (Million Tons)
	2005	**2015**	**2030 (Target)**	**2005-2015**	**2015-2030**
Newfoundland and Labrador	10.1	10.3	7.1	0.02	-0.02
Prince Edward Island	2.1	1.8	1.4	-0.03	-0.02
Nova Scotia	23.2	16.2	16.2	-0.7	0.0
New Bronwick	20.3	14.1	14.2	-0.6	0.0
Quebec	88.9	80.1	62.2	-0.9	-1.2
Ontario	204.0	166.0	142.8	-3.8	-1.5
Manitoba	20.6	20.8	14.4	0.02	-0.4
Saskatchewan	69.5	75.0	48.7	0.6	-1.8
Alberta	**233.0**	**274.0**	**163.1**	**4.1**	**-7.4**
British Columbia	63.9	60.9	44.7	-0.3	-1.1
Total (Canada)	735.6	719.2	514.8	-1.6	-13.6

3.3 Environmental Impact of the Oil Sands

Table 6 presents the oil sands criteria air contaminants (CAC) emissions versus the Canadian total. Extracting the viscous, bituminous sands and processing into products that are usable on a large scale is a technically complex and energy-intensive process that also creates associated environmental impact making it correspondingly troublesome and costly to reduce. Though billions have been spent by producers to reduce both local pollution and global greenhouse gas impacts with significant success, oil sands production results in more land disturbance, more use of water, and more greenhouse gas (GHG) emissions per barrel produced than conventional light oil production.

In Canada, the constitution grants responsibility for management of natural resources to provinces. As a result, most oil sands exploration, production and upgrading lies within the jurisdiction of the province of Alberta and do not therefore require any approval from the federal government. The federal government however plays a larger role in pipeline and other inter-provincial and international transportation, as well as when a project triggers federal authority such as Parks Canada or Health Canada. The Canadian federal government has not yet become involved in regulating GHG emissions and this has been left to the provinces to take action.

3.3.1 Air pollution

Oil sands extraction and upgrading as with many industrial processes, produces regional air pollution that can cause huge damage to both terrestrial and aquatic ecosystems if accumulated in significantly enough concentrations. Furthermore human health can be endangered by air pollution as witnessed in the most polluted cities and industrial areas around the world today. Oil sands processing emit criteria air contaminants (CAC: NO_x, SO_x, Particulate Matter, Volatile Organic Compounds, CO, and NH_3), heavy metals (cadmium, mercury, lead and vanadium), polycyclic aromatic hydrocarbons (PAHs) and Total Reduced Sulphur (including H_2S). Though the CAC emission levels are substantial, in most cases they make up only a small percentages of Canada’s total (see Table 6)

Mining emissions, typically higher in volatile organic compounds (VOCs), arise from open-face mines, tailing ponds, and evaporation of froth extraction solvents. In-situ production drives air pollution through the large-scale combustion of natural gas in the steam generation process. Similar to a typical oil refinery, oil sands upgraders contribute the most air pollution, with their SO_x emissions being most disturbing. Because of specific regulations that provide incentives for cleaner operations, the ability of producers to reduce emissions of CACs has witnessed an impressive success. Table 6 demonstrates the improvements made over a seven-year period. Heavy metal and PAH pollution from the oil sands have been shown to be relatively small compared when compared to other industrial activity in Canada, though particulate PAH are often wind-dispersed and deposited in surrounding lakes. Ecological damage can occur potentially but none has been demonstrated to-date. Also worrying is the issue acidification of soil and lakes from the acidification of NO_x and SO_x. Northern Alberta soils and the nearby lakes of the sister province of Saskatchewan are highly sensitive to acidic deposits and have little buffer capability. Improved continuous monitoring and further testing is being conducted to minimize environmental impact.

Table 6: Oilsands CAC Emissions Vs Canadian Total (Tons (T))

Process	**Pollutant**							
	TPM	**PM10**	**PM2.5**	**SOx**	**NOx**	**VOC**	**CO**	**NH_3**
Mining	751	372	199	2,885	3,826	18,947	3,461	162
In-Situ	686	671	670	9,433	14,397	1,947	13,498	-
Upgrading	4,379	2,638	1,256	99,545	26,445	24,819	14,201	1,197
Oil Sands Total	5,816	3,681	2,125	111,863	44,668	45,713	31,160	1,359
Can Total	22,731,744	7,081,067	1,368,325	1,287,662	1,861,718	2,026,674	8,254,128	495,522
Oil Sands (% of Can)	**0.03%**	**0.05%**	**0.16%**	**8.69%**	**2.40%**	**2.26%**	**0.38%**	**0.27%**

Source: Environment Canada, Pollutant Inventories and Reporting Division, 2014

4. PROJECT DESCRIPTION

4.1 Forced-Flow Catalytic Membrane (FFCM) Reactor for Flue Gas Methane Reforming

In this research the use of a catalytic membrane reactor for the conversion of power plant flue gas has been successfully proofed. We have created an inorganic catalytic membrane reactor and operated it in a forced-flow through configuration as shown in Figure 3. Two different temperatures have also been tested for the reaction. The hydrogen to carbon monoxide (H_2: CO) ratio obtained was optimum for Fischer-Tropsch synthesis (FTS). Most importantly, scale-up has been demonstrated for membrane pore size, membrane size and superficial flow area. We believe the highly encouraging results achieved support the case to initiate a pilot study leading to the eventual commercialization of the process. The approach envisions development of a system ultimately able to take flue exhaust gas such as from natural gas fired power stations, tar sand up-grader plants and other facilities and rehabilitate the CO_2 component into valuable and highly useful chemical components such as hydrogen, methanol and ammonia. The underlying technology is known as inorganic hybrid membrane (IHM) technology. In its current laboratory scale rig, the device consists of porous ceramic tubes, which provide a structure onto which a coating/catalyst is applied. In the laboratory, simulated flue gas comprising carbon dioxide, nitrogen and oxygen are fed (together with a methane feed) into the catalytic membrane reactor (CMR) at temperature. As depicted in Figure 3, the F3R™ Process reaction results in the direct production of synthesis gas with desirable H_2/CO ratio. The synthesis gas is available for onward processing by existing technologies such as FTS.

Dry and auto-thermal reforming are catalytic methods that convert both the CH_4 and CO_2 into H_2 and CO (syngas). This work has shown that a Rh/Al_2O_3 catalyst is successful in flue gas reforming methane to syngas without deactivation from carbon formation at CH_4/CO_2 ratios of one or lower. In CH_4 rich mixtures, auto-thermal reforming (ATR) is effective because it provides additional oxidant that eliminates carbon formation and combusts a portion of the CH_4 in-situ to provide the heat needed for the endothermic reforming reactions. This work also investigated the effect of NO_2 and SO_2 on the activity of CH_4 flue gas reforming using an Rh/Al_2O_3 catalyst. It was determined that parts per million introductions of NO_2 and SO_2 into the reforming reaction did not adversely affect catalyst activity. Therefore, O_2 or air co-feeding produces H_2O and additional heat from the CH_4 combustion reaction and it keeps the Rh/Al_2O_3 catalyst clean of carbon thereby maintaining the activity and selectivity of the catalyst for conversion of flue gas into syngas.

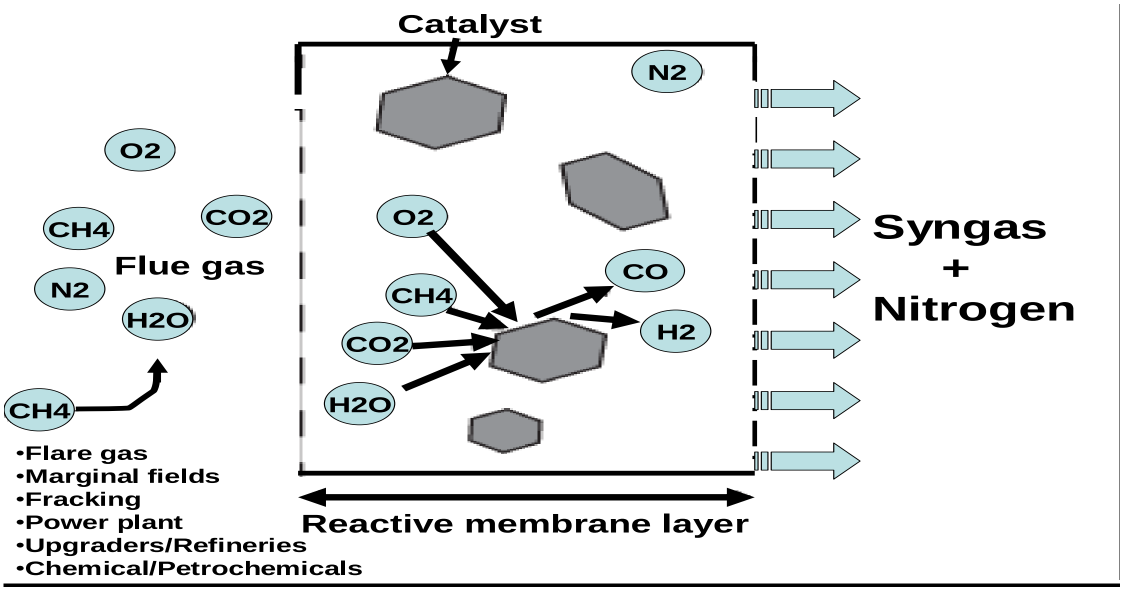


Figure 3: Schematic Diagram of the Flue Gas Methane Tri-Reforming (F3R™) Operating in the Forced Flow-through Catalytic Membrane (FFCM) Configuration

4.2 Feed Delivery and Reactor System

Figure 4 shows the schematic representation of feed delivery and reactor flow system used for the flue gas reforming experiments. The catalytic activity experiments were performed with two tubular ceramic reactors at defined temperature and pressure. The membrane geometry allows for a degree of control of the contact time as it is operated in the FFCM configuration in which all of the reactants are forced to flow through the membrane by supplying the feed in the shell side with one exit on the permeate side closed exit (Figure 4; insert)

