

# Ethyl Chloride Gas Production

Submitted to

Dr. Clémence Fauteux-Lefebvre  
CHG 3127 Professor

By

Ilia Negovora (300070880)  
Fadi Oussta (7958597)  
Alexander Karmazin (8786600)  
Ebiarede Odibo-Satu (300065337)  
Tareq Mareh (300096483)

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## Executive Summary

To complete the CHG3127 design project group 22 members elected to design a packed bed reactor (PBR) model consisting of two reactors, meant to facilitate a multi-step reversible reaction between ethanol (EtOH) and hydrochloric acid (HCl) to produce ethyl chloride (EtCl), a chemical with a wide variety of uses in industry. The main task of the design project was the creation of a model in excel, which could demonstrate the ability of students to apply material regarding chemical reaction design learned in class and apply it to the chosen chemical reaction, using a sophisticated mathematical method to solve for ordinary differential equations to obtain necessary values. Group 22 members used the RK45 ODE solution method to solve for said equations, calculating molar flow rates, reaction rates, temperatures, pressures, and selectivity, and comparing said values against varying initial conditions. It was found that though it was possible to achieve a desired output of the product under optimal conditions using said reactor design, the design was deemed too inefficient to be put in practice for industrial purposes, which correlated with relevant findings from literature. To ameliorate results perhaps a different reactor type able to withstand high pressures could be used, and a route facilitating liquid-phase reactions of the same type could be implemented.

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## Nomenclature Table

Symbol	Definition
DEE	Diethyl ether
$k_i$	Rate constant
$E_A$	Activation energy
SBET	Nitrogen fixation surface area
PBR	Packed-bed reactor
$F_i$	Molar flow rate
$r_i$	Reaction rate
W	Catalyst weight
P	Density
K	Equilibrium constant
$U_i$	Heat transfer constant
$C_i$	Concentration
D	Diameter

# 1. Introduction

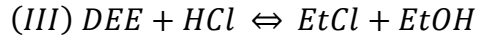
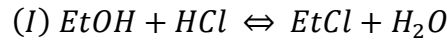
This report contains the design information and simulation for ethyl chloride production from the reaction of Ethanol and HCl in a series of Packed Bed Reactors. Chloroethane is the simplest and least toxic member of the class of chloroethanes, that is ethane in which a single hydrogen is substituted by a chlorine. A colorless gas at room temperature and pressure (boiling point;12°C) National Center for Biotechnology Information,<sup>[2]</sup> Ethyl chloride has a wide variety of uses across different industries in the medical industry. It also functions as a topical anesthetic to numb skin prior to medical procedures such as skin biopsies and sports injuries, Axiall Corporation.<sup>[1]</sup> In the petrochemical industry it is used to produce Tetraethyl lead which in turn is added to gasoline and acts as an anti-knock agent. Ethyl Chloride is also used in the production of Ethyl Cellulose resins which function as coating, film forming and binding for various products such as industrial coatings and pharmaceuticals; According to one of our sources this is the biggest use for ethyl chloride in the United States Axiall Corporation.<sup>[1]</sup> Even with the countless uses of ethyl chloride in various industries there are some disadvantages and harmful by-products in the production of ethanol. Some of the disadvantages of ethyl chloride production are -

- Ethyl chloride is a hazardous air pollutant (HAP). Axiall Corporation,<sup>[1]</sup>
- Suspected of causing cancer. National Center for Biotechnology Information,<sup>[2]</sup>
- Harmful to aquatic life. National Center for Biotechnology Information<sup>[2]</sup>

Two methods of production of chloroethane were discussed in the reference paper Bukhanko et al.,<sup>[3]</sup>. The reaction between Ethanol and HCl. The second model was “based on the assumption that ethyl chloride is produced from ethanol and diethyl ether, but via intermediate states”. This reaction pathway can be found in the literature Bukhanko et al.,<sup>[3]</sup>. The current production techniques discussed in the literature make use of plug flow packed bed reactors. This is the method adopted in our simulation as we used multiple PBRs to ensure maximum conversion of Ethanol.

## 2. Reactions and Parameters

The reaction that is being studied between ethanol and HCl is a “green route” for producing ethyl chloride which has various industrial applications Bukhanko et al.,<sup>[3]</sup>. The reactions involved in this process along with their kinetic parameters were obtained from the research conducted by Buhanko et al. titled “Kinetic modeling of gas phase synthesis of ethyl chloride from ethanol and HCl in fixed bed reactor”. Two reaction models were provided for this process and scheme 1 was chosen as the target for the simulation experiments. The main reaction for production of the desired product ethyl chloride as well as the side reactions, are as follows:



In addition, the reaction rates of each are as follows:

$$r_1 = \frac{k_{1s} * \left( C_{EtOH} C_{HCl} - \frac{C_{EtCl} C_{H_2O}}{K_{eq1}} \right)}{D^2} \quad (eq. 1 - 1)$$

$$r_2 = \frac{k_{2s} * \left( C_{EtOH}^2 - \frac{C_{DEE} C_{H_2O}}{K_{eq2}} \right)}{D^2} \quad (eq. 1 - 2)$$

$$r_3 = \frac{k_{3s} * \left( C_{DEE} C_{HCl} - \frac{C_{EtCl} C_{EtOH}}{K_{eq3}} \right)}{D^2} \quad (eq. 1 - 3)$$

$$Where D = 1 + K_{HCl} C_{HCl} + K_{EtOH} C_{EtOH}$$

It must be noted that the values for  $K_{HCl}$  and  $K_{EtOH}$  were inaccurate, and the error values were far too large. The authors stated that these constants provided little to no change in the final calculations and were not accounted for during their final run. In this simulation, D was assumed to be equal to 1 for simplicity.

Next, the equilibrium constants calculated by the authors corresponding to reaction scheme 1 are as follows:

Table 1: Equilibrium constants calculated from the thermodynamic theories from model 1

<b>T (°C)</b>	<b>Keq<sub>1</sub></b>	<b>Keq<sub>2</sub></b>	<b>Keq<sub>3</sub></b>
<b>200</b>	635.6	14.12	45.01
<b>250</b>	332.6	8.45	39.38
<b>275</b>	251.6	6.8	37.02
<b>300</b>	195.0	5.59	34.90
<b>325</b>	154.4	4.68	32.99

The values of the estimated kinetic parameters for reaction scheme 1 are:

Table 2: Estimated kinetic parameters for reaction scheme 1

<b>Parameter</b>	<b>Value</b>	<b>Error</b>
<b>k<sub>1</sub></b>	9.67 x 10 <sup>-7</sup>	± 8.82 x 10 <sup>-8</sup>
<b>k<sub>2</sub></b>	4.27 x 10 <sup>-8</sup>	± 2.12 x 10 <sup>-8</sup>
<b>k<sub>3</sub></b>	3.66 x 10 <sup>-11</sup>	± 2.88 x 10 <sup>-11</sup>
<b>Ea<sub>1</sub></b>	1.05 x 10 <sup>5</sup>	± 4.44 x 10 <sup>3</sup>
<b>Ea<sub>2</sub></b>	4.48 x 10 <sup>4</sup>	± 5.26 x 10 <sup>4</sup>
<b>Ea<sub>3</sub></b>	2.35 x 10 <sup>4</sup>	± 2.12 x 10 <sup>4</sup>

where:

$$k_{is} = k_i e^{\frac{1}{T} - \frac{1}{T_{mean}}} \text{ where } T_{mean} = 300^\circ\text{C} (eq. 2 - 1)$$

The catalyst properties that were used are:



Table 3: Catalyst Properties for  $Al_2O_3$

<b>SBET</b>	$4.23 \times 10^2 \text{ m}^2/\text{g}$
<b>Pore size</b>	$1.8 \times 10^{-8} \text{ m}$
<b>Pore Volume</b>	$1.9 \times 10^{-6} \text{ m}^3/\text{g}$
<b>Porosity</b>	0.37
<b>Particle diameter</b>	$5.0 \times 10^{-6} \text{ m}$

The fluid properties were estimated by averaging the properties of all the substances present in the flow. The properties are assumed to be constant throughout the system.

