

A COMSOL Multiphysics® Study of the Temperature Effect on Chemical Permeation of Air Supply Tubes

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Abstract—Permeation of chemicals through pipes or hoses may have hazardous effects upon inhalation. A simulation model using COMSOL Multiphysics for diffusion of one such chemical, in this case MEK, across a PVC pipe is described. The simulation model is based on experimental data from Bromwich and Parikh⁽¹⁾. The transport of MEK species across the pipe is studied at various temperatures and the simulation results of the diffusion process trend with the experimental results.

Keywords— Diffusion, Transport of chemical species, COMSOL Multiphysics Simulation Model, Non-isothermal Environment, MEK, PVC Pipe, Polymer Diffusion, Permeation

I. INTRODUCTION

Often situations arise where workers in a contaminated environment require the use of a respirator attached to an air-supply hose. Air supply hoses are also predominantly used in the medical industry to aid in patient oxygen intake. In many situations, the outside of the hose can be contaminated with chemicals, especially if the hose lies on the ground in an environment where chemicals are easily found. Permeation and transport of chemicals into the walls of air supply hoses is a noteworthy problem in the chemical industry. Sometimes permeation may only be evident by the taste or smell in the air from the hose. The transport of chemicals through the walls of the hose occurs in a similar manner as through gloves and chemical suits, driven by the chemical concentration gradient.

An experimental test method was developed by Bromwich and Parikh⁽¹⁾ in which chemical permeation through homogeneous hoses could be calculated by sealing a short section of the hose with the chemical and weighing it at different time intervals to show the chemical had permeated the hose wall and evaporated. To further expand on this test method, Bromwich and Parikh⁽¹⁾ measured the effect of temperature through designing an isothermal rig which would permit testing at temperatures above ambient. Testing was performed at 19, 30, 40, 50, 60,

and 70°C to represent possible workplace environments. The trials lasted between 25-360 hours and cumulative permeation was calculated in milligrams per meter of hose.

A model of the transport processes involved in the experiment by Bromwich and Parikh⁽¹⁾ can be reasonably simulated within the capabilities of COMSOL Multiphysics®. The model proposed will take experimental data and simulate the transport process with COMSOL. The COMSOL simulation is used to develop quantitative insight into the transport process and to appropriately characterize the transport process. Although the experimental paper studied the effects of various steady state, above ambient temperatures, the model proposed tries to predict the effects of a non-isothermal environment at various temperature on the diffusion through the tube wall.

II. MODEL INPUTS

A 2-D axisymmetric geometry was selected to create the model due to assumed cylindrical symmetry of the PVC pipe. The physics selected in the COMSOL time-dependent study included heat transfer in fluids and chemical species transport. Parameters that were required to be input into COMSOL are listed in Tables I-III. Table I displays the geometry of the PVC pipe, the initial temperature of the MEK solute, and weight fractions of the MEK assumed at different locations in the pipe. Table II and III lists material properties of MEK and PVC which were manually input into COMSOL since they were not included in the built-in library. The ratio of specific heats is assumed to be a value of 1 because both materials are not gases. A molar mass of 54.1328 gram/mole is used for MEK and 93.92 gram/mole is used for PVC.

TABLE I
EXPERIMENT GEOMETRY

Property	Name	Value	Unit
Outer Radius of PVC pipe	R1	9	mm
Inner radius of PVC pipe	R2	5	mm
Length of PVC pipe	L	10	cm
Initial Temperature	To	19	°C
Weight Fraction of MEK at Inner Surface of PVC pipe	wo	1	--
Weight Fraction of MEK at Outer Surface of PVC pipe	wh	0	--

TABLE II
METHYL ETHYL KETONE ⁽²⁾ PARAMETERS

Property	Name	Value	Unit
Thermal Conductivity	k	0.000358	cal / (cm.s.°C)
Density	rho	0.8037	g/cm ³
Heat Capacity at constant pressure	Cp	0.549	cal/(g. °C)
Ratio of Specific Heats	gamma	1	1

TABLE III
POLY VINYL CHLORIDE ⁽³⁾ PARAMETERS

Property	Name	Value	Unit
Thermal Conductivity	k	1.1	(BTU.in) / (h.ft ² .°F)
Density	rho	1.4	g/cm ³
Heat Capacity at Constant Pressure	Cp	0.25	BTU / (lb.°F)
Ratio of Specific Heats	gamma	1	1

III. BOUNDARY CONDITIONS

Boundary conditions are necessary to limit the solution found with COMSOL. Since two different physics were selected in modeling, chemical species transport and heat transfer, multiple boundary conditions exist and are required accurately predict the experimental results.