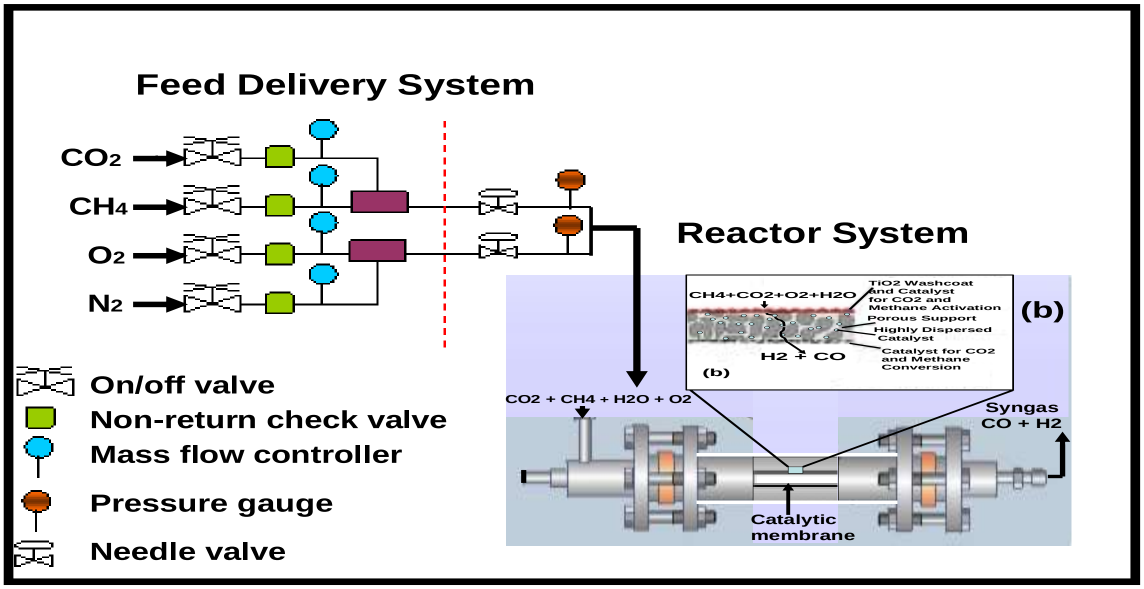


Figure 4: Schematic Diagram of the Feed Delivery and Reactor System

4.3 Reactor/Reaction Flow System

Figure 5 shows details of the reactor flow system used for permeation as well as reaction experiments. The reactor is heated up externally by an electric furnace using a power controller. The reaction temperature was monitored by strategically located thermocouples and zonal controlled using thermocouples. The experiments were carried out using a gaseous stream composed of O_2, CH_4, CO_2 and N_2. Two membrane sizes were used for the evaluation with the same length in each case. Tests were performed controlled pressure, temperature and volumetric flowrates. Before the reaction, the entire flow system was flushed with N_2. Subsequently, it was heated up to the desired reaction temperature. Once the desired temperature had been attained, the N_2 flow was switched off and the reactant feed gases were introduced to initiate the reaction. A condenser placed at the reactor outlet collected any water produced during the experiments. The gaseous products were analyzed using an Agilent Technologies Model 7890B equipped with an Agilent Technologies 5977A MS detector and a Varian CP – 3800 gas chromatograph equipped flame ionization detector (FID) and thermal conductivity detector (TCD) respectively. With the recovered water and the product gaseous stream compositions, the CH_4, O_2 and CO_2 conversions and the H_2/CO rations were calculated using an iterative method and closing the mass balances to within a ± 5 % error margin.

Figure 5: COMMERCIAL CONFIDENCE

The reactor consists of a high temperature ceramic catalytic tube enclosed in a furnace with zoned heating and a power controller to control the temperature of the membrane centralized inside a stainless steel tube as shown in Figure 6. The two ends of the stainless steel shell are fitted with screw caps which through tightening create the seal by compression of moulded seal rings located at the top and bottom of the membrane tube as previously shown in Figure 5. Five Ni-Cr thermocouples (Cole – Palmer, London, UK) are inserted in to the furnace (Figure 6) at the top middle and bottom through bored-through fittings. The furnace used in the reactor set-up is custom designed and has four split zones (Horst, Frankfort, Germany). The first zone serves to preheat the incoming feed gases, second and third zones serve to maintain the isothermal conditions for the membrane, and fourth zone maintains the reactor temperature in order to avoid any condensation of water vapor inside the reactor. The four heating zones of the furnace heater are digitally controlled using separate two-point (heat only) temperature controllers (Horst R2400, Frankfort, Germany) with LCD Display). The temperatures in each of the four zones are adjustable based on the top and the bottom temperature. By maintaining the four temperatures in each zone the entire membrane reactor is operated at a desired reaction temperature.

Figure 6: Photograph of the Two Membrane Reactors Enclosed in the Heating Furnace (Heating Jacket) with Power Controllers between the Reactors and Showing the Thermocouples

4.4 Membrane Catalyst Preparation

Unlike in traditional fixed-bed catalysts, where maintaining the location of the catalyst bed inside the reactor is critical for reproducible data, in the membrane reactor this is not an issue because the catalyst is deposited uniformly throughout the porous tubular support. This is an important characteristic of the membrane reactor that enables it to obtain consistent reading as the length of the membrane is always constant and so too is the distance of the membrane from either end of the reactor. In this work, we developed a method optimized to ensure uniform deposition of catalyst on the membrane. Membranes were prepared and evaluated with different loadings of catalyst.

Figure 7: COMMERCIAL CONFIDENCE

4.5 Membrane Catalyst Characterization

The membranes were characterized by scanning electron microscopy (SEM) coupled with energy dispersive x-ray (EDAX) and the Brunauer-Emmett and Teller (BET) gas adsorption method using liquid nitrogen.

4.5.1 Surface Area, Pore size Distribution and Porosity Measurement

Figure 8 (Left) shows the Quantachrome Model 2013 automated gas sorption analyzer (Hartley, Wintney, UK) used for the BET surface area measurements, average porosity, and pore size distribution of fresh and catalyst impregnated support respectively. This analysis is based on the adsorption-desorption principle. Before to the analysis itself, small fragments of the support or catalytic membrane sample was degassed. This degasification removes trapped impurities in the pores, such as air and other gases. The degasification process is carried out under elevated vacuum at a temperature ramp of 1 °C/min for 30 minutes to 50 °C. It was then heated to 100 °C at 1 °C/minute and soak for 60 minutes. The final stage the sample was heated to 300 °C at 1 °C and soak for 180 minutes. After degasification the amount of the sample in the cell is carefully weighed and then loaded onto the analysis port of the instrument. The Dewar flask is then filled with liquid nitrogen and kept directly underneath the analysis port. The analysis is initiated and the Dewar rises automatically to immerse the sample completely in the liquid and maintain the cell temperature at −196 °C. The amount of nitrogen gas that is adsorbed at various relative pressures is recorded. From the data obtained a plot of $p/p0$ versus $1/[w((p0/p) - 1)]$ (where p and p0 are the equilibrium and the saturation pressure of adsorbates at the adsorption temperature, and w is the quantity of volume that is adsorbed) is drawn and the surface area is calculated using the BET equation. The linear relationship between $p/p0$ and $1/[w((p0/p) - 1)]$ is maintained only in the range of $0.05 < p/p0 > 0.35$

Similarly, a witness sample of support or catalyst impregnated support is characterized by its distribution of pore sizes. Each pore size in the material contributes to the total adsorption isotherm in a proportion as the fraction of the total area for that particular sample. Isotherms of mesoporous materials are usually measured over a pressure ranging from 1 torr to approximately 760 torr. Once the details of the isotherm curve have been accurately expressed as a series of pressure vs. quantity adsorbed data pairs, a variety of different theories or models can then be applied in order to determine the pore size distribution. One if these are the Barrett, Joyner and Halenda method (BJH) and T-Plot analysis used to calculate the pore size.

Figure 8 (Middle)) shows the Zeiss EVO scanning electron microscope (Germany) used for the SEM imaging and Figure 8 (Right) shows an Oxford Instruments INCAx-act (Oxfordshire, England, UK) used for the EDXA analysis. SEM is an imaging technique that employs electrons while EDXA (or EDS) is an x-ray spectroscopic technique for determining elemental compositions. When EDAX is used in conjunction with imaging in SEM, signal can be acquired from a spot, area, line profile or a 2D map. SEM is used to determine the morphological aspects of the sample including shape and size of particles. With EDXA information can be obtained on the chemical composition.

Figure 8: The Quantachrome Model 2013 Automated Gas Sorption Analyzer (Left); the Zeiss EVO Scanning Electron Microscope used for the SEM Imaging (Middle) and Energy Dispersive X-ray Analysis System (Oxford Instruments INCAx-act) used for the EDAX Analysis (Right)

4.6 Membrane Deployment

The membrane is deployed exactly at center of the stainless steel tube so as to take advantage of the uniform furnace heat as previously shown in Figure 5. This is achieved through the use of high precision moulded rings. The membrane is placed such that it is possible to measure the temperature at the top and bottom of the reactor respectively (See Figure 5) Care was also exercised to obtain an ideal flow-through reactor system such that the feed gases have maximum contact with all the dispersed catalyst. Initially the membrane reactor is heated to the desired temperature with a ramp rate of 10 °C per minute under the flow of inert N_2 (99.999% pure, BOC Gases, UK). Catalytic tests were carried out by allowing the feed gas mixture entering the reactor where it is maintained in a preheating zone before entering the main reactor high-temperature or ‘hot’ zone.

4.7 Flow Controllers

The gases were supplied to the reactor through 1/4 inch lines fitted with a non-return valves to prevent any back flow that may occur due to any pressure build up within the system (as shown previously in Figure 4). Digital pressure gauges are located on each line to indicate the pressure. The feed lines for the inert gas have a 7 μm size filter fitted between the supply gas cylinder and the mass flow controller. The mass flow controllers were initially calibrated with the actual gas reactants. The inert gas N_2 was used as the internal standard for the gas chromatograph and also as a carrier gas through the membrane reactor system.