Table 4: Average fluid properties for the flow

<b>Average molar mass</b>	40 kg/mol
<b>Average viscosity</b>	$2.43 \times 10^{-5} \text{ P}$
<b>Average density</b>	$189.31 \text{ kg/m}^3$

Finally, the starting parameters desired outputs for this system are as follows:

Table 5: Starting parameters and desired outputs

<b>Inlet Pressure</b>	100 atm
<b>Inlet temperature</b>	200°C
<b>Inlet EtOH flowrate</b>	100 mol/s
<b>Inlet HCl flowrate</b>	80 mol/s
<b>Inlet Inert flowrate</b>	15 mol/s
<b>Target outlet EtCl flowrate</b>	25 mol/s
<b>Target conversion</b>	0.99

### 3. Design Procedure

#### Problem Description

The objective of the given design project is to adjust performance of PBR reactors system to produce 25 mol/s of ethyl chloride. This system operates isothermally (at the current stage) and assumes single phase (gas phase) for all components. Most of the inlet conditions were adjusted freely, however some limitations were imposed by the experimental conditions provided in the research paper used during the design process. Namely, experiments were conducted at temperature ranging from 200 C to 325 C, same temperature constraints were enforced upon the designed system. Temperature constraints imply a constraint for pressure (to maintain single gas phase). However, pressure constraint was violated in order to produce feasible design (this issue will be discussed in the **Results and Discussion** section). To further discuss the design procedure the following aspects of the design will be discussed: **Operating Conditions, System Assumptions, Mathematical Model and Design Proposal.**

#### Operating Conditions

Current design includes a system of PBR reactors operating in isothermal regime. Certain inlet conditions were selected and kept fixed, in this section each of the fixed conditions will be mentioned and discussed. In addition, the effect of variable parameters on the system will be discussed.

##### Fixed Parameter #1: Temperature

It was decided to keep the temperature fixed at average experimental temperature (300 C). The research paper used during the design procedure has defined experimental temperature range from 200 C to 325 C and average temperature for the reaction scheme #1 at 300 C. Since current design assumes isothermal operating condition, it appeared to be the most optimal choice.

##### Fixed Parameter #2: Diameter of Reactor

Diameter of reactor will affect such parameters as pressure drop and length of the reactor. It was decided to select sufficiently high diameter of 0.1 m to keep superficial velocity at around 10 m/s for selected pressure.

### Fixed Parameter #3: Pellet Size

While research paper used in modelling used glass beads mixed with  $\text{Al}_2\text{O}_3$  powder or pellets (the paper has not decisively stated what form of  $\text{Al}_2\text{O}_3$  was used). It was decided to use commercially available ¼ inch sized pellets of  $\text{Al}_2\text{O}_3$ , since analysis of a mixture of beads and reactant pellets of different size is beyond the scope of this design project. In a scenario beyond simulator, this would be a small pellet size which would cause significant pressure drop due to the dense packing of the PBR.

### Fixed Parameter #4: Flowrate of EtOH

EtOH is an abundant and cheap component. After quick research it was found that on a per mole basis, HCl have significantly higher costs if purchased commercially. It was decided to select 100 mol/s inflow of EtOH as a basis for our optimization.

### Variable Parameter #5: Pressure

While technically speaking pressure is variable parameter, we decided to select a basis for pressure at 100 atmospheres. The reasoning behind the selection was high initial total concentration leading to the high rates of formation of desired product. Reaction mechanism proposed in paper was not optimized for scaling, and indeed, design was found to be poorly scalable. The crude and simple solution to this problem was to drastically increase the pressure of the system. Such a decision has number of critiques, namely formation of liquid phase and non-ideal behavior of gas (critiques are discussed in **Results and Discussion** section).

### Variable Parameter #6: Flowrate of HCl

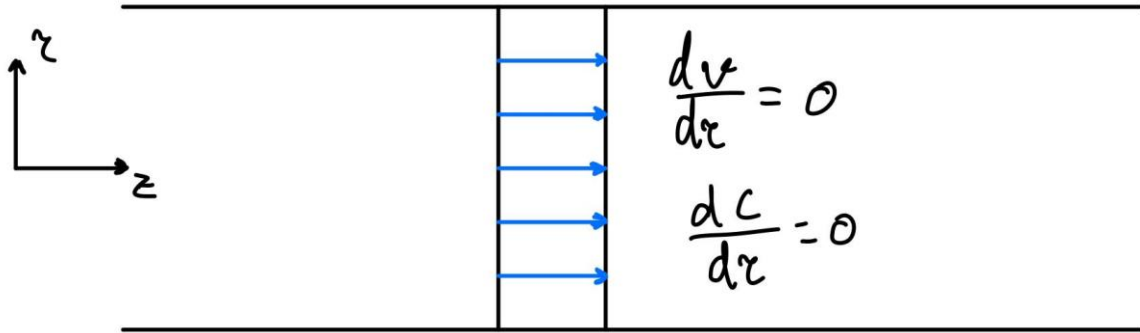
As was previously discussed, HCl is a specie that we optimize due to its excessive cost. To optimize initial rate of production of desired product, various inflows of HCl were tested with fixed EtOH to find the most optimal HCl inflow (see details on this optimization technique in **Results and Discussion**).

## **System Assumptions**

### Assumption 1: Plug-Flow PBR

Constant concentration across any cross-section of the PBR was assumed. Analogously to constant concentration distribution, constant velocity distribution is also a part of plug-flow assumption. This set of assumptions lead to the conclusion that both velocity and concentration

at any infinitesimal cross section of PBR can be assumed constant along  $r$  (radius) axis. The following schematic depicts a typical case of plug flow:



*Figure 1: Typical plug flow*

#### Assumption 2: Ideal Gas

To model a given system, it was assumed that gas always behaves as an ideal. This assumption means that particles of gas behave as particles of mass with negligible volume, collide elastically (do not lose energy during collision), and do not interact with each other. It is well known that gases at large pressure (over 1 atm) deviates from ideal behavior, but in current design procedure this deviation is not accounted for.

#### Assumption 3: Single Phase System

It is assumed that a given system exists in a single gas phase only. While temperature of the reactor is kept well beyond the boiling point of all species, various effects can come at play during chemical reactions and interaction of gas molecules. Currently, all components of the system are assumed to always exist in the gas phase.

