Introduction

The project goal is to design a process capable of converting methane, obtained from remote sites, to a more easily transportable fuel, methanol. The design should focus on minimizing the overall footprint of the process by utilizing micro-unit operations wherever feasible. All utilities required by this process are to be generated from the natural gas feed, which represents a direct loss to the process.

The methane well sites are located on the north slope of Alaska, just outside of Prudhoe Bay. The exact coordinates for one of the well sites are "70.350,-149.328." A satellite image of the well site is displayed in Figure 1.

Figure 1. Satellite image of potential methane source located just outside of Prudhoe Bay.[1]

The methane obtained from the sites is expected to be derived from natural gas hydrates and will be available as methane at 0°C, at approximately 27 atm, containing approximately 5% nitrogen and saturated with water vapor at these conditions.

Refineries located in the Prudhoe Bay area use methanol as a de-icing agent, since the melting point is -97°F. Currently, 8.5 million gal/y of methanol are shipped to Prudhoe Bay from the lower 48 using the transportation route displayed in Figure 2[2].

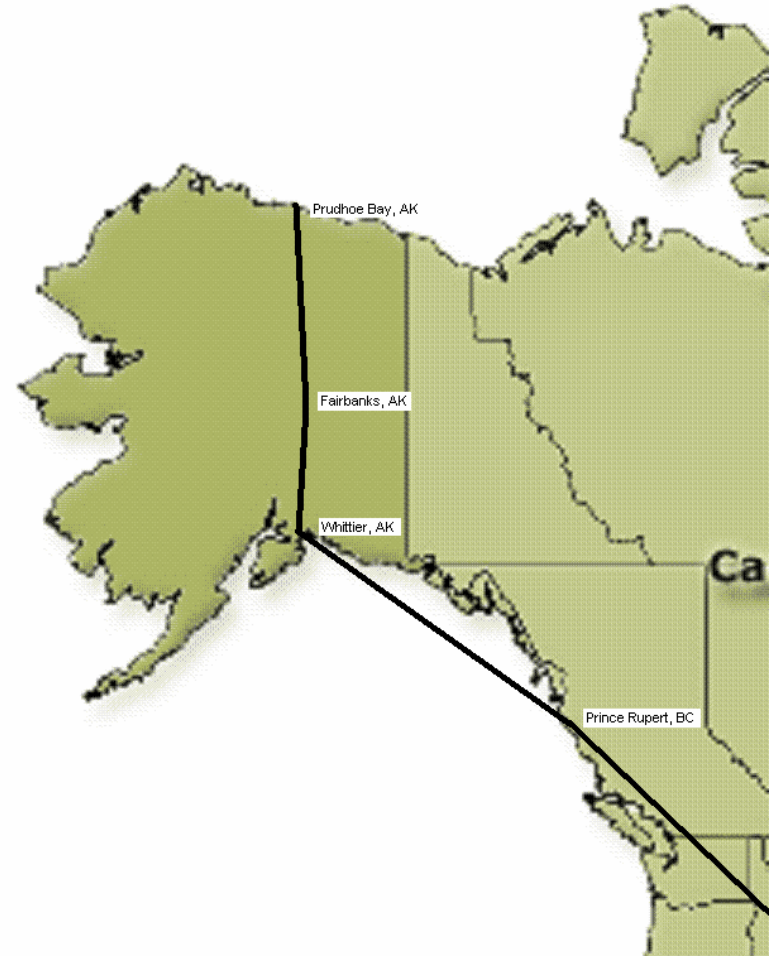

Figure 2. Current Methanol Shipping Route from the lower 48 to Prudhoe Bay, AK.[2]

The methanol is shipped by rail car to Prince Rupert, BC, from the lower 48. From there, the methanol is put on a rail barge to Whittier, AK. Then, railroads are used to get to Fairbanks, AK. Finally, the methanol is transported by truck to Prudhoe Bay. Alaska West Shipping Company

operates a transfer facility in Fairbanks that transfers the product from the truck to the rail car, or vice versa. Aqua-Train Company is in charge of all rail and rail barge transportation.[2] Converting the North Slope natural gas to methanol would give refineries a local methanol source and eliminate the need for this lengthy and expensive shipping route.