4.8 Condenser, Gas Liquid Separator and Moisture Trap

Figure 9 shows a photograph of the condenser used to condense any produced water that exits from the reactor. The condenser is constructed of stainless steel material with a spiral coil inside having a surface area of about 150 cm^2. The shell side of the condenser is maintained at 0°C using ice blocks which are constantly renewed and the product coming out from the bottom of the reactor is directed through the coiled section of the condenser using 1/4 inch outside diameter (OD) stainless steel (SS) 316 line. Because of very little water production (since no water was added in the feed) there was no left over uncondensed water vapor from the condenser and the effluent gases leaving this section go through a moisture trap shown in Figure 9 to extract only trace quantities of water vapor. The dry gases are then fed online to the GC for analysis. Carrier gases are passed through a gas purifier (Figure 10) before entering the GC.

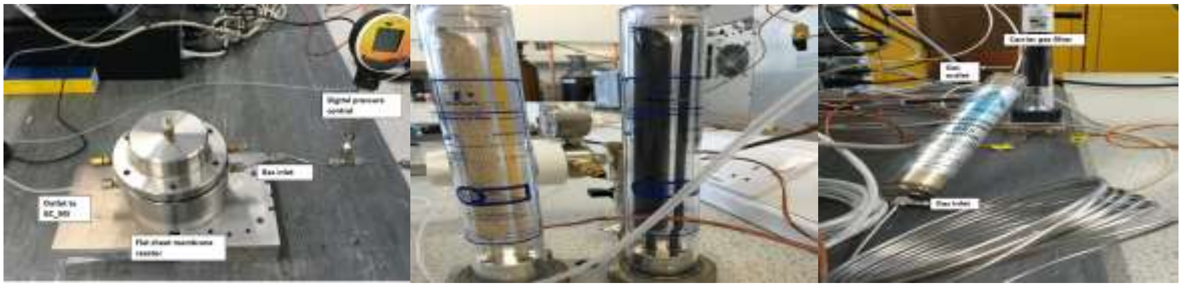


Figure 9: Condenser and Gas-Liquid Separator (Left); Perkin Elmer Moisture Trap from Llantrisant, UK (Middle) and Chemical Ionization Gas Purifier (Right

4.9 Gas analysis

The gases exiting the membrane reactor system mainly contains generated gas (H_2 and CO), unreacted gases (CH_4, O_2, and CO_2) and inert gas (N_2). These gases are sent to the online GC shown in Figure 10 (Left; Agilent Technologies, Santa Clara, California, USA) equipped with a mass spectrometry detector (MS) for analysis equipped with an automated 6-port gas sampling valve (Agilent Technologies, Santa Clara, USA) and Figure 10 (Right; Varian gas chromatograph equipped with three automated gas sampling valves – Valco Instruments, Houston, Texas, USA). The gas automated gas samplers enable introduction of a fixed quantity of gas samples through an automated operation, at ambient temperature conditions. The sample volume can be selected in 1, 2, or 5 milliliters by adjusting the valve operation. In our work a 1 ml loop was operated throughout the experiments reported. Hayesep Q 80-100 MESH_packed SS column (2 m x 1/8’’ x 2.0 mm), and 2 SS columns each packed with Molecular sieve 60-80 MESH (2m x 1/8’’ x 2mm) were used for gas separation. For the Varian GC, the temperature of the injector port, column temperature, and TCD temperature were all maintained at 150 °C with a TCD current of 60 mA. Helium is used as a carrier gas for GC for the detection of all the gases exiting the reactor. The exit gas sample was injected every 15-30 mins until a steady state was attained which was indicated by a constancy of the chromatogram areas for all the components being sampled.

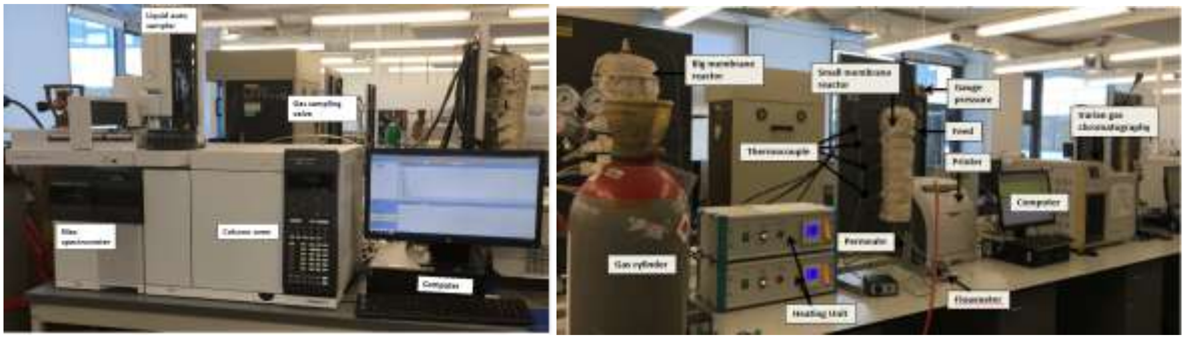


Figure 10 Picture Showing the Agilent Technologies Gas Chromatography Coupled with Mass Spectrometry (Left) and the Varian Gas Chromatograph (Right)

4.10 Mass balance

The main assumption here is that the reaction of feed gases produces a mixture consisting of CO_2, CO, CH_4, O_2, H_2, H_2O and solid carbon (C). The basis for calculating all outlet flow rates assumes that oxygen, carbon, and hydrogen mass balance equations are described by equations 1-4.

4.10.1 Carbon balance

$$[CH_4]\text{feed} + [CO_2]\text{feed} = [CO]\text{product} + [CO_2]\text{product} + [\text{Carbon}]\text{product} \tag{1}$$

4.10.2 Oxygen mass balance

$$[H_2O]\text{feed} + 2[CO_2]\text{feed} = [CO]\text{product} + 2[CO_2]\text{product} + [H_2O]\text{product} \tag{2}$$

4.10.3 Hydrogen balance

$$2[CH_4]\text{feed} + [H_2O]\text{feed} = 2[CH_4]\text{product} + [H_2O]\text{product} + [H_2]\text{product} \tag{3}$$

Where [ ]product and [ ]feed are product outlet flow rates [mol/h] and feed inlet flow rates [mol/h], respectively. The gases coming out from the reactor are directed through the condenser and gas liquid separator sequentially to extract any unreacted H_2O. Thus, the gas being fed to the GC contains only CO, N_2, H_2, and unreacted CO_2, O_2, and CH_4. These species are related by the mass balance equation given in equation 4:

$$[H_2]\text{wf out} + [CH_4]\text{wf out} + [CO]\text{wf out} + [CO_2]\text{wf out} + [O_2]\text{wf out} = 1. \tag{4}$$

Where [ ]wf out are dry mole fractions (water-free) of the outlet stream and are obtained through GC results.

Deposition of carbon is one of the major causes of catalyst deactivation. The amount of deposited carbon can be estimated using the mass balance equations already described above. Since no carbon deposition and catalyst deactivation was observed when the membrane was removed from the reactor run at temperature. Formation of carbon has therefore been assumed to be zero throughout the calculations i.e. Cout. = 0.

4.11 Reactant Conversion and Syngas Ratio

From the flowrates of the various components in the feed and product the reactant conversions and hydrogen and synthesis gas ration were calculated as shown in equations 5-8

(1) Methane conversion: $\mathbf{X}_{CH_4}$ (%) = ($\mathbf{V}_{CH_4}$ in - $\mathbf{V}_{CH_4}$ out) / $\mathbf{V}_{CH_4}$ in .100 (5)
(2) Carbon dioxide conversion: $\mathbf{X}_{CO_2}$ (%) = ($\mathbf{V}_{CO_2}$ in - $\mathbf{V}_{CO_2}$ out) / $\mathbf{V}_{CO_2}$ in .100 (6)
(3) Oxygen conversion: $\mathbf{X}_{O_2}$ (%) = ($\mathbf{V}_{O_2}$in - $\mathbf{V}_{O_2}$out) / $\mathbf{V}_{O_2}$ in .100 (7)
(4) (H_2/CO)out molar ratio: (H_2/CO)out = ($\mathbf{V}_{H_2}$ / $\mathbf{V}_{CO}$)out (8)

Where **X** is the reactant conversion and **V** is the volumetric flowrate.

4.12 Issues Encountered/Limitations

Recruitment of researchers with the required skills, long lead times for supply of the gas mixtures due to stability issues, expansion/contraction issues in the stainless steel reactor holder following high-temperature operation, water condensation in flow lines, pressure gauges and flow metering equipment causing damage, need for specialized pressure regulators and the need for multiple detectors for monitoring all the reaction products simultaneously. Some suppliers never even honoured supply contracts.

4.13 Results

4.13.1 Effect of NO_2 Contaminant on the CO_2, CH_4 and O_2 Conversions

Conversion rates of different types of catalysts were assessed and compared for different membranes. One membrane was selected to study the effect of exposure to NO_2 contaminant on catalyst performance due to the superior performance of this system compared to the other systems studied.

Figure 11: COMMERCIAL CONFIDENCE

4.13.2 Time-Dependent Stability Conversions of CO_2, CH_4 and O_2 in SO_2 and NO_2 Contaminants

The time-dependent activities (stability) of the membranes for NO_2 and SO_2 contaminants catalysts were investigated. No significant deactivation occurred. One membrane type was selected to study the effect of exposure to NO_2 contaminant and a different pore size membrane selected to study the effect of exposure to SO_2 contaminant on catalyst performance

Figure 12: COMMERCIAL CONFIDENCE

4.13.3 Effect of Inlet Carbon Dioxide Concentration in the Feed on Syngas Quality

Carbon dioxide re-forming is typically influenced by the simultaneous occurrence of the reverse water gas shift (RWGS) reaction (equation 8), which results in H_2/CO ratios of less than 2. In traditional fixed-bed reactors, this ratio is usually less than unity. Results of flue gas reforming of CH_4 by three catalysts (Ni/Ce – ZrO_2, Ni/ZrO_2 and Haldor Topsoe R-67-7H) have revealed that the coke on the reactor wall and the surface of catalyst were reduced dramatically. It was found that the weak acidic sites, basic site and redox ability of Ce-ZrO_2 play an important role in methane conversion. This is an important finding. It confirms that the FFCM can be used to carryout reforming of other feedstocks apart from flue gas. Enormous quantities of co-produced gas are flared as a waste by-product during gas processing. In the upgrading of bitumen, the offgas is wasted to the atmosphere instead of being utilised and in landfills the current practice involves the separation of methane and CO_2 with the CO_2 being vented into the atmosphere. The concentration of CO_2 in these applications varies and our results show that the syngas produced by varying the CO_2 concentration in the feed from 5 to 40% has an H_2: CO ratio varying from 2 – 1.7 respectively. This syngas quality range is within the desired window for the production of several value-added carbon-based products such as hydrogen, methanol, ammonia and gas-to-liquids (GTL).