#### Assumption 4: Density of Gas

In current design, it is assumed that density of gas can be approximated as average density of each specie in a gas mixture. It might or might not be true. Interactions between particles of gas can significantly affect the density of mixture, and the current system does not account for such interactions.

#### Assumption 5: Viscosity of Gas

It was challenging to find experimental data for mixture of given gases or even individual gases. Therefore, the viscosity at various temperatures was modelled after air at equivalent temperature. Therefore, fundamental system assumption regarding gas viscosity is that it behaves similarly to air.

#### Assumption 6: Sufficiently high flowrate of coolant

In this system, the flowrate of the coolant was assumed to be sufficiently high, so that temperature of coolant ( $T_a$ ) stays constant throughout the process. Cheap price of cooling liquid (tap water at 25C was assumed to be a coolant) combined with low reaction rate (not a lot of heat released) further justifies this assumption.

#### Assumption 7: No resistance to heat transfer in pipe materials

Since the applicable materials for the given pipes were not specified, it was decided to assume no resistance to thermal conductivity in pipe materials. Therefore, convective only transfer with cooling liquid was assumed. In practical design context, convection of gas mixture and resistance of pipe should be considered

### **Mathematical Model**

In order to simulate the system, ideal plug flow PBR reactor was modelled. The following formula represents a typical plug-flow PBR reactor

$$\frac{dF_i}{dW} = r'_i \quad (eq. 3 - 1)$$

This model assumes that  $r'_A$  is expressed as a function of catalyst weight. However, proposed kinetic parameters proposed in research paper used during design procedure are not related to catalyst weight. Model proposed in research paper can be expressed as follows

$$\frac{dF_i}{dV} = r\rho_B \quad (eq. 3 - 2)$$

However, in research paper,  $dV$  was aliased as  $dx$  (since term was not property noted or mentioned in nomenclature section, it was the logical conclusion made).

Suggested reaction scheme consists of 3 reactions, which can be summarized for isothermal ideal gas system as follows

$$\begin{aligned}
r_1 &= k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( C_{EtOH} C_{HCl} - \frac{C_{EtCl} C_{H2O}}{K_{Eq1}} \right) \\
&= k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} \\
&\quad * \left( (C_{T0} \frac{F_{EtOH}}{F_T} p)(C_{T0} \frac{F_{HCl}}{F_T} p) - \frac{(C_{T0} \frac{F_{EtCl}}{F_T} p)(C_{T0} \frac{F_{H2O}}{F_T} p)}{K_{Eq1}} \right) (eq. 4 - 1) \\
r_2 &= k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( C_{EtOH}^2 - \frac{C_{DEE} C_{H2O}}{K_{Eq2}} \right) \\
&= k_2 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( (C_{T0} \frac{F_{EtOH}}{F_T} p)^2 - \frac{(C_{T0} \frac{F_{DEE}}{F_T} p)(C_{T0} \frac{F_{H2O}}{F_T} p)}{K_{Eq2}} \right) (eq. 4 - 2) \\
r_3 &= k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( C_{DEE} C_{HCl} - \frac{C_{EtCl} C_{EtOH}}{K_{Eq3}} \right) \\
&= k_3 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} \\
&\quad * \left( (C_{T0} \frac{F_{DEE}}{F_T} p)(C_{T0} \frac{F_{HCl}}{F_T} p) - \frac{(C_{T0} \frac{F_{EtCl}}{F_T} p)(C_{T0} \frac{F_{EtOH}}{F_T} p)}{K_{Eq3}} \right) (eq. 4 - 3)
\end{aligned}$$

PBR model equation can be expressed in terms of  $r_1$ ,  $r_2$ ,  $r_3$

$$\begin{aligned}
\frac{dF_{EtOH}}{dV} &= \rho_B(-r_1 - 2r_2 + r_3)(eq.4 - 4) \\
&= \rho_B(-k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}}) \\
&\quad * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{H2O}}{F_T} p \right)}{K_{Eq1}} \right) - 2 * k_2 \\
&\quad * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right)^2 - \frac{\left( C_{T0} \frac{F_{DEE}}{F_T} p \right) \left( C_{T0} \frac{F_{H2O}}{F_T} p \right)}{K_{Eq2}} \right) + k_3 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} \\
&\quad * \left( \left( C_{T0} \frac{F_{DEE}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right)}{K_{Eq3}} \right) (eq.4 - 5)
\end{aligned}$$

$$\begin{aligned}
\frac{dF_{HCl}}{dV} &= \rho_B(-r_1 - r_3) \\
&= \rho_B(-k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}}) \\
&\quad * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{H2O}}{F_T} p \right)}{K_{Eq1}} \right) - k_3 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} \\
&\quad * \left( \left( C_{T0} \frac{F_{DEE}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right)}{K_{Eq3}} \right) (eq.4 - 6)
\end{aligned}$$

$$\begin{aligned}
\frac{dF_{EtCl}}{dV} &= \rho_B(r_1 + r_3) = \rho_B \left( k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \right. \right. \\
&\quad \left. \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{H2O}}{F_T} p \right)}{K_{Eq1}} \right) + k_3 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( \left( C_{T0} \frac{F_{DEE}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \right. \\
&\quad \left. \left. \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right)}{K_{Eq3}} \right) \right) (eq.4 - 7)
\end{aligned}$$

$$\frac{dF_{H_2O}}{dV} = \rho_B (r_1 + r_2) = \rho_B \left( k_1 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right) \left( C_{T0} \frac{F_{HCl}}{F_T} p \right) - \frac{\left( C_{T0} \frac{F_{EtCl}}{F_T} p \right) \left( C_{T0} \frac{F_{H_2O}}{F_T} p \right)}{K_{Eq1}} \right) + k_2 * e^{\frac{1}{T} - \frac{1}{T_{mean}}} * \left( \left( C_{T0} \frac{F_{EtOH}}{F_T} p \right)^2 - \frac{\left( C_{T0} \frac{F_{DEE}}{F_T} p \right) \left( C_{T0} \frac{F_{H_2O}}{F_T} p \right)}{K_{Eq2}} \right) \right) \quad (eq. 4 - 8)$$

However, the proposed model does not account for pressure drops. Pressure fraction (p) can be expressed as 4th d

$$\frac{dp}{dV} = \rho_B \frac{-a}{2p} \frac{F_T}{F_{T0}} \quad (eq. 5 - 1)$$

In addition to a non-isobaric design, the system was calculated to be non-isothermal. The differential equation is as follows:

$$\frac{dT}{dW} = \frac{r'_A \Delta H_{RX} - \frac{Ua(T - T_a)}{\rho_b}}{\sum F_i C_{P_i}} \quad (eq. 6 - 1)$$

In addition, the model of the cooling system is as follows:

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m} C_{P_c}} \quad (eq. 6 - 2)$$

In such a way, the entire system can be modelled using derived coupled ODEs. Such a system can be solved using numerical methods such as Euler or RK45. Current final design uses the RK45 method to solve the system of ODEs.