Results

Due to the variable methane flowrates over the life of the project, 14 modules will be required, with each being brought online as needed. The proposed process flow diagram for a single module is displayed in Figure 3.

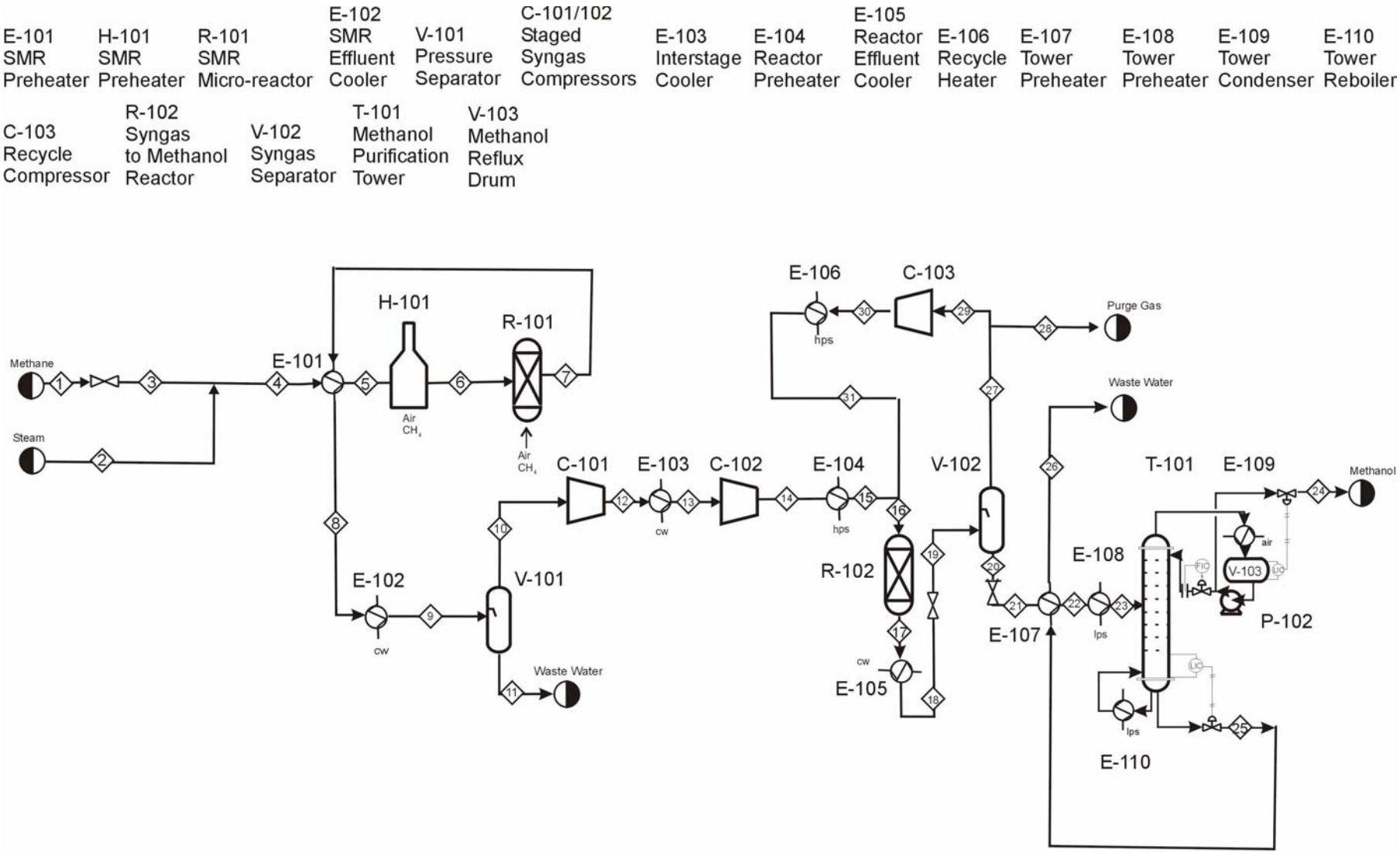

Figure 3: Process Flow Diagram For Unit 100 – Methane Reforming to Methanol

Referring to Figure 3, the methane is supplied to the process directly from the well head at a pressure of 27 atm, 0°C, and saturated with water vapor. The methane feed pressure is reduced to 10 bar before being mixed with steam. Steam then mixes with the methane feed at a 3:1 water-to-methane molar ratio, and the resulting stream, Stream 4, is preheated using R-101 effluent to 950°C in E-101. A fired heater is required for the final heating stage to ensure that R-101 feed, Stream 6, is at the reaction temperature of 1000°C. Stream 6 is sent to R-101, a gas-phase isothermal micro-channel reactor packed with an Rh/MgO catalyst on an Al_2O_3 support structure to produce synthesis gas (syngas). The reactor effluent, Stream 7, is then cooled to 30°C and flashed to separate the residual water from the syngas. The syngas-rich stream, Stream 10, is compressed to 50 bar, heated to 230°C, and mixed with syngas recycle before being sent to R-102, a gas-phase, adiabatic packed bed reactor to convert the syngas to methanol. The reactor effluent, Stream 17, is then cooled to 10°C and flashed at 50 bar to separate the residual syngas from the methanol-water solution. The vapor leaving V-102 is then recycled to increase the overall methanol conversion. The methanol-water stream, Stream 20, is then heated to 95°C and sent to HIGEE system T-101 to separate the water from the methanol. In this tower, a methanol-rich stream, containing approximately 99.86 wt% of methanol is taken as a top product and sent to V-105*, a central methanol storage vessel.