Chemical Species Transport

Since the tube is initially completely filled with MEK solute, the first assumed boundary condition is that initially the inner radius of the tube, $r < R_2$, is assumed to have a weight fraction of 1, $\omega_1 = 1$. Due to presence of the air flow, which continuously sweeps away any permeate in the experiment modeled and maximizes the gradient, the second boundary

condition is at the outer radius, $r = R_1$, where it is assumed the mole fraction of MEK is zero, $X_{w1} = 0$, due to presence of the air flow which continuously sweeps away any permeate and maximizes the gradient. There is a no flux condition specified on the outer wall of the tube as well as on the bottom and top regions to ensure the second boundary condition is met as well.

Heat Transfer

Initially the model was isothermal to produce just chemical species transport. The boundary condition needed to produce this phenomenon is a no heat flux condition all around the perimeter of the 2-D cylinder. Providing a boundary from the external environment and keeping the temperature set at T_0 kept the cylinder in an isothermal state for the transient. The intent of the model was to evaluate unsteady state heat transfer with the MEK solute being the thermal source. Difficulties came with setting up a temperature dependent model which would simulate the given transport process which will be elaborated on in the discussion.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 depicts the diffusion of the solvent MEK across the PVC pipe. As can be seen in the figure, the mass fraction of the solvent MEK is at a maximum at the center of the PVC pipe and a gradual decrease in the mass fraction is observed when moving along the radial coordinate to the outer surface of the pipe. The mass fraction of the MEK at the outer wall of the PVC pipe was assumed to be negligible. Bromwich and Parikh⁽¹⁾ experimental testing chamber was set up so that the air flow across the outer wall of the PVC pipe was fast enough that the mass fraction on the outer wall of the pipe was assumed to not increase. This assumption would be consistent with a Biot number of infinity, where the external diffusion resistance was negligible. The experiment done by Bromwich and Parikh⁽¹⁾ also set the initial weight fraction inside the pipe to 1, by filling the pipe with neat MEK at the beginning of the experiment.

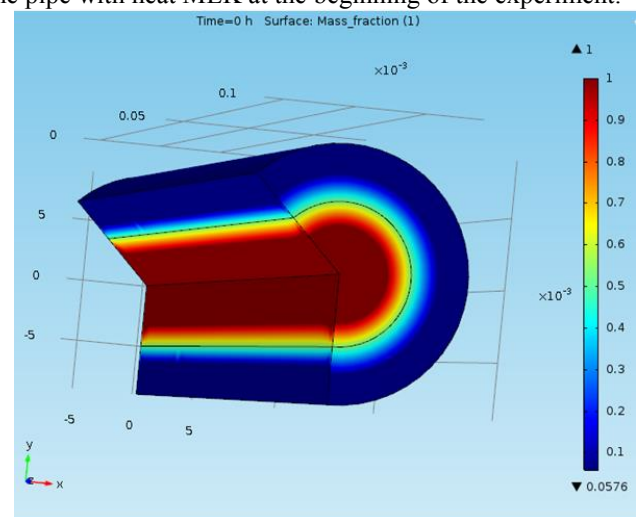


Fig. 1 3-D View of Mass Diffusion of MEK Across PVC Pipe

The diffusion coefficient (D_p) was estimated using the method detailed in Chao, Lai, Lin and Hsu⁽⁴⁾. The method can be used for polymer films and involved Equation 1 below:

$$D_p = \frac{L^2}{6t_1} \quad \text{Equation 1}$$

where L is the thickness of the polymer membrane and t_1 is the lag time. The lag time can be calculated by determining the x intercept of the initial linear portion of the experimentally generated cumulative permeation versus time plot⁽⁴⁾. In order to determine the diffusion coefficient for the data from Bromwich and Parikh⁽¹⁾, the lag times reported in the paper were used along with Equation 1. The calculated diffusion coefficients are shown in Table IV.

TABLE IV.

DIFFUSION COEFFICIENT AND LAG TIME FROM BROMWICH AND PARIKH⁽¹⁾

Temperature (°C)	Lag Time (1) (hr)	Lag Time (2)(hr)	Average Lag Time (hr)	D_p (m ² /s)
19	15	13.9	14.45	5.13E-11
30	10.1	10.7	10.4	7.12E-11
40	7.8	7	7.4	1.00E-10
50	5.6	5	5.3	1.40E-10
60	4.3	4.9	4.6	1.61E-10
70	4.2	3.8	4	1.85E-10

In order to fully investigate the lag times found in Bromwich and Parikh, the data was re-analysed. However, since a raw table of the cumulative permeation versus time data for each temperature tested was not included in the paper, the graphs had to be reproduced using approximation. One issue found with determining the lag time was that the so called initial linear portion of the data was not always clear. For instance, in the case of 19°C, multiple initial linear portions could have been chosen. Figure 2 shows the cumulative permeation versus time plot for the first 15 hours.