## Design Proposal

After building and evaluating mathematical models, it became clear that the rate of production of desired species was relatively low even at high pressure (100 bar). In order to achieve the target production rate, it was decided to parallelize PBRs. It was decided to put 2 units of 5 parallel PBR, units are arranged in series. The following schematic represents the proposed design



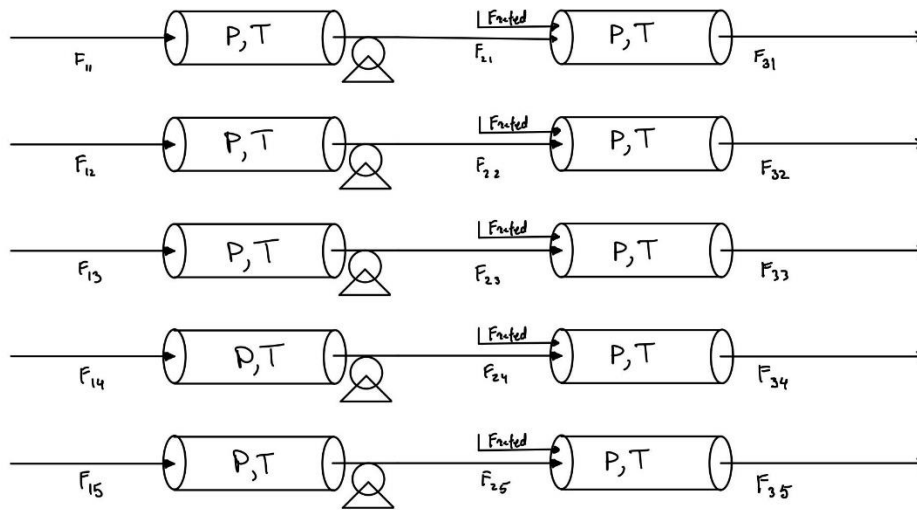


Figure 2: Proposed reactor design

## Design Parameters

Table 6: PBR Design Parameters

Parameter	Value	Units
Pellet Diameter	6.35E-03	m
Pellet Density	3950	kg/m <sup>3</sup>
Bed Diameter	0.1	m
Bulk Density	2.39E+03	kg/m <sup>3</sup>
Voidage (Found through literature)	3.96E-01	

Table 7: Initial Conditions for Reactor Unit 1

Parameter	Value	Units
F <sub>A</sub>	100	mol/s
F <sub>B</sub>	80	mol/s
F <sub>C</sub>	0	mol/s
F <sub>D</sub>	0	mol/s
F <sub>E</sub>	0	mol/s
F <sub>I</sub>	18	mol/s
T	300	C

P	10132500	Pa
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Table 8: Cooling Parameters for Reactor Unit 1

Parameter	Value
U	0.1
T <sub>a</sub>	25

Table 9: Initial Conditions for Reactor Unit 2

Parameter	Value	Units
F <sub>A</sub>	96.538	mol/s
F <sub>B</sub>	76.538	mol/s
F <sub>C</sub>	3.462	mol/s
F <sub>D</sub>	3.462	mol/s
F <sub>E</sub>	0.00018	mol/s
F <sub>I</sub>	18	mol/s
T	287.800	C
P	10132500	Pa

Table 10: Cooling Parameters for Reactor Unit 2

Parameter	Value
U	0.1
T <sub>a</sub>	25

Table 11: Reactor Refeed Parameters

Parameter	Value	Units
F <sub>A0</sub>	3.46	mol/s
F <sub>B0</sub>	3.46	mol/s
F <sub>I0</sub>	1.80	mol/s

## 4. Results and Discussion

### Case study on effect of variable and design parameters:

In this study, the variables that are being manipulated are the inlet conditions which consist of the inlet flowrate, initial temperature, and initial pressure. Upon increasing the flowrate of EtOH, the selectivity and conversion of EtOH will decrease. The higher concentration of EtOH might push the 2<sup>nd</sup> reaction further than it does the main reaction that contains our desired product. Increasing HCl flowrate on the other hand will result in higher selectivity since HCl is not involved in the side reaction that produces the undesired product and will instead push the main reaction to synthesize EtCl. Increasing the inlet pressure would increase yield and selectivity. This is a result of a lower drop in pressure throughout the reactor when the inlet pressure is high. Finally, increasing the temperature would result in a drop in yield and not much change in selectivity. As the temperature increases, the kinetic parameters will drop in value which will cause the reaction to proceed more slowly for the same amount of catalyst.

### Result Interpretation:

To begin, an initial determination study was performed to find the ideal flowrate of HCl to be used in order to achieve maximum optimization.

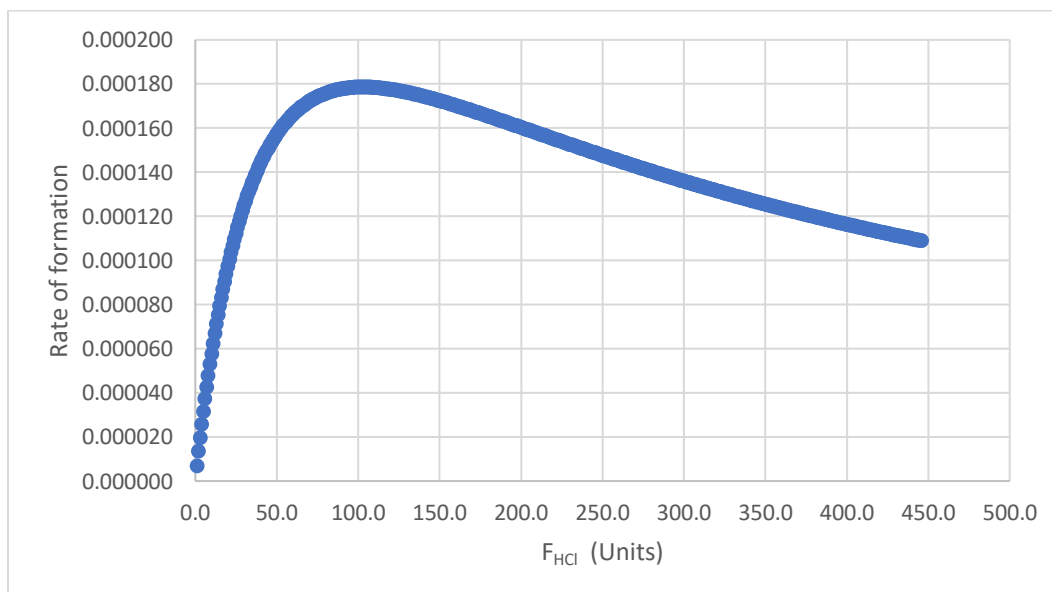


Figure 3: Rate of formation of EtCl as a function of inlet HCl flowrate

It was found that the optimal starting flowrate for HCl would be between 80 to 100 mol/s. This result corresponds with the data achieved by the authors of the research paper. In their

supplementary information, they showed that the setup with the highest conversion of EtOH would be that of when EtOH was in slight excess to HCl.

The reaction in the first reactor was deemed complete after the rate of reaction dropped by 10% from its initial value as is shown by the following graph. After this point, the 2<sup>nd</sup> unit was added the material was refed to the unit. Five of these setups were placed in parallel in order to achieve the desired flowrate of 25 mol/s.