Figure 13: COMMERCIAL CONFIDENCE

5. PROJECT OUTCOMES

Introduction of renewable energy resources into the energy supply chain will to large extent focus on production of syngas. Reforming of methane with flue gas is of interest (equation 9) as it can produce syngas with low H_2/CO ratio (around 1) from the most common carbon containing waste streams, namely H_2O, O_2, and CO_2. This mixture of gases eventually combined with syngas from steam methane reforming is well suited for Fischer-Tropsch synthesis. The reaction also has important environmental implications since both methane and CO_2 are greenhouse gases.

$$CH_4 + CO_2 + O_2 + N_2 \Rightarrow 2CO + 2H_2 + N_2 \qquad (9)$$

Methane steam reforming and methane dry reforming reactions are highly endothermic and usually require large flame combusting units to supply heat to catalytic converters resulting in high emissions of NO_x. The application of reformers based on porous catalytic membranes gives a new solution to this problem.

5.1 Requirement for Membrane Support Pore Size Limit

The requirement for the pore size limit on the ceramic substrates can be less rigid, i.e., bigger pore-sized substrates are acceptable to fabricate continuous membranes without defects when the bigger grain-sized alpha-Al_2O_3 crystal is applied as the modification layer. From a practical point of view in the flue gas methane reforming process, bigger pore-sized substrate is more economical due to the low pressure feedstock and easier to obtain since bigger-sized powders are easier to manufacture on a commercial scale. In addition, bigger pore-sized substrate has a higher permeability which means a low pressure feed gas (which is typical of flue gas streams) can be utilized without additional compression. The preparation processes of the intermediate/modification layer and the catalyst layers are both based on the simple dip-coating (sol–gel) technique which can be easily adapted to industrial applications for scale-up. The permeation measurements as a function of temperature were useful for predicting the transport regimes involved at high temperature in a membrane reactor configuration. Tailoring the membrane porosity is very important because the porosity, pore size distribution, pore connectivity and tortuosity of the membrane pore network are the parameters which define the permeability of the porous membranes. With conventional sol-gel routes, the pore size distribution is usually broad and the tortuosity is important with the presence of constrictions. Thus, ordered interconnected pore networks with a constant pore size, are strongly attractive. Hierarchical porosity and adaptive porosity are also fascinating approaches to increase or manage the permeability of ceramic membranes.

5.2 Mode of Catalytic Membrane Reactor Operation

In the forced flow-through catalytic membrane (FFCM) operation, the premixed reactants flow through the catalytic membrane in a single-pass resulting in complete conversion of CH_4, O_2, and CO_2. This takes advantage of the high catalytic efficiency caused by the intimate contact between the reactants and the catalyst resulting in process intensification. It is noted that this is the first study to attempt the use of flow-throw catalytic membrane for flue gas methane reforming. The use of a catalytic membrane reactor for the flue gas reforming of methane has been proofed. Scale-up of the catalytic membrane flue gas methane reforming process has been successfully demonstrated in pore size, tube diameter and superficial flow area. Flue gas CH_4 reforming reactions have been studied under controlled temperature programs with the optimum temperature range has been found. The membrane support affects in a major way, the activity of the supported rhodium (Rh) catalyst for the flue gas methane reforming. Basic oxides have shown to promote the reaction and are also thought to catalyze the gasification of coke with steam and so help prevent deposition of carbon and are therefore the most promising supports as they both provide high surface areas and are thermo-stable. In flue gas methane reforming, several reactions are occurring simultaneously and finding the correct ratios of reactants is not easy, but it was found that oxygen (O_2) was always completely consumed as it seems to have a high affinity for active sites on the catalyst causing it to react very quickly. Active sites or those where O_2 disassociation had already occurred are available for the remaining reactants. The membranes were stable to NO_2 and SO_2 environment for up to 2 hours without any deterioration in activity. Increasing the CO_2 concentration in the feed stream reduced the H_2: CO ratio. The experimental CO_2 conversions and H_2/CO ratios achieved are sufficiently high to form the bases to initiate a pilot study.

5.3 Cost/Selling Price for Hydrogen

We have employed HYSYS simulations flow sheet for CO_2 reforming of CH_4, steam reforming of methane and flue gas reforming of methane over a Rh based catalyst to calculate the cost/selling price for hydrogen for each process. The hydrogen cost/selling price was US$0.796/kg (CAN$1.02/kg) for dry methane reforming, US$1.1/kg (CAN$1.41/kg) for flue gas methane reforming and US$2.4/kg (CAN$3.07/kg) for steam methane reforming. This result suggests that the flue gas methane reforming system could replace an SMR for hydrogen production since the cost/selling price is 100% lower than that of the SMR.

5.4 Energy Efficiency (Thermo-Neutrality of the Reforming Reaction)

Thermodynamically, in order to produce synthesis gas with H_2/CO ratio of 2, the energy requirement for the three processes (dry reforming of methane, steam reforming of methane and partial oxidation of methane) involved in the flue gas reforming must be calculated. This calculation shows that if the amount of energy consumed by absorption is taken into account (as it is supplied as a reactant to produce synthesis gas with desired ratio) then it can be estimated that to produce one mole of hydrogen and two moles of carbon monoxide, 0.233 mol CH_4 is consumed and produces 0.013 mole CO_2 emission per ($CO + 2H_2$) in modern oxy-CO_2-steam – reforming which is far lower than either the CO_2 dry reforming or steam methane reforming. The presence of H_2O provides a source for surface oxygen and hydroxyl-radicals, O(s) and OH(s), which in turn can result in very high methane conversion, higher H_2 and lower CO selectivity. This is highly desirable for catalytic membrane reactors as hydrogen can aid the stabilization of the post-catalyst gaseous combustion zone located in the bore of the membrane tube. To enable complete conversion of CH_4, an additional 0.42 moles of O_2 will be supplied in addition to the O_2 in the original flue gas. The large endothermic heat of steam methane reforming is compensated for by the large exothermic heat of the partial combustion reaction on the same catalyst surface without any additional supply of heat from outside of the reactor. This results in an extremely compact size of the F3R™ system compared to converters packed with catalysts results in high conversions in a single pass and if extended to the downstream Fischer-Tropsch process will result in highly effective ultra-clean fuels such as DME, MeOH and high octane number gasoline (sulfur-free & non-aromatic) to be produced effectively and economically.

5.5 Reactor Configuration

The FFCM reactor has shown better conversion performance compared to the state-of-the-art technology due to an optimized reactant contact with catalysts and a design that circumvents mass and heat transfer resistances which means only a tiny amount of catalyst loading increment results in a large increase in reactant conversion. The requirement for the pore size limit to the ceramic substrates can be less rigid, i.e., bigger pore-sized substrates are acceptable to fabricate continuous membranes without defects when the bigger grain-sized aluminium oxide crystal membrane is applied as the modification layer. From a practical point of view in the flue gas methane reforming process, bigger pore-sized substrate is more economical due to the low pressure feedstock and easier to obtain since bigger-sized powders are easier to manufacture on a commercial scale. In addition, bigger pore-sized substrate has a higher permeability which means a low pressure feed gas can be utilized. The preparation processes of the intermediate/modification layer and the catalyst layers are both based on the simple sol–gel technique which can be easily adapted to industrial applications for scale-up. The permeation measurements as a function of temperature were useful for predicting the transport regimes involved at high temperature in a membrane reactor configuration

5.6 Effect of CO_2 Feed Concentration on Syngas Quality

Enormous quantities of co-produced gas are flared as a waste by-product during gas processing. In the upgrading of bitumen, the offgas is wasted to the atmosphere instead of being utilised and in landfills the current practice involves the separation of methane and CO_2 with the CO_2 being vented into the atmosphere. The concentration of CO_2 in these applications vary and syngas produced by varying the CO_2 concentration in the feed from 5 to 40% is 2 – 1.7 respectively. These syngas ration range is within the desired window for the production of several value-added carbon-based products such as hydrogen, methanol, ammonia and gas-to-liquids (GTL).

5.7 The Time-Dependent Activities (Stability) of the Membrane Catalysts for SO_2 and NO_2 Contaminants

The time-dependent activities (stability) of the membranes for SO_2 and NO_2 contaminants on membrane supported catalysts have been studied. The conversions of CH_4 and O_2 in the membranes tested, remained unchanged during the seven-hour testing period of study. CO_2 also showed a stable conversion during the period of study and its conversion improved steadily. Initially, the CO_2 conversions were slightly lower than those observed for CH_4 and O_2 but increased noticeably after the first 2 hours, and again after the first 5 hours to become almost unchanged from 6 to 7 hours. No significant deactivation occurred.

6. SUITABILITY OF THE F3R™ TECHNOLOGY FOR ALBERTA

Synthesis gas can be produced by CO_2 reforming of methane, steam reforming of methane and flue gas reforming of methane using catalysis. The production capacity of each of these processes was selected to be 13,930 metric tons of H_2 per year (1,589 kg hr^{-1}). This was based on Air Products and Chemicals INC's hydrogen plant located in Geismar, LA, with the production capacity of 15 million cubic feet per day (13,920 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). Using the HYSYS flow sheet for each process, the cost/selling price for hydrogen for each process was US$0.796/kg (CAN$1.02/kg) for dry methane reforming, US$1.1/kg (CAN$1.41/kg) for flue gas methane reforming and US$2.4/kg (CAN$3.07/kg) for steam methane reforming as shown in Table 7.