Water is obtained from tundra lakes located within a mile of the centralized facility using pump P-101*. A desalination unit, D-101*, is required in order to purify the water for feed and utility requirements. Desalination occurs through reverse osmosis, and it will be powered by electricity produced through methane combustion turbines. The desalinated water will be used as feed, boiler feed water in steam production, and cooling water. For both steam and cooling water systems a loop will be in place to conserve most of the water; however, small water losses

will be incurred due to evaporation. Approximately 15% of the water is lost in the steam system, while 2% is lost in the cooling water system. The desalination unit will run continuously to replenish the water losses.

High-pressure steam used for feed and utility requirements is produced at a centralized facility, H-102*. Waste water streams, Streams 11 and 26, are treated in V-106* to remove any residual methanol before sending water back to the tundra lakes.

In addition to methane being consumed to produce high-pressure steam and electricity for the desalination unit, methane is also consumed in combustion turbines, J-101, J-102, and J-103* to turn the shafts of compressors C-101, C-102, and C-103. J-103 is also connected to a generator to supply electricity to the HIGEE drive and reflux pump P-102.

*Not depicted in Figure 3. Shown on plot and elevation diagrams not included in this synopsis.

Gas Production Schedule

As specified by our contract, a maximum of four wells will be dug every year, with new wells being put into service approximately every three months. By operating year four, all sixteen wells will be completed and online. Assuming a project life of fifteen years, the maximum output possible from the entire well site by year is given in Figure .

Of the methane obtained from the well sites, 48% is sent to the process as feed and 52% is used for utility requirements. The projected methane flowrates and utility requirements were taken into account to determine when new modules will have to be brought online. The schedule is displayed in Table .