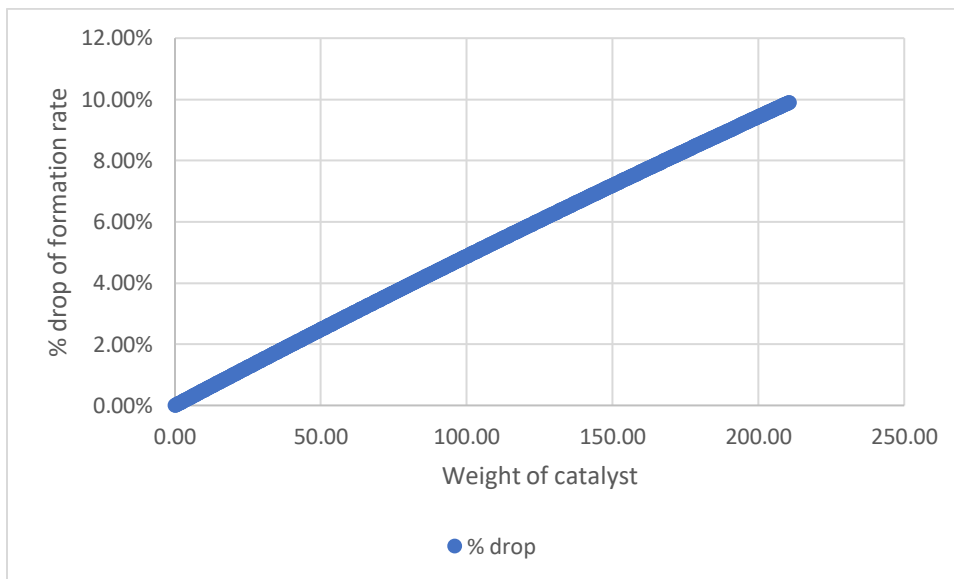


Figure 4: % drop of rate of formation of EtCl as a function of the weight of catalyst

The pressure chosen for this system is high, around 100 atm. The kinetic parameters in the rate laws for all the reactions are incredibly small. Furthermore, the error associated with each of them is of the same order of magnitude as the parameters themselves and one can conclude that the parameters provided are inaccurate and unreliable. That means that the reaction is inefficient and not much product is being produced and the theoretical amounts produced by the reaction could not be representative of the actual amounts produced. The conversion at the calculated optimal catalyst mass of 210.63 kg will result in a conversion of 0.00343 for EtOH and 0.0387 for HCl. This is an expected result due to the small kinetic parameters. To push the reaction forward and achieve our desired flowrate of 25 mol/s of EtCl, the inlet pressure was the main variable being manipulated. To that end, the pressure had to be increased to 100 atm. While this gets the required results in a simulation, this would not be feasible. At the pressure and temperature that this process is running, there will be some phase separation where some of the

reactants will condense into the liquid phase. This will result in the simulator being inaccurate since it only accounts for the gas phase in the calculations. While the specifications and goals for this project were achieved numerically, it is very likely that this will not be the case in execution.

The temperature drop was only around 15.82 degrees for the whole system. This is reasonable given that the reaction rate is very slow so not much heat is going to be generated. Because of the cooling present, it resulted in cooling of the system. This is actually beneficial to the system. The reaction constants are inversely proportional to the temperature, according to the data presented by the reference paper. So, dropping the temperature as the reaction goes would help the reaction move forward increasing its efficiency.

The synthesis of EtCl from EtOH in the gaseous phase is very inefficient based off data retrieved from literature. So, this system is very difficult to optimize. As stated previously, it is unreasonable to have that high of pressures in a PBR reactor. In the research, the authors were getting  $1/1000^{\text{th}}$  the amount of initial reagents as EtCl. Realistically, with the information provided, this reaction cannot be scaled. If one were to try and execute the proposed design, it would incur costs that are far more than the expected return of the desired product. For instance, the diameter of the pipe being used is 0.1 m and the length required will be around 10 m. 5 units of the proposed design are required to achieve the required output flowrate and obtaining pipes of that size is simply too expensive. In addition, acquiring a pump which can provide pressures of 100 atm will also be too costly. The waste produced from this reaction will also be high. A large amount of HCl and EtOH will remain unreacted. In order to purify and reuse the materials will again be costly. This is a reaction that, while feasible on a lab scale, is not scalable on an industrial scale.

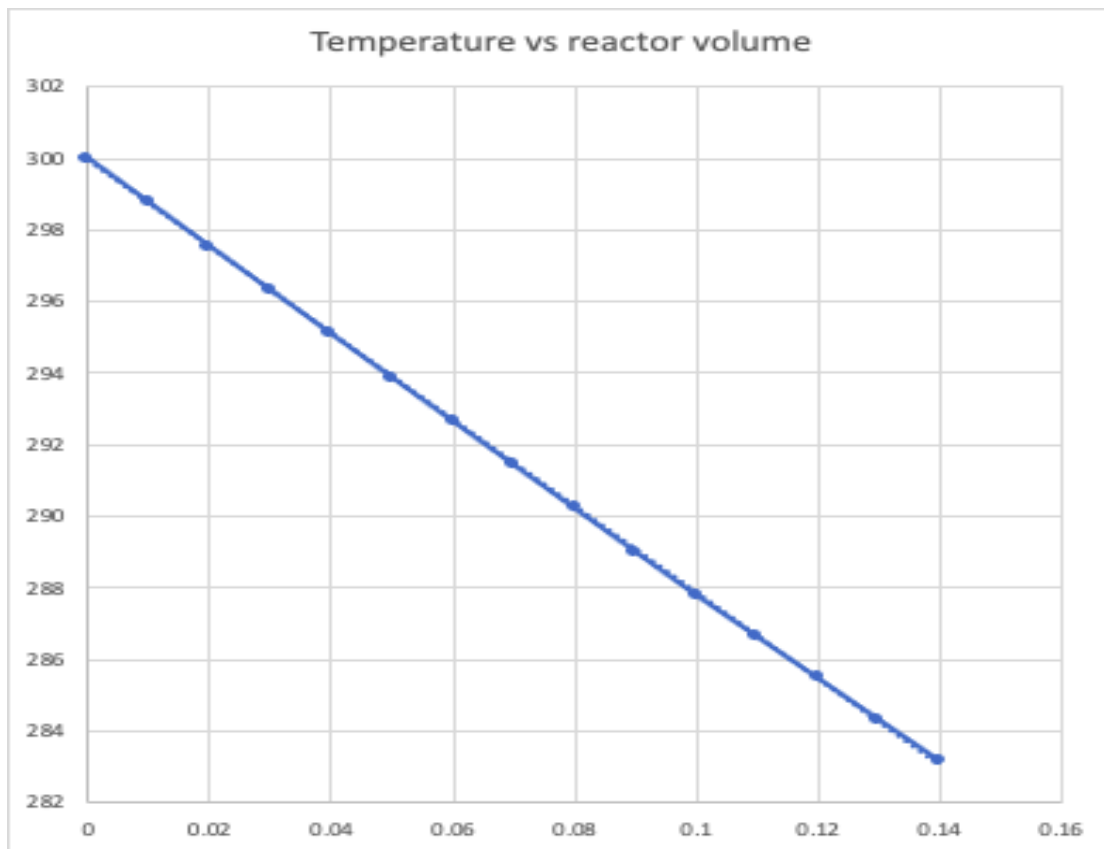


Figure 5: Temperature vs reactor volume. From volume 0.0 till 0.1 the reactions were taking place in the first unit reactor. From volume 0.1 till 0.14 the reactions were taking place in the second unit reactor.