Firstly, the thermodynamics suggest optimum syngas production is obtainable at temperatures in the region to those normally used in existing steam methane reformers despite the nitrogen dilution. Accordingly we do not envisage increasing the temperature in our flow-through catalytic membrane beyond that. This is due to the good reactant/catalyst contacting, no necessity for catalyst separation from the product (as is the case with slurry-phase reactor systems) and good catalyst accessibility (less catalyst metal necessary). Second, in the flow-through catalytic membrane the effective reaction rate is not influenced by mass transfer limitations (reduced pore diffusion) resulting in the attainment of integral conversions under differential conditions and the selectivity for the desired product (syngas) can therefore be increased without the need for excessive pressures. Third, by avoiding the nitrogen removal (or carbon capture) process we can reduce energy consumption significantly. These three factors when taken together favour F3R™ technology compared to the 380,000 tons/year CO_2 emissions for a conventional SMR (without carbon dioxide sequestration). A disadvantage with SMR (apart from the very high pressures) is that CO_2 capture and sequestration may be necessary in the future, which will result in additional capital and operating costs (CAPEX and OPEX) and very high GHG implications. Therefore, in a GHG constrained future our flow-through catalytic membrane flue gas conversion process is the clear technology of choice the technology can therefore replace SMR (*SEE RESULTS USING HYSSYS MODEL IN TABLE 7*). In addition, it will enable existing SMRs to comply with these future stringent GHG regulations by utilizing the CO_2. The conversion of methane and CO_2 respectively for a single pass (as observed in our study) was taken to be 100% (which is typical of our experimental results) and therefore there was no need to attain total conversion by recycling in the flue gas methane reforming case. However, for the CO_2 reforming of methane and steam reforming of methane processes, HYSIS utilised a methane recycle to enable complete conversion. The following reactions where each assumed in each of the HYSYS flow sheet:

- steam methane reforming (SRM) $CH_4 + H_2O \rightarrow CO + 3H_2$ ***Equation (10)***
- dry methane reforming (DRM) $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ ***Equation (11)***
- partial oxidation of methane (POX) $CH_4 + 0.5O_2 \rightarrow CO + 2H_2$ ***Equation (12)***
- flue gas methane reforming process involving various reactions ***Equation (10)***+***(11)*** + ***(12)*** simultaneously

Canada is home to vast natural gas resources and a significant amount of this is being flared. Additionally, the oil sands industry emits large amounts of CO_2 and flue gas to the atmosphere from processing/upgrading and power generation. This technology can therefore replace current steam methane reformers and simultaneously reduce the cost of hydrogen production by as much as 100%.

Table 7: Economic Results for the HYSYS Simulated Process for Hydrogen Production by CO_2 Methane Reforming (DMR), Flue Gas Methane Reforming (the F3R™ Process) and Steam Methane Reforming (SMR) for the Production of CO and H_2

Product/Raw Material	Flow Rate from HYSYS Simulation (kg/hr)	H_2 Cost/Selling Price (US$/kg)
Carbon Dioxide	17,350	0.003
Methane	6,324	0.172
Hydrogen*	1,589	0.796
Hydrogen**	1,589	1.1
Hydrogen***	1,589	2.4

steam methane reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H^o = +206.3$ kJ/mol ***(10))

*dry methane reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H^o = +247.3$ kJ/mol ***(11)***))

flue gas methane reforming reactor (the F3R™ process); *(10)*** + ***(11)*** + ***(12)***

6.1 Synthesis of Petrochemical Products from Flue Gas via Syngas

Carbon dioxide capture, transportation and storage pose significant problems. Various methods involving adsorption, membrane technology and absorption of CO_2 from flue gas, etc. are widely discussed. Another and probably the most effective and elegant way is to produce energy dense liquid compounds (e.g. gasoline and petrochemicals) from flue gas via syngas is shown in Figure 14 and then transport or store the products for later use. Building on Alberta's huge supply of propane, and upgrader off gases the Petrochemicals Diversification Program (PDP) capitalized on the growing global demand for related higher value products and promoted greater energy processing in Alberta. This helps to build a broader petrochemical industry and the related light alkane mid-stream sector while simultaneously diversifying Alberta's economy and creating jobs. Successful integration of the F3R™ Process will generate over $500 million in royalty credits, encourage investment in Alberta's petrochemicals industry, specifically methane and propane upgrading, credits paid out over three years after facility begins production and generate up to 3,700 – 4,200 jobs during construction and over 240 full-time jobs when projects are operating. The new giant petrochemicals complexes hosting the F3R™ Process represents a potential capital investment approaching up to $50 billion to Alberta. This type of diversification will create jobs and economic activity that will help to increase and broaden Alberta's tax base over the long term, supporting important services such as health care and education. Many other industry sectors including metals fabrication, engineering, manufacturing, construction, and transportation and business services, such as professional, scientific and technical services will also benefit from the F3R™ Process. Oil sands upgrading involves vacuum distillation, cracking (thermal or catalytic), and desulphurization processes. These processes are used in various upgrading configurations to extract out lighter hydrocarbon streams then purify the heavier crude, and extract the asphalt. The upgrading process also removes nitrogen, trace metals and sulphur impurities in the lighter streams by the application of hydro-treating before blending the final output streams to generate synthetic crude oil (SCO) which is transported by pipeline. The light hydrocarbons are particularly useful as the feedstock for flue gas reforming using the F3R™ Process.

As an example of giant petrochemical complexes identified in Alberta are Williams' (NYSE: WMB) offgas liquids extraction plants. On Wednesday, March 23, 2016 Williams announced the startup of its second upgrader offgas liquids extraction plant. The plant constitutes a key asset in the company's midstream and petrochemicals complex in Canada. The plant boosts petrochemicals feedstocks domestically and reduces emissions in the oil sands production process significantly while also recovering natural gas liquids (NGLs) and olefins which are valuable petrochemicals feedstocks. The new plant serves an oil sands upgrader facility located north of Fort McMurray, Alberta and is designed to reduce greenhouse gas (CO_2 emissions) – by an average of 200,000 tonnes per year and also reduce emissions of sulphur dioxide (SO_2) which is a contributor to acid rain – by an average of approximately 2,800 tonnes per year. The company's two offgas processing plants in Canada will in total eventually reduce CO_2 emissions by more than 500,000 tonnes and SO_2 emissions by 5,500 tonnes annually respectively. This level of CO_2 emissions reduction equates to taking 105,000 cars off the road annually and corresponds to the total yearly energy needs of 45,000 homes. To achieve the same level of CO_2 reduction through sequestration would require approximately 12.8 million seedlings to be grown for 10 years. If the offgas from all oil sands upgraders in Alberta were captured and processed, the CO_2 emissions would be reduced by total of 1 million tonnes each year.

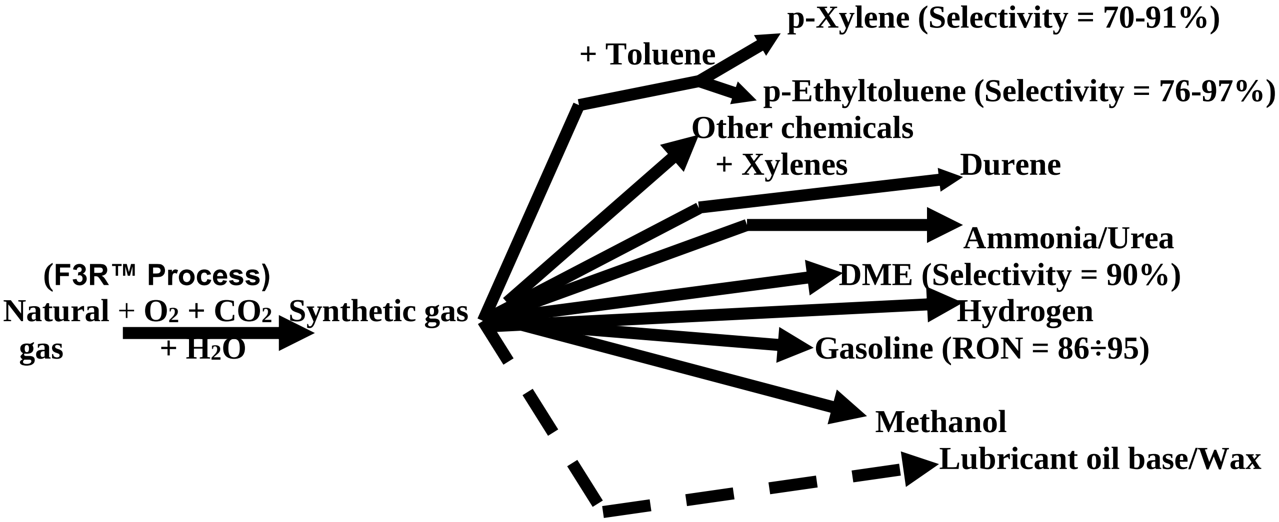


Figure 14: Scheme for Synthesis of Petrochemicals from Flue Gas via Syngas.