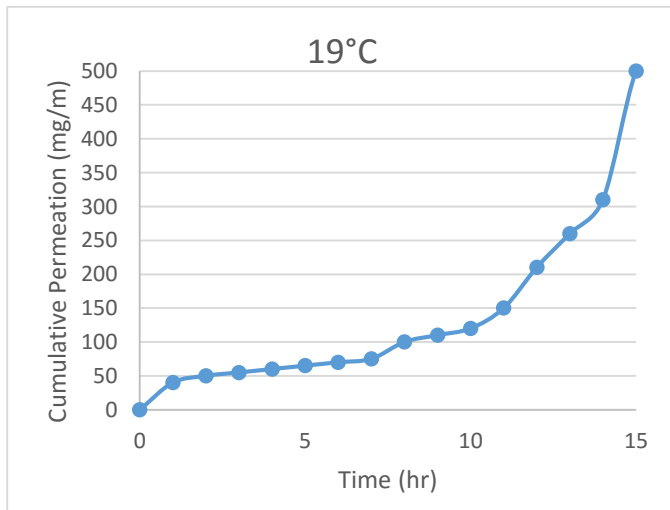


Fig. 2 Cumulative Permeation Versus Time for 19°C Showing the First 15 hr

Figure 3 and 4 show the data for the 19°C case where the chosen linear portion was changed from 1 to 10 hrs to a smaller portion from 1 to 7 hours. The smaller portion was more linear however only a few points were used in that case. The lag times for these two linear portions are ~3 and ~6 hours respectively. From the example shown the lag time can change by a factor of two depending on the selection of the linear portion. Also the data from Bromwich and Parikh⁽¹⁾ was not taken vary often for the initial portion of the study. To better determine the correct linear portion, the experiment should be repeated where the cumulative permeation is measured every ten minutes for the first 10 hours. The lag times calculated were a lot lower than those reported by Bromwich and Parikh⁽¹⁾.