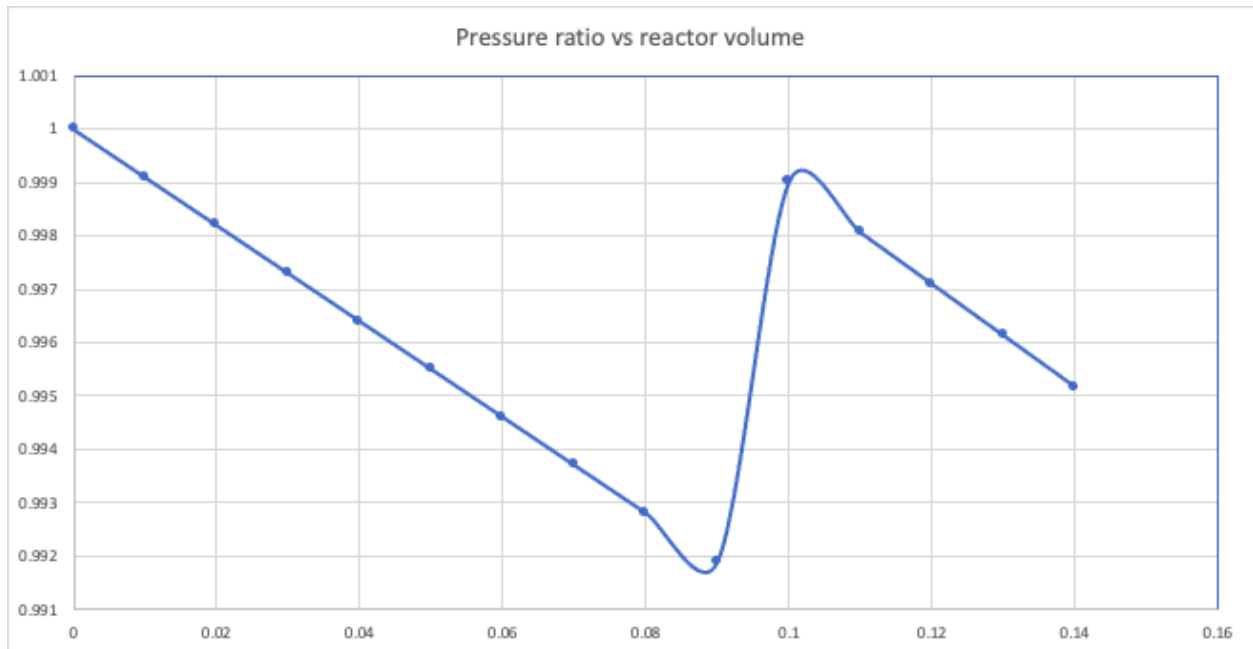


Figure 6: Pressure ration vs reactor volume. From volume 0.0 till 0.1 the reactions were taking place in the first unit reactor. From volume 0.1 till 0.14 the reactions were taking place in the second unit reactor (with refeed).

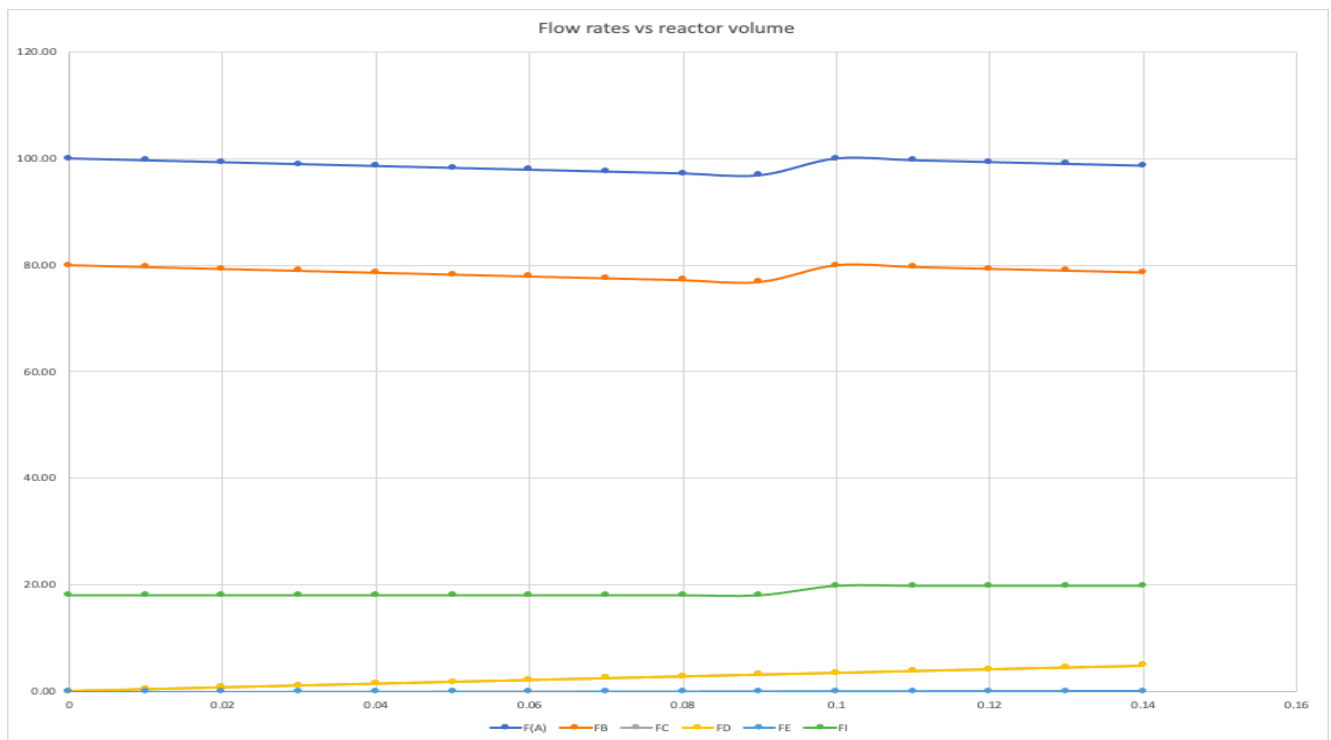


Figure 7: Flowrates vs reactor volume. From volume 0.0 till 0.1 the reactions were taking place in the first unit reactor. From volume 0.1 till 0.14 the reactions were taking place in the second unit reactor.

In reference to figure 7, the small changes in product formation and reactant consumption speak to how low the reaction rates are. Notice at volume 0.1 there is an increase in FA and FI, which is explained by the refeed into that reactor.