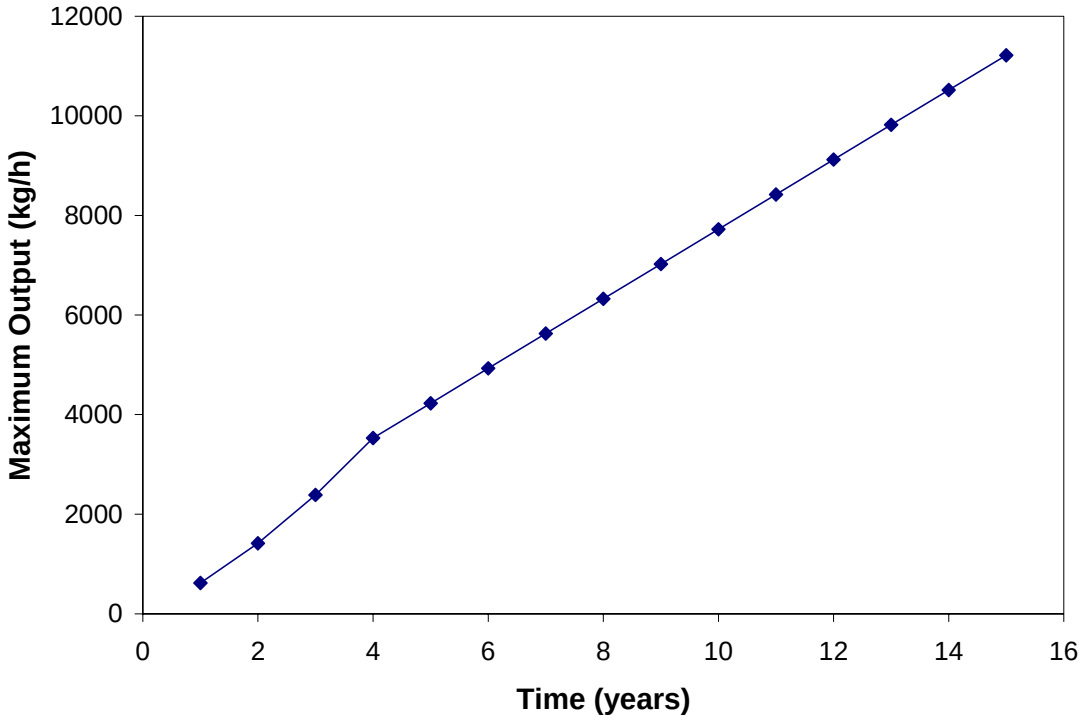

Figure 4. Maximum methane output from entire well site.

Table 2. Schedule for bringing new modules online based on projected methane flowrates

Year	Estimated Methane Production from Wells (kg/h)	Methane used as raw material (kg/h)	No. of Required Modules
1	621	397	1
2	1416	794	2
3	2386	1191	3
4	3530	1985	5
5	4229	2382	6
6	4927	2382	6
7	5626	2779	7
8	6325	3176	8
9	7023	3573	9
10	7722	3970	10
11	8420	4367	11
12	9119	4764	12
13	9818	4764	12
14	10516	5161	13
15	11215	5558	14

Reaction Equations and Kinetics

The first reactor, R-101, is a steam methane reforming reactor. The reactions that take place in this reactor are shown in Equations 1 and 2.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \quad (2)$$

Equation 1 is the reforming reaction. It is highly endothermic and produces more moles of products than reactants. This makes conversion favored by high temperatures and low pressures. Equation 2 is the water-gas shift reaction. This reaction is exothermic, independent of pressure, and favored by low temperatures. Both reactions are equilibrium limited and are controlled by reaction kinetics shown in Equations 3-12.[3] The catalyst used in these reactions is Rh/MgO on Al_2O_3 support structure.

$$r_1 = k_1\left(P_{CH_4}P_{H_2O} - \frac{P_{CO}P_{H_2}^3}{K_1}\right) \quad (3)$$

$$k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) \quad (4)$$

$$A_1 = 1.275\text{x}10^8 \quad (5)$$

$$E_1 = 1.605\text{x}10^8 \quad (6)$$

$$K_1 = \exp\left(\frac{-26830}{T} + 30.114\right) \quad (7)$$

$$r_2 = k_2\left(P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_2}\right) \quad (8)$$

$$k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \quad (9)$$

$$A_2 = 1.466\text{x}10^3 \tag{10}$$

$$E_2 = 6.713\text{x}10^7 \tag{11}$$

$$K_2 = \exp\left(\frac{4400}{T} + 4.036\right) \tag{12}$$

In Equations 3-12, the reaction rate is in kmol/m^{3}cat/s, the pressure is in bar, and the temperature is in Kelvin. The activation energy units are J/kmol.