7. GREENHOUSE GAS AND ECONOMIC IMPACTS

7.1 Estimation of the Scale of CO_2 Emissions Reductions and Energy Savings

Table 8 shows advantages and economics of value-added products obtained from flue gas methane reforming. The production of useful synthesis gas by flue gas reforming of methane will prevent a large amount of CO_2 from getting into atmosphere. This will occur by utilising the CO_2, O_2, and H_2O already present in the flue gas to reform methane. The simultaneous reforming consumes far less amount of methane when compared to the conventional methane steam reforming process and in addition does not involve a dedicated steam generation plant. In order to have a starting point with high energy efficiency and low baseline emissions the attention for this project is focused on natural gas combined cycles (NGCC). In Alberta, the intent is to PHASE OUT coal fired power plants by 2030. So, the most likely scenario for this technology would be a NGCC. This flue gas can be used to reform methane to produce synthesis gas according to equation 9.

$$1.23CH_4 + 0.55CO_2 + 1.1H_2O + 0.15O_2 + 3.2N_2 \leftrightarrow 0.27CH_4 + 1.03CO + 2.06H_2 + 0.33CO_2 + 0.66\,H_2O + 3.2\,N_2 \qquad (9)$$

Assuming the amount of carbon dioxide coming out of a 400 MWe natural-fired power plant is equal to 1.47 million tons of CO_2 a year, and CO_2 conversion = 40%; O_2 conversion = 100%; CH_4 conversion = 78% and H_2O conversion = 18%, the amount of methanol, ammonia and hydrogen produced per year and the contribution to the world's capacity is specified in Table 8. By knowing the amount of methane consumed in current state-of-the-art conventional steam reforming of methane, we have thus compared the effectiveness of the oxy-CO_2-steam reforming of methane to produce synthesis gas with H_2/CO ratio 2. This comparison is based on heat of combustion of methane and assuming the natural gas delivered cost is US$6.73/MMBTU. The amount of energy that can be saved using flue gas reforming and the cost of each product (methanol, hydrogen and ammonia) based on current-state-of-art steam reforming of methane compared flue gas methane reforming also is specified in Table 8.

Table 8: Advantages and Economics of Value-added Products Obtained from Flue Gas Methane Reforming

Final Product	**%CO_2 Emissions Avoidance**	**% Fuel Saving**	**% World Capacity**	**Cost based on current-state-of-art steam reforming of methane**	**Cost based on oxy-CO_2-steam reforming**	**By-products or significant waste streams**	
						Flue gas methane reforming	**Current-state-of-art steam methane reformer**
Methanol	50	25.3	4.56	US$510/ton	US$381.5/ton	N_2, H_2O	CO_2, N_2, H_2O
Hydrogen	24.5	72.5	0.08	US$2.4/kg	US$1.1/kg	N_2, H_2O	CO_2, N_2, H_2O
Ammonia	33.6	11.0	1.19	US$290/ton	US$236/ton	H_2O	CO_2, H_2O

7.2 Sustainable Emissions Reduction

Table 9 shows an estimate of the resultant CO_2 consumption and supporting evidence for this estimate. It also shows a comparative evaluation of the GHG impact for flue gas methane reforming (combined steam reforming, partial oxidation and dry reforming process), dry reforming, and steam reforming. The produced synthesis gas (a mixture of H_2 and CO) is the precursor for the production of methanol, hydrogen and ammonia and a multitude of other heavy chemicals. It can also be used to generate electricity. Methane, carbon dioxide, steam and oxygen are the four reactants involved in the F3R™ Process. The last three reactants are already present in the flue gas from the natural gas-fired power plants (viz: CO_2, O_2 and H_2O) and can be used in the F3R™ Process (combined steam reforming, partial oxidation and dry reforming process) to produce the synthesis gas. The composition of flue gas from natural gas-fired power plants demands the addition of methane, to produce synthesis gas with H_2/CO ratio of 2:1. The flue gas methane reforming process results in an overall endothermic process, but consume the least amount of energy when compared to steam reforming or dry reforming of methane (See Table 9). Thermodynamically, in order to produce synthesis gas with H_2/CO ratio of 2, the energy requirement for the three processes (dry reforming of methane, steam reforming of methane and partial oxidation of methane) must be calculated. This calculation is tabulated in Table 9. It also shows that if the amount of energy consumed by absorption is taken into account (as it is supplied as a reactant to produce synthesis gas with desired ratio) then it can be estimated that to produce one mole of hydrogen and two moles of carbon monoxide, 0.233 mol CH_4 is consumed and produces 0.013 mole CO_2 emission per (CO + $2H_2$) in modern oxy-CO_2-steam – reforming which is far lower than either the CO_2 dry reforming or steam methane reforming. This can be further enhanced by using advanced membrane reactors where 0.00 mole CO_2 emissions per (CO + $2H_2$) are produced with the least overall energy requirement. The presence of H_2O provides a source for surface oxygen and hydroxyl-radicals, O(s) and OH(s), which in turn can result in very high methane conversion, higher H_2 and lower CO selectivity. This is highly desirable for catalytic membrane reactors as hydrogen can aid the stabilization of the post-catalyst gaseous combustion zone located in the bore of the membrane tube. To enable complete conversion of CH_4, an additional 0.42 moles of O_2 will be supplied in addition to the O_2 in the original flue gas. As shown in Table 9, the catalytic combustion of methane has been avoided as a result of carrying out the reaction in a catalytic membrane reactor.

Table 9: Energy Requirement for the Three Processes (DRM, SRM and the Membrane-Enhanced Flue Gas Reforming of Methane

Process	**Reactions**	**Energy (kJ/mol)**	**Key GHG Impact**
			CO_2 emission/ ($CO+2H_2$)
CO_2 dry reforming (H_2/CO ratio = 2).	$0.75\ CH_4 + 0.75\ CO_2 \leftrightarrow 1.5\ CO + 1.5\ H_2$	+182.5	0.18
	$0.5\ CO + 0.5\ H_2O \leftrightarrow 0.5\ CO_2 + 0.5\ H_2$	- - -	
	CO_2 from absorption (0.75 x 160)	+120	
	Total	**+302.5**	
Conventional steam methane reforming (H_2/CO ratio = 2).	$0.75\ CH_4 + 0.75\ H_2O \leftrightarrow 0.75\ CO + 2.25\ H_2$	+154.5	0.04
	$0.25\ CO_2 + 0.25\ H_2 \leftrightarrow 0.25\ CO + 0.25\ H_2O$	+10.2	
	CO_2 from absorption (0.25 x 160)	+40	
	Total	**+204.7**	
Flue gas reforming (H_2/CO ratio = 2).	$0.22\ CH_4 + 0.22\ CO_2 \leftrightarrow 0.44\ CO + 0.44\ H_2$	+ 54.34	0.00
	$0.44\ CH_4 + 0.44\ H_2O \leftrightarrow 0.44\ CO + 1.32\ H_2$	+90.64	
	$0.12\ CH_4 + 0.06\ O_2 \leftrightarrow 0.12\ CO + 0.24\ H_2$	-4.32	
	Total	**+115.48**	

7.3 Potential Economic Impacts of Additional Hydrocarbon Value-Added Processing in Alberta

Projected expansions in the petrochemical, fertilizer and refining industries are outlined and the net economic impacts of upgrading various products in terms of contributions to Gross Domestic Product (or GDP/output/value added), labour income, employment and provincial government revenues are presented in Table 10. There are no particular environmental or climatic issues specific to Alberta which has a negative impact on the feasibility of operating the technology in Alberta. There are in fact a number of drivers making the technology particularly suitable for deployment in Alberta:

1. Significant fossil fuel burn from the electricity generating industry - close to 50% of total generating capacity is still attributed to coal fired power stations with around 30% from plants fired by natural gas.
2. Growing petrochemical industry - significant business opportunities in the processing of petroleum off gases: Alberta's natural gas industry offers an important feedstock for Alberta's petrochemical industry. Secure supply and current price levels contribute to an attractive business case for more value-added processing of key derivatives such as methanol, ammonia and urea (Alberta's Industrial Heartland). The proposed technology offers potential efficiency gains in respect of CO_2 emission against production of key feedstocks towards production of higher value derivative products such as ethane/propane and ethylene and propylene.
3. Oil Sand processing - increasing demand for hydrogen - Alberta's oil sands continue to drive national and provincial economic growth; however, the oil sands industry requires increasing amounts of hydrogen. The 2020 projected hydrogen consumption for oil sands processing in Alberta has been estimated at over 3.19 million tons which would be the same as the entire captive hydrogen consumption in the U.S. refining sector back in 2004. Surface mining operations typically range from 13,000 to 274,000 b/d with the median around 50,000 b/d [Alberta Department of Energy, 2004]. This means that half of the oil sand production facilities may have hydrogen requirements of around 46,000 tons/year.

A study carried out by Schlenker Consulting Ltd. (SCL) (1) in 2013 commissioned by the Alberta's Industrial Heartland Association (AIHA) estimated the potential economic impacts of expanding value added processing of provincial energy resources such as natural gas liquids (NGLs), raw natural gas and bitumen.

7.3.1. Oil Sands Offgas Processing Expansions

Upgrading bitumen into synthetic crude oil simultaneously produces a by-product (offgas) that is comprised roughly of 40% methane, 20% hydrogen, and 40% olefins (ethylene and propylene) and natural gas liquids (ethane, propane and butane). After extracting natural gas liquids (NGLs) and olefins from the offgas a methane and hydrogen-rich stream is obtained. If this methane/hydrogen waste stream is used for flue gas reforming we estimate that for a 15,000 barrels per day (bpd) upgrader the average annual operating impacts could be expected to include roughly CAD$5.7 million in GDP, CAD$2.4 million in labour income and CAD$5.4 million in provincial government revenues. Average annual operating employment would amount to 21 jobs per year.

7.3.2. Methanol

The profitability of methanol production in North America has improved considerably given lower gas prices in the last few years as a result of the shale gas boom. So much so, in fact, that Methanex is proposing a debottlenecking of its Medicine Hat facility that would increase capacity by 10-20%. When an adjustment is made to the feedstock costs to account for more recent forecasts, the results indicate that a new methanol plant could in fact be profitable. Assuming a 900 kt/year plant, roughly CAD$800 million in GDP, CAD$640 million in labour income, CAD$65 million in provincial government revenue and 4000 person years of employment would be created during construction. Annual operating impacts would include CAD$270 million in GDP, CAD$50 million in labour income, CAD$20 million in provincial government revenue and 540 jobs. The cost structure for the methanol facility is more capital intensive resulting in relatively larger construction phase versus operating phase impacts.

7.3.3. Ammonia (and Urea)

Ammonia and urea are two products that represent some of the most favourable investment opportunities in hydrocarbon derivatives in Alberta. Like with methanol, the projections of future gas prices suggest that a new urea plant could be economically viable. The net annual economic impacts of a 600 kt/year urea plant in Alberta would include about CAD$80 million in GDP, CAD$35 million in labour income, CAD$10 million in provincial government revenue and 340 jobs.