### **Case Study**

For this reaction system, several variables were manipulated to test the functionality of the system. The variable that had the biggest impact on the system was the pressure. In order for the system to run properly, a very high pressurization was required. When lower pressures were used, the reaction rate was too low and no product was being produced. So, very large pressures were required. When it comes to temperature, lower temperatures resulted in better reaction rates. This is due to the fact that the reaction constants provided by the research paper were inversely proportional to temperature. However, the lowest temperature presented in the paper was 300 C and that was the initial temperature that was decided. The reaction constants were incredibly small with very high error values to there was no confidence in an interpolation to lower temperatures where there could have potentially been better results. Finally, when increasing the starting reagents, the yield also increases but this is due to the higher amount of material going in. The amount of reagent could not be increased arbitrarily due to the effects it would have on pressure. Finally, different sized pellets were tested and smaller sizes resulted in very high pressure drops, which is unfavorable.

## **5. Conclusion**

The target of this study was to scale up the synthesis of ethyl chloride from ethanol using a packed bed reactor setup with  $\text{Al}_2\text{O}_3$  catalyst and a desired output flowrate of 25 mol/s of ethyl chloride. Although the study met project expectations numerically, it would not be possible to implement the design realistically due to the poor performance of the reaction. This was apparent by the results obtained in the simulator which makes use of the mathematical models from the referenced paper. Based on our findings, it would be better to use a different reaction for the synthesis of ethyl chloride from the one under study. When such a reaction is obtained, the rate calculations would be updated to fit the new reaction model and a better design that is scalable could be made. As it stands currently, the reaction is unfortunately unscalable and a different reaction scheme must be used.



## 6. References:

1. Corporation, A. (2016, October). *Product Stewardship Summary: Ethyl Chloride*. Product Stewardship Summary. Retrieved November 9, 2021, from <https://www.westlake.com/sites/default/files/Ethyl%20Chloride%20Summary%20Ed1.pdf>.
2. National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 6337, Chloroethane. Retrieved November 10, 2021 from <https://pubchem.ncbi.nlm.nih.gov/compound/Chloroethane>.
3. Bukhanko, N., Wärnå, J., Samikannu, A., & Mikkola, J.-P. (2016). *Kinetic modeling of gas phase synthesis of ethyl chloride from ethanol and HCl in fixed bed reactor*. Science Direct. Retrieved November 9, 2021, from <https://www.sciencedirect.com/science/article/pii/S0009250915007824>.

## 7. Appendices

### Sample calculations:

Concentration of Species A

$$C_A = C_{T0} * \frac{F_{A0}}{F_A} * p = 2126.37 * \frac{100}{195} * 1 = 1.09 * 10^3 \text{ M}$$

Flowrate of Species A:

$$F_A = F_{A0} + r'_A * s = 100 - 0.155 * 10^{-2} * 0.0001 = 99.99 \text{ mol/s}$$

- Reaction Enthalpy:

$$C_{Pi} \neq \text{const}; C_{Pi} = f(T)$$

$$H_i(T_R); T_R = 25^\circ \text{C}$$

$$\Delta H_{RX}(T)_1 = \frac{1}{1} H_{H_2O}^\circ + \frac{1}{1} H_{EtCl}^\circ - \frac{1}{1} H_{HCl}^\circ - \frac{1}{1} H_{EtOH}^\circ + \frac{1}{1} \int_{T_R}^T C_{P_{H_2O}} dT + \frac{1}{1} \int_{T_R}^T C_{P_{EtCl}} dT - \frac{1}{1} \int_{T_R}^T C_{P_{HCl}} dT - \frac{1}{1} \int_{T_R}^T C_{P_{EtOH}} dT$$

$$\Delta H_{RX}(T)_2 = \frac{1}{2} H_{DEE}^\circ + \frac{1}{2} H_{H_2O}^\circ - \frac{2}{2} H_{EtOH}^\circ + \frac{1}{2} \int_{T_R}^T C_{P_{DEE}} dT + \frac{1}{2} \int_{T_R}^T C_{P_{H_2O}} dT - \frac{2}{2} \int_{T_R}^T C_{P_{EtOH}} dT$$

$$\Delta H_{RX}(T)_3 = \frac{1}{1} H_{EtOH}^\circ + \frac{1}{1} H_{EtCl}^\circ - \frac{1}{1} H_{HCl}^\circ - \frac{1}{1} H_{DEE}^\circ + \frac{1}{1} \int_{T_R}^T C_{P_{EtOH}} dT + \frac{1}{1} \int_{T_R}^T C_{P_{EtCl}} dT - \frac{1}{1} \int_{T_R}^T C_{P_{HCl}} dT - \frac{1}{1} \int_{T_R}^T C_{P_{DEE}} dT$$

$$\tau_1 = 1.63 \times 10^{-8} (e^{\frac{1}{300}} - e^{\frac{1}{300}}) ((1.07 \times 10^3)(8.59 \times 10^2) - 0) \\ \approx 1.5 \times 10^{-2}$$

$$\tau_2 = 7.12 \times 10^{-10} (e^{\frac{1}{300}} - e^{\frac{1}{300}}) ((1.07 \times 10^3)^2 - 0) \approx 8.21 \times 10^{-4}$$

$$\tau_3 = 6.10^{-13} (e^{\frac{1}{300}} - e^{\frac{1}{300}}) (0 - 0) = 0$$

$$F_{Ail} = F_{Ai} + p_b (-\tau_1 - 2\tau_2 + \tau_3) \Delta V = 100 + 2385.4 (-1.5 \times 10^{-2} \\ - 2(8.21 \times 10^{-4}) + 0) (0.0001) \approx 100$$

$$P_{ii} = P_i - \left( \frac{a}{2P_i} \right) \frac{F_{Ti}}{F_{T0}} (\Delta V) \approx 1 - \left( \frac{0.34198}{2(1)} \right) \left( \frac{198}{198} \right) (0.0001) \\ \approx 1$$

### Code usage:

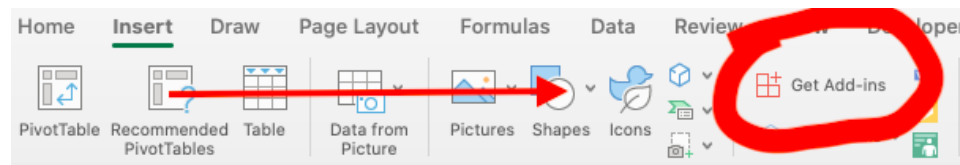
It should be noted that the bulk of the program designed was written in JavaScript. The RK45 algorithm that calculated the desired parameters is linked to the submitted Excel file via an API.