The second reaction in this system is the production of methanol from the syngas produced in the steam-methane reforming reaction. Equations 13 and 14 detail the reactions that take place in the production of methanol.

$$\text{CO} + 2\text{H}_2 \Leftrightarrow \text{CH}_3\text{OH} \tag{13}$$

$$\text{CO}_2 + \text{H}_2 \Leftrightarrow \text{CO} + \text{H}_2\text{O} \tag{14}$$

Equation 13 is the desired reaction in the production of methanol. It is highly exothermic and produces fewer moles than it reacts. This makes conversion favored by low temperatures and high pressures. Equation 14 displays the water-gas shift reaction. Both reactions are equilibrium limited and are controlled by reaction kinetics shown in Equations 15-20. The constants in the reaction rate are taken from a case study conducted at 225°C.[4]

$$r_1 = k_1 \frac{K_{CO} K_{H_2}^2 \left(p_{CO} p_{H_2}^2 - p_{MeOH} / K_{eq}\right)}{\left(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2}\right)^3} \tag{15}$$

$$k_1 = 1.064 \tag{16}$$

$$K_{CO} = 12.52 \tag{17}$$

$$K_{H_2} = 1.77 \tag{18}$$

$$K_{eq} = 9034 \tag{19}$$

$$K_{CO_2} = 39.62 \qquad (20)$$

In Equation 15, the reaction rate is in mol/g cat/h and the pressure is in atm.

HIGEE® Separation System

The project scope requested a detailed design of separation system T-101. This is the final unit operation required to produce a pure methanol product from a gas hydrate raw material. The rotating packed bed or HIGEE® was determined to be best suited for this application, in part due to its small footprint. A diagram of the HIGEE® system is shown in Figure .

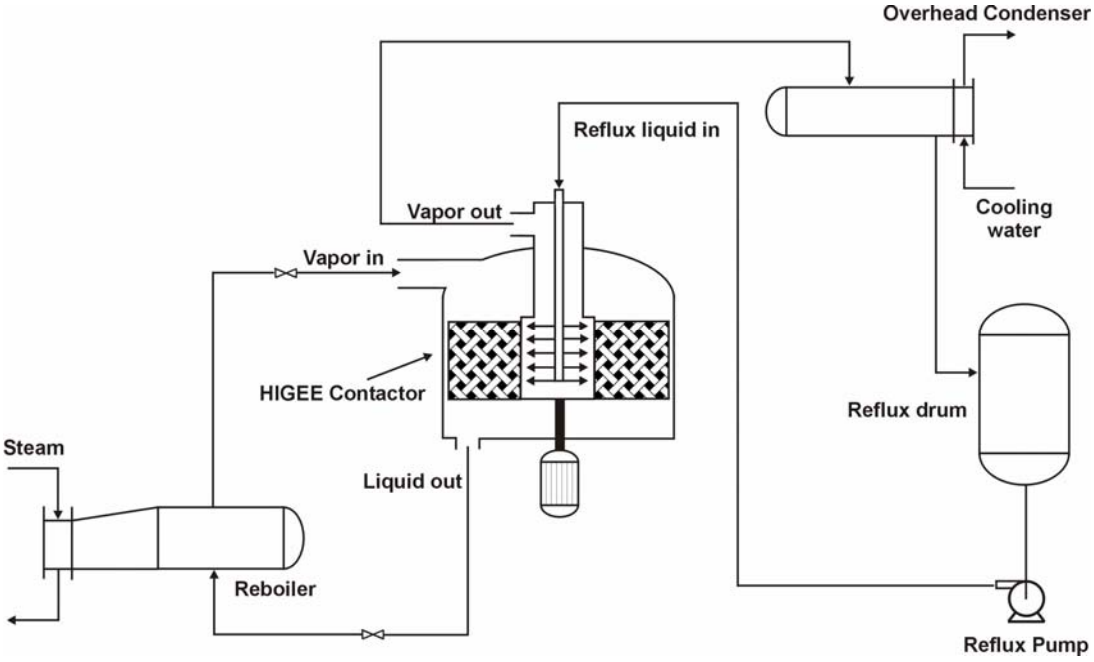

Figure 5. HIGEE® system with auxiliary equipment[5]

A detailed layout and design description is included in Table .