7.3.4. Hydrogen

In Alberta, on average, 21,000,000 m^3 of hydrogen are required to upgrade 125,000 m^3 of bitumen per day in the oil sands mining projects in Northern Alberta. Northwest Redwater Partnership (NWR) has sanctioned the construction of 50,000 barrels per day (bpd) bitumen refinery in Alberta’s Industrial Heartland scheduled to start in 2015 with future expansion anticipated by NWR to bring the capacity of the refinery to 150,000 bpd of bitumen. NWR’s 50,000 bpd bitumen refinery could be expected to generate roughly CAD$670 million in GDP, CAD$200 million in labour income, CAD$70 million in provincial government revenues and 2100 jobs per year when in operation. Should the refinery ultimately be expanded to its planned long-term capacity of 150,000 bpd of bitumen, the operating impacts would triple.

7.3.5. Fischer-Tropsch Gas-to-Liquids (GTL)

Synthesis gas with a H_2/CO ratio of 2 is perfect for conversion via Fischer-Tropsch into products such as diesel fuel and naphtha in a GTL plant. Sasol was contemplating the initiation of engineering and design for 96,000 barrels per day (bpd) GTL plant in Alberta, but recently delayed those plans given their proposed development of GTL facilities on the US Gulf Coast. A 96,000 bpd GTL plant could be expected to generate roughly CAD$1.8 billion in GDP, CAD$360 million in labour income, CAD$180 million in provincial government revenues and 3800 jobs per year when in operation.

7.3.6. Polyethylene and Polypropylene

NOVA Chemicals is currently planning an expansion of its polyethylene facilities at Joffre. The company expects to add a third polyethylene reactor, with the capacity to produce up to 1.1 billion pounds of linear, low-density polyethylene annually. The impacts of this polyethylene expansion would include roughly CAD$840 million in GDP, CAD$670 million in labour income and about CAD$70 million in provincial government revenues. The average annual operating impacts could be expected to be approximately CAD$360 million in GDP, CAD$120 million in labour income and CAD$35 million in provincial government revenues. Average annual operating employment would amount to about 1300 jobs while overall construction employment would be roughly 4100 person years. A 300 kt/year polypropylene plant could be expected to generate roughly CAD$130 million in GDP, CAD$35 million in labour income, CAD$10 million in provincial government revenues and 370 jobs per year. Williams has recently sanctioned construction of a propane dehydrogenation (PDH) facility in Strathcona County with a capacity of to provide enough feedstock for about 450 kt/year of polypropylene production. The H_2 offgas is a good feedstock for the production of methanol, ammonia and merchant hydrogen.

Table 10: Potential Annual Economic Impacts in Alberta of Chemical Industry Expansions Using Hydrocarbon Feedstocks over the Next Decade (Values are in millions of 2012 CAD$)

Product - Annual Volume	GDP	Labour Income	Provincial Government Revenue	Employment (person years)
Methanol – 900 kt/year	270	53	21	541
Urea – 600 kt/year	78	34	10	343
NGLs/Olefins from Oilsands Offgas	537	197	54	2062
Propylene – 900 kt/yr	398	174	46	1890
Polyethylene – 900 kt/yr	712	236	72	2542
Polypropylene – 900 kt/yr	396	102	33	1113
Total	2391	796	236	8491

(1) Economic Impacts of Adding Value to Alberta's Hydrocarbon Resources, Report prepared for Alberta's Industrial Heartland Association, Schlenker Consulting Ltd., April 15, 2013.

8. INTELLECTUAL PROPERTY, PROJECT COSTS AND ROUTE TO MARKET

8.1 Intellectual Property Status

Robert Gordon University holds significant background IP in this technology space. Relevant patent families established by RGU are identified in Table 11. The University maintains confidentiality around unpublished results and know-how through operation of its IP Policy.

Table 11: Relevant Patent Families

WO2004/098750	Published 18-Nov-04 Granted in multiple territories.	"Gobina & Olsen": *A membrane apparatus & method of preparing a membrane & method of producing hydrogen*
WO2009037469	Published 26-Mar-09 Granted & Pending in multiple territories	"Gobina & Umoh" *Process & apparatus for the production of alcohols*
WO02074421	Published 26-Aug-02 Granted and Pending in multiple territories	"Gobina" *Apparatus & method for separating gases*

8.2 Business and Commercialization Strategy

The possible routes to market are illustrated in Figure 15 along with the expertise that has already been developed at the Centre for Process Integration and Membrane Technology and the tangible benefits of the proposed project. We believe there are several non-competing routes to commercial exploitation including:

- A product model at a subsystem level i.e. reactors for carbon conversion/stranded gas
- A data services model for carbon trading/offset strategies.
- An integrated product model for utilisation.

8.3 Business Strategy

Figure 15 shows our Business and Commercialization Strategies for FFCM reactor (forced-flow catalytic membrane) process. Our objective is to be the leading provider of CO_2-rich/lean flue gas conversion and related technologies for the production of value-added chemicals.

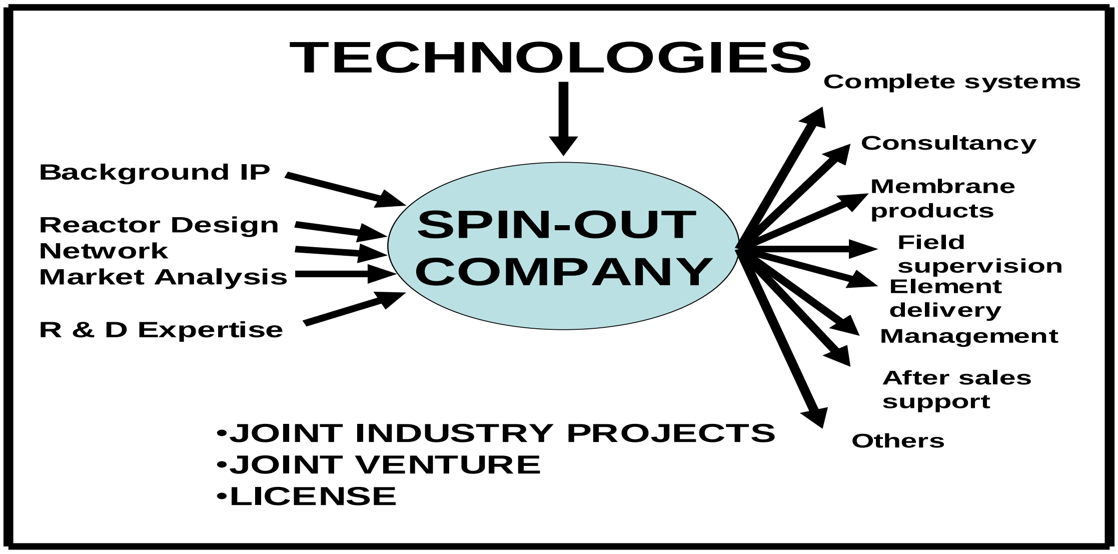


Figure 15: Business and Commercialization Strategies for F3R™ Process

8.4 Research Environment

The Centre for Process Integration & Membrane Technology (CPIMT) at The Robert Gordon University conducts research on hydrogen, natural gas, gas-to-liquids and carbon capture using its state-of-the-art laboratories and pilot plants. The Centres' laboratories are one of the highest quality research facilities in North Scotland and feature equipment such as an X-Ray Diffractometer, Scanning Electron Microscope/ Electron Probe Microanalysis, Nuclear Electron Probe Microanalysis, Gas Chromatography-Mass Spectrometer, Fourrier Transform Infrared Spectroscopy, and High Performance Liquid Chromatography and Nitrogen Adsorpsion surface area and pore size characterization using cryogenic nitrogen (BET, BJH). Researchers at the Centre study thin-film metallic composites, formulated/design reactor development and testing, impregnation and membrane development, process flow configurations, multilayer and integrated process studies, simulation and modelling and downhole technologies. Our mission is to develop the most economic, effective, and versatile energy efficient and greenhouse gas reduction solutions possible with research on carbon capture with carbon rehabilitation as a key focus. CPIMT conducts R&D on advanced ceramic hybrid membrane separation and recovery of industrial gases from waste streams and industrial processes. Researchers are also investigating membrane/catalyst development, gas/solid interactions, and surface characterization to enhance the ability of filters to separate and capture such impurities as CO_2, VOCs, and hydrogen from fuel gas and waste streams. Catalytic membrane reactors have been developed for a wide range of temperatures and for use with different fuel gas/waste streams and researchers are developing fundamental models for calculating reaction rates and equilibrium associated with the combustion and gasification of fossil fuels, chemistry of production of ultra-clean fuels, hydrogen separation and storage technology, and surface science and catalysis. Models that predict CO_2 separation efficiency and the conversion of CO_2 during dry reforming with methane are being developed to demonstrate how carbon conversion to chemicals can dramatically mitigate potential impacts of greenhouse gas emissions.