To use the RK45 package please do the following:

- 1- Open the project file submitted
- 2- Click on **Insert** in the top taskbar of the Excel page



- 3- Click on **Get Add-ins** in the taskbar selections under **Insert**

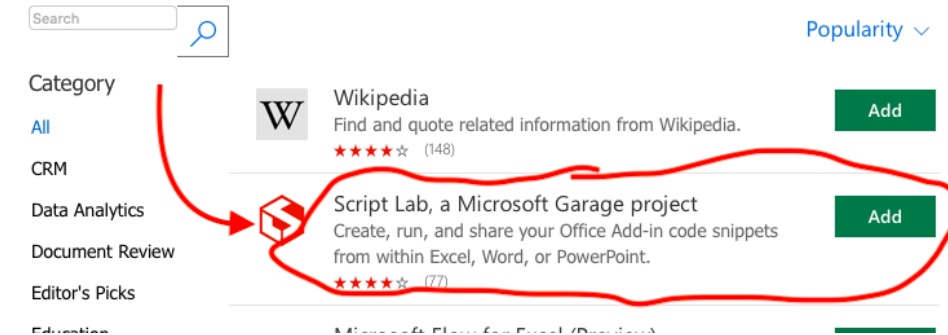


4- Add **Script Lab** search if it does not immediately popup.

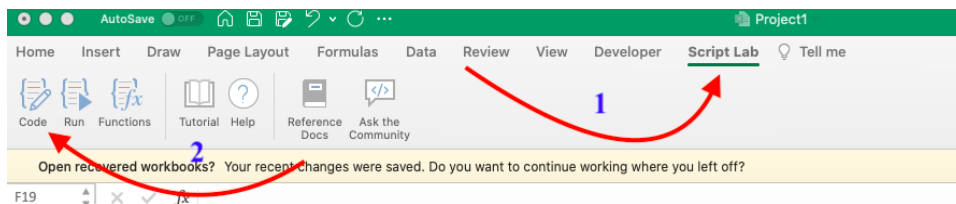
## Office Add-ins

MY ADD-INS | ADMIN MANAGED | [STORE](#)

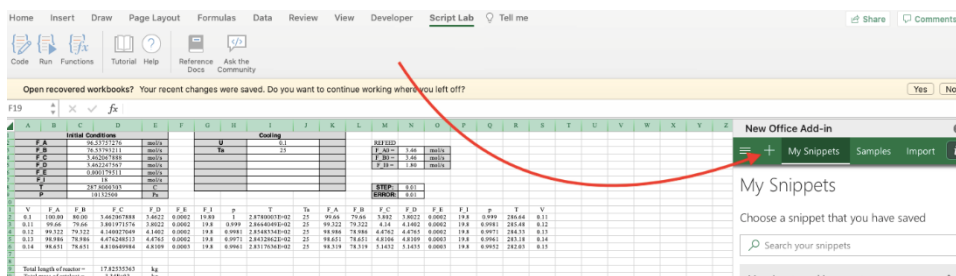
Add-ins may access personal and document information. By using an add-in, you agree to its Permissions, License Terms and Privacy Policy.

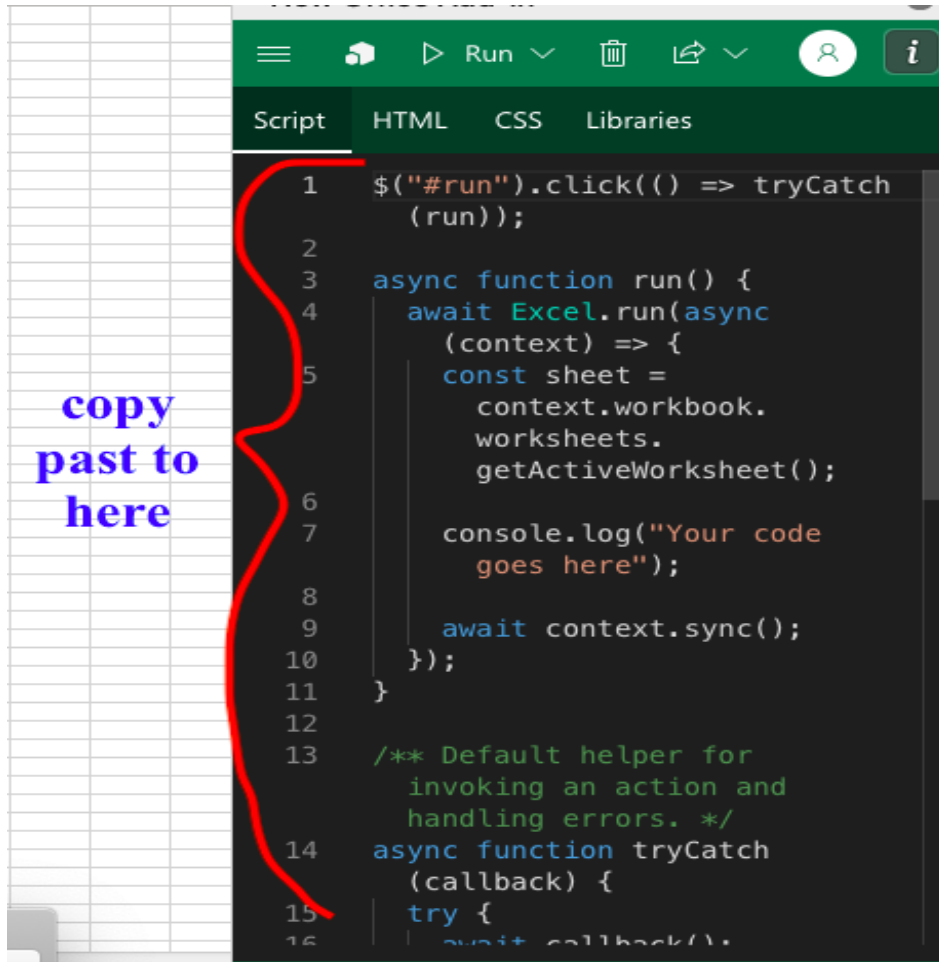


5- Now go to **Script Lab** in the Excel page taskbar and click on **Code**



6- click on the + sign, it will open a programming environment. In the environment delete all the available code, and copy-paste the code provided in the **RK45.txt** text file that was attached.





7- The function downloaded is called **PFR()**. To ensure that the software was downloaded properly go to the Excel page labeled **Unit2-RK45** and click on cell **K12** (Follow same procedure for **Unit1-RK45**). Go to its equation (fx) click on its equation and press ENTER and you should see the cells around **K12** update to (BUSY!) then numerical values. NOTE: do not change anything in **K12**'s equation!



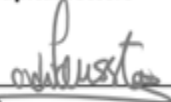
**Personal Ethics Agreement Concerning University Assignments**

**Group Assignment**

We submit this assignment and attest that we have applied all the appropriate rules of quotation and referencing in use at the University of Ottawa. We also confirm that we have taken knowledge of and respected the *Beware of Plagiarism!* brochure found at <http://www.uottawa.ca/plagiarism.pdf>. We attest that this work conforms to the rules on academic integrity of the University of Ottawa. We understand that this assignment will not be accepted or graded if it is submitted without the signatures of all group members.

FADI OUSSTA

Name, Capital letters

  
Signature

7958597

Student number

12/6/2021

Date

ILLIA NEGOVORA

Name, Capital letters

  
Signature

300070880


Student number

12/6/2021

Date

Tareq Mareh

Name, Capital letters

  
Signature

300096483


Student number

12/6/2021

Date

EBIAREDE ODIA-SMTU

Name, Capital letters

  
Signature

30006337


Student number

12/6/2021

Date

ALEXANDER KARMAZIN

Name, Capital letters

  
Signature

8786600

Student number

12/06/2021

Date