Table 3. Key design variables for HIGEE® system T-101

Pressure	bar	4
Temperature	°C	95
Volume	m^3	12.7
Outer Radius	m	0.818
Height	m	6.05
Packing Radius	m	0.489
Packing Height	m	0.55
Surface Area of Packing	m^2/m^3	2500
Reflux Ratio		1.1
Condenser Duty	MJ/h	-365.3
Reboiler Duty	MJ/h	985.8
Outlet Purity	mol%	99.7
ATU	m^2	0.0273
NTU		25
RPM		1000
Drive Power	kWh	28.5
Pressure Drop	kPa	3.56
Annualized Capital Cost	$/y	$ 12,602

Micro-Reactor Design

The reactor configuration for R-101 has been defined as a cross-flow, micro-channel heat exchanger. The reactor configuration is illustrated in Figure .

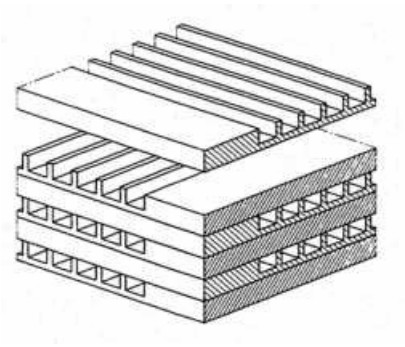

Figure 6. Cross-flow reactor configuration[6]

The endothermic steam methane reforming reaction takes place at 950ºC. The heat is supplied to the process through combustion of methane in adjacent channels. Since the reactor is running isothermally, the temperatures of both sides are very similar. The temperatures and properties of both streams are shown in Table .

Table 4. Stream properties for R-101

	Methane Combustion	Process Side
T_{in} (ºC)	1005	1000
T_{out} (ºC)	1005	1000
m (kg/h)	3152	1622
ρ (kg/m^3)	7.74	1.43
μ (kg/m-s)	1.06×10^{-5}	4.31×10^{-5}
C_p (kJ/kg-K)	2.25	3.05
k (kW/m-K)	0.39	0.16
v (m/s)	5.36	1.49

With a heat duty of 4005 MJ/hr, a heat transfer area of 105.45 m^2 was necessary. The dimensions of both the overall reactor and interior channels are shown in Table . With the dimensions listed, the process-side pressure drop was found to be 20.6 kPa, while the methane

Table 5. Dimensions for R-101

		cm
Overall	Length	44.997
	Width	44.997
	Height	113.10
Methane	Channel Width	0.026
	Channel Height	0.013
	Wall Thickness	0.010
Process	Channel Width	0.026
	Channel Height	0.130
	Wall Thickness	0.010

side pressure drop was 19.3 kPa. The dimensions yield a reactor volume of 0.0945 m^3. The reactor was designed to have 500 layers for each fluid, totaling to 1000 layers. The overall heat transfer coefficient for the reactor was found to be 2,110 W/m^2K.

R-101 Materials of Construction

The material of construction for the micro-channel reactor/heat-exchanger is Inconel 617, a highly temperature-resistant, nickel alloy. Inconel is ideal for the micro-channel heat exchanger primarily because of its melting point of 1335ºC. Other physical properties of Inconel 617 are shown in Table 1.

Table 1. Physical Properties of Inconel 617[7]

Density, lb/in^3	0.302
Mg/m^3	8.36
Melting Range, °F	2430-2510
°C	1332-1380
Specific Heat at 78°F (26°C)	
Btu/lb-°F	0.100
J/kg-°C	419
Electrical Resistivity at 78°F (26°C)	
ohm-circ mil/ft	736
μΩ-m	1.22

The fabrication of the heat exchanger with Inconel is unlike conventional methods. Inconel is a difficult metal to machine using traditional techniques due to the rapid work hardening. Work hardening tends to deform elastically either the work piece or tool after the initial machining pass. There are two alternatives to classical machining: mechanical stamping and photochemical machining (PCM). For the application of R-101, photochemical machining will be the most economical. A manufacturing cost estimate from Velocys, Inc., showed that the reactor should cost around $280,000[8].

References

1. www.maps.google.com

2. Weide, D., Alaska West Shipping Company, personal communication.

3. Tonkovich, A., "From Seconds to Milliseconds Through Tailored Microchannel Reactor Design of a Steam Methane Reformer," *Catalysis Today*, 120 (2007): 21-29.

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5. Kelleher, T., "Distillation Studies in a High-Gravity Contactor," *I&EC Research*, **35** (1996): 4646-4655.

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