8.5 Principal Investigator (PI) Experience

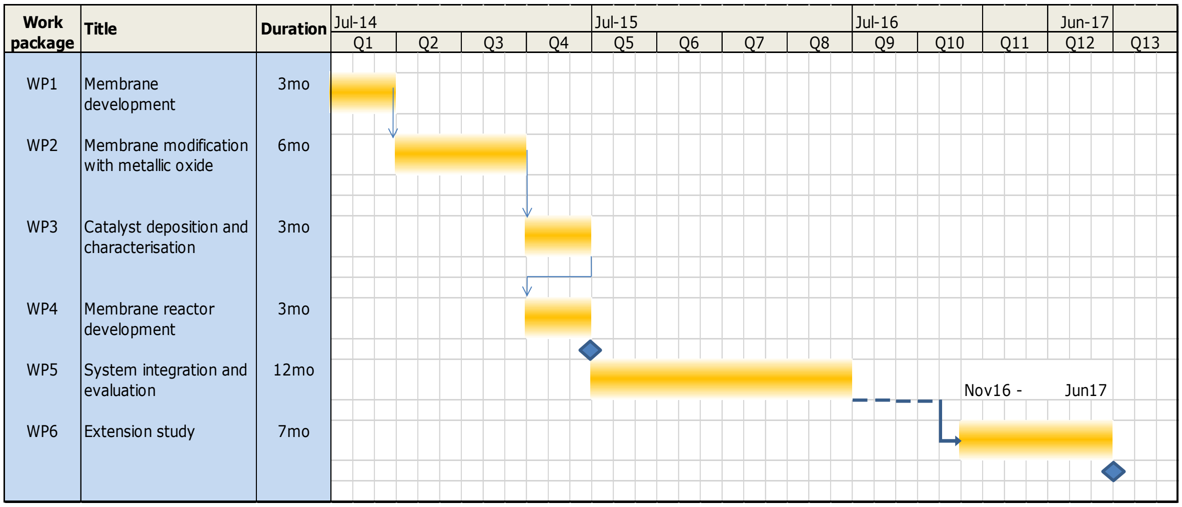
8.5.1 Professor Edward Gobina

Edward Gobina is the current Director of CPIMT with over 33 years research and teaching experience in environmental engineering, petrochemical reaction engineering, and catalysis and membrane technology. He has over 20 awarded patents and over 50 patent applications and has been published extensively with over 350 publications in international scientific journals and 25 books including a volume on carbon dioxide utilisation and recovery. His research has resulted in the creation of up to three Spin-out companies including focused on bringing to market a new generation of natural gas to liquid reactors based on proprietary catalytic porous membrane technology. He has worked on other commercially led projects including a carbon capture and high-density hydrogen production project funded by Scottish Enterprise through the Proof-of-Concept Scheme, Conoco Phillips, Carbon Trust and Oil Industry Technology Facilitator. Professor Gobina has 15 years in-depth experience in Industry Market Analysis and has carried out numerous custom studies in this regard. Professor Gobina is a member of the European Membrane Society (EMS), the North American Membrane Society (NAMS), and the New York Academy of Sciences (NYAS).

8.6 Project Gantt Chart

Table 14 presents the project Gantt chart including the ‘’Extension Study’’. The Extension Study was approved by CCEMC in order to assess experimentally the effect of contaminants such as NO_2 and SO_2 on membrane catalyst stability.

Table 12: Gantt Chart



Work package	Title	Duration
WP1	Membrane development	3mo
WP2	Membrane modification with metallic oxide	6mo
WP3	Catalyst deposition and characterisation	3mo
WP4	Membrane reactor development	3mo
WP5	System integration and evaluation	12mo
WP6	Extension study	7mo

8.7 Role of Edmonton Facilities in the Phased Commercialization Approach

Table 15 identifies the role of Edmonton facilities in our phased approach to the F3R™ Process commercialization.

Table 13: Role of Edmonton Facilities in the Phased Commercialization Approach

PHASE	PERIOD	ROLE OF EDMONTON FACILITIES
2, 3 & 4	2018 – 2023	Edmonton Facilities will assist in the sourcing of the membrane supports, the catalysts, and the seals for the reactor, connections, tube sheets, headers, gaskets, mountings, baffles. They will also help in identifying the manufacturers of the shell housing the membranes. We have identified the university of Alberta as a suitable host to test the components of the experimental reactor, take care of the system design and optimization, and assist in building the pilot scale reactor. The system will be finally installed and operated at an NGCC plant (not yet identified) in Alberta to perform the environmental life cycle assessment of the system. We have also identified Enerkem's waste-based facility in Edmonton or a slip stream from the Shell Scotford's upgrader complex for our Demonstration Facility which will be bolted-on to produce ultra-clean diesel fuel and jet fuel (subject to certification) from flue gas using the F3R™ Process.

9. NEXT STEPS AND FUTURE WORK

9.1 Potential for Follow-on Projects

The project at this stage has been very much at the level of applied research and with respect to recognised technology readiness levels has met the goal of progressing to TRL3/TRL4. The project has provided a laboratory scale proof of concept for up-grading of flue gas with methane (tri-reforming) into high quality syngas through catalytic reforming reactions using a catalytic membrane reactor over activated in-lab prepared rhodium membrane catalyst using two membrane dimensions. The "extension study" conducted over the period Jan – Aug 2017 further cemented the proof-of-concept to show process tolerance to trace quantities of NO_2 and SO_2 contaminants.

Given the early stage of technology and process development a great many follow-on projects can be contemplated and ultimately will be necessary to build a compelling case for investment towards commercialisation (Please see more details in the **TECHNOLOGY TRANSFER PLAN REPORT**).

Figure 16: COMMERCIAL IN CONFIDENCE

9.2 Long-term Plan for Commercialisation of the F3R™ Technology

The university is fully aware that technology development from a low level of readiness towards commercial realisation will requires significant investment to overcome the technical challenges and build a business case for commercial deployment. Our early thinking towards these issues is to engage at an early point with a large industrial partner. The ideal partner should be capable of sustaining the high levels (£million) of investment required to support the technology development and have the relevant market footprint to be able to realise its investment.

From the university perspective, commercialisation of the project will be achieved through technology licensing, coupled with on-going consultancy and technology development support into the partner where relevant and required. The university will always seek to retain rights in the technology to conduct further research and teaching as per its core mission. Appropriate agreements will be executed to ensure commercial interests are protected, for example around data confidentiality and publications.

The present F3R™ Process is recognised to be a technology "module" to a wider process pathway. Thus whilst we have demonstrated that F3R^{TM} Process can produce syngas at an appropriate quality for subsequent gas-to-liquid hydrocarbon synthesis, there is a requirement for a compatible Fisher Tropsch process to be available for making suitable market quality products. A downstream technology process partner is likely to be in the petrochemicals or closely related sector. We believe that this does mean that successful technology uptake will be global and our commercialisation activities will be of an international outlook from the beginning.

We believe that the F3R™ Process will be an attractive solution for companies reviewing methods of reducing and/or elimination CO_2 emissions and those involved in producing their natural gas reserves that may contain unacceptably high CO_2 concentrations using non-traditional methods. We believe the F3R™ Process will enable owners of flue gas sources and invaluable natural gas reserves to monetize a portion of these resources by converting them into synthetic liquid hydrocarbons in the form of ultra-clean fuels and that these products can be:

- produced substantially free of undesirable products normally found in fuels and specialty products made from crude oil;
- used as blending stock to upgrade conventional fuels and specialty products made from crude oil;
- used unblended in traditional internal combustion engines to reduce emissions;
- used in advanced internal combustion engines and fuel-cells that require sulphur-free fuels; and
- transported through existing distribution infrastructures for crude oil and refined products.

Aside from the climate change benefits, the economic benefits of the technology will accrue in three significant areas. The large scale manufacture of the ceramic tubes coated in the membrane layer is a significant new industrial activity – a single power station will require many millions of catalytic tubes to convert >90% of its CO_2 production. The engineering design and installation of the technology at major emission sources will be a significant driver of design and construction-related employment. The operation of this system, and the associated carbon conversion systems, represents an entire new waste-disposal industry with significant employment opportunities.

9.2.1 Phase 2 Work packages

PHASE 2 will involve the fabrication of the miniature industrial scale prototype unit, followed by live testing at various power stations (natural gas fired power plant). This is an industrialisation and prototype development project. This will address the challenges of the different methods for catalyst preparation and influence catalyst activity for CO_2 reforming, designing the system to avoid membrane degradation due to particulates and acid gases; manufacturing the membrane technology in large quantities; and assessing the issues associated with operating the membranes at a real power plant where there are substantial variations in operating parameters day-to-day.

9.2.2 Phase 3 Work packages

PHASE 3 work would entail a 2 year “follow on” project and would scale-up to demonstration plant scale (~250MW), This development will deliver a competetively low energy CO_2 conversion system in time to serve the large and completely new market for carbon capture.

9.2.3 Phase 4 Work packages

PHASE 4 will culminate with the first full scale power plant tests implementation.

9.3 Other Actions to Facilitate Commercialisation

The following identifies other key actions to underpin commercialisation activities:

9.3.1 Consolidate Intellectual Property.

- The technology is currently protected as confidential information and all research students who have undertaken aspects of this work have assigned their IPR to the university.
- An initial Invention Disclosure of the technology has been reviewed for patentability and whilst there are no particular concerns around novelty, the attorneys have flagged potential issues around inventive step.
- New experimental data, and in particular that concerning the formulation and characterisation of the catalyst, and performance of the system are to be reviewed for patentability and patent filings established.
- TM registration for terms such as F3R™ is to be considered and international registrations made where appropriate.

9.3.2 Undertake Full Market Assessment and Business Model Planning

- Project team to work with Aberdeen Business School MBA programme to undertake market segment analysis, economic case development and business model planning. Results to inform senior management decisions around the suitability of a university spin-out company creation versus a technology licencing option.
- External consultants to be sought and relevant industry experts to be identified as commercialisation champions.

9.3.3 Identify Development Partners and Build Consortia

- Some supply chain partners and interested development partners already have visibility of the project and are identified in the **TECH TRANSFER REPORT**
- A strategic approach to partner identification will be taken and this will be informed by the business model planning and economic case modelling.

9.3.4 Further Develop and Implement Project Dissemination Strategy

- Strategic publication to target appropriate industry journals.
- Attendance at selected conferences to generate interest but ensure contact follow-up with potential commercialisation or research partners in all instances.
- Existing network relationships, particularly with agencies in Aberdeen such as the Oil and Gas Innovation Centre, the Oil and Gas Technology Centre and the Industry

Technology Facilitator will be leveraged to support partner identification, and next level funding opportunities.

9.3.5 Maintain an On-going Research Activity

- The pace of on-going research will be subject to level of funding that can be attracted from funding councils or other agencies. Any new data is recognised to consolidate the technical case, the IPR position, de-risk commercialisation decisions and thereby aid potential partner engagement.
- Strategic thinking will be required to ensure any funding which is dependent of industry partner contribution, maintains freedom to commercialise internationally and to multiple industrial sectors.