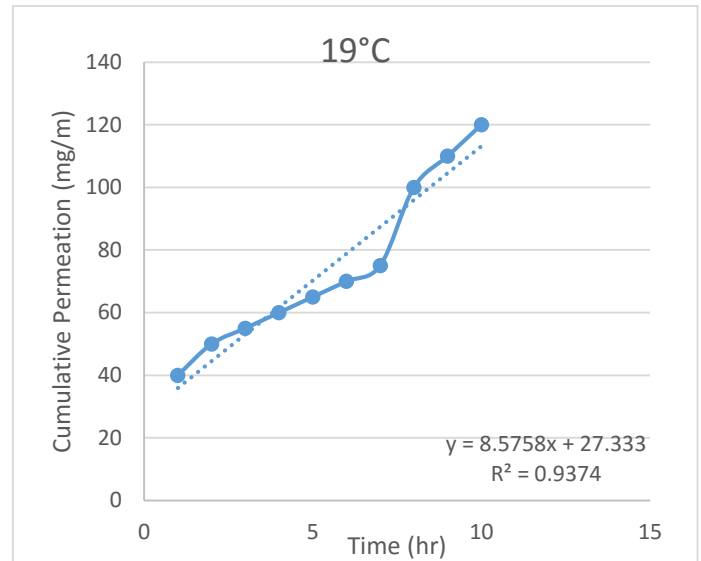


Fig. 3 First Attempt at Linear Portion for 19°C- 1 to 10 Hours

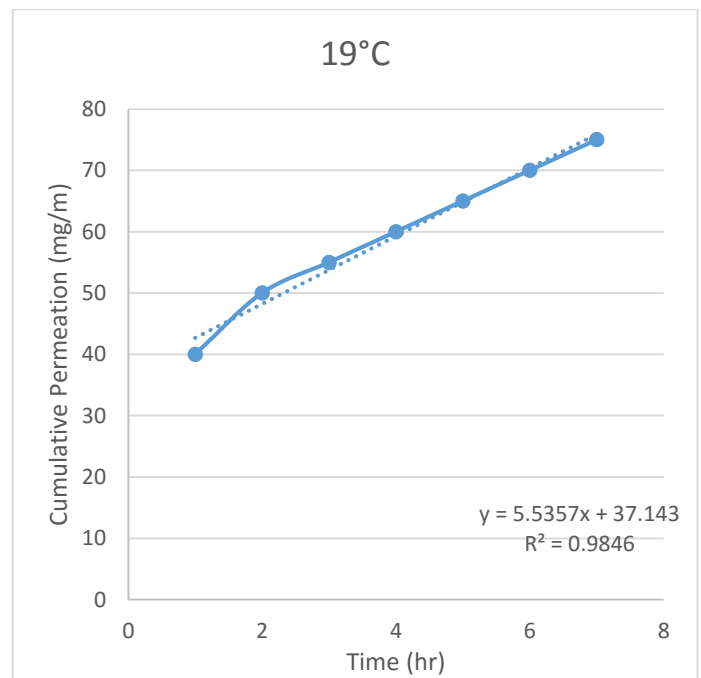


Fig. 4 Second Attempt at Linear Portion for 19°C- 1 to 7 Hours

Table V shows the calculated lag times and diffusion coefficients that were determined during the modelling project discussed.

TABLE V

CALCULATED DIFFUSION COEFFICIENT AND LAG TIME USING PLOTS FROM BROMWICH AND PARIKH⁽¹⁾

Temperature (°C)	Lag Time (hr)	Dp (m ² /s)
19	3.19	2.32E-10
30	1.52	4.88E-10
40	3.91	1.90E-10
50	1.39	5.35E-10
60	2.39	3.10E-10
70	0.86	8.63E-10

When the lag times calculated by Bromwich and Parikh⁽¹⁾ are compared to the values calculated in the project overall the values are a lot lower than the ones references in Bromwich and Parikh⁽¹⁾. Due to the inconsistency in the calculated lag times the values in Bromwich and Parikh⁽¹⁾ were used to calculate the Dp of the system. Figure 5 shows a comparison of the lag times measured by Bromwich and Parikh⁽¹⁾ versus the ones calculated for the model.

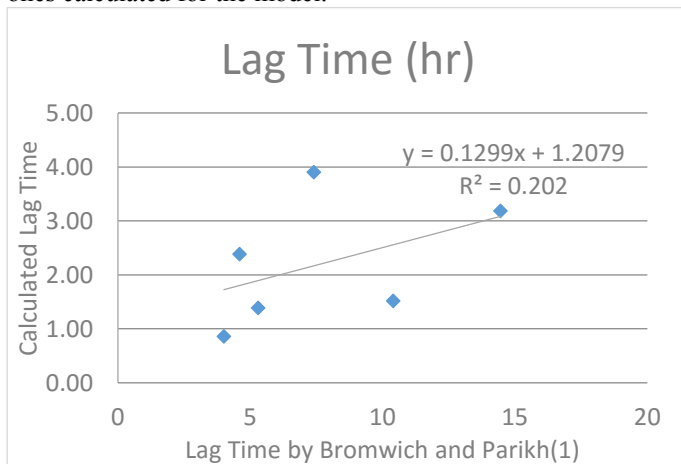


Fig. 5 Calculated Versus Reported Lag Time⁽¹⁾

Using the data from Table V, a linear relationship with D_p and temperature was found. The results are shown in Figure 6.

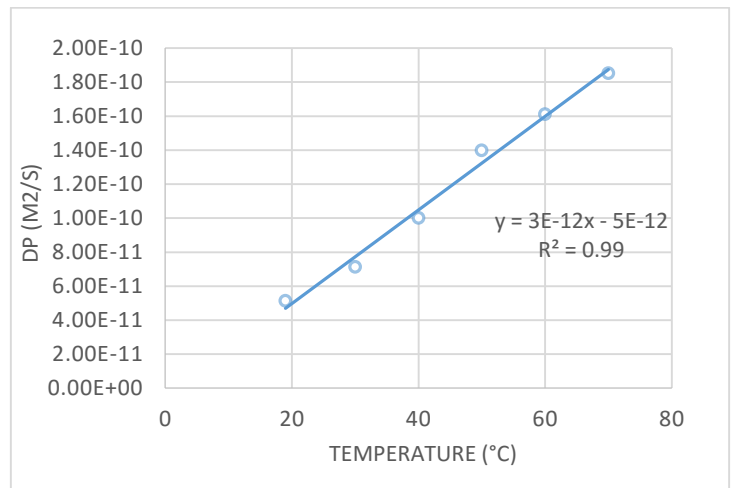


Fig. 6 A Diffusion Coefficient versus Temperature Relationship

Initially the COMSOL simulation assumed no heat flux, so the calculated D_p for the 19 °C case was used. A cut line was taken between 0 and R1 at L/2, the weight fraction of MEK versus the radius was then plotted for various times. Figure 7 shows the change in the weight fraction profile along the pipe over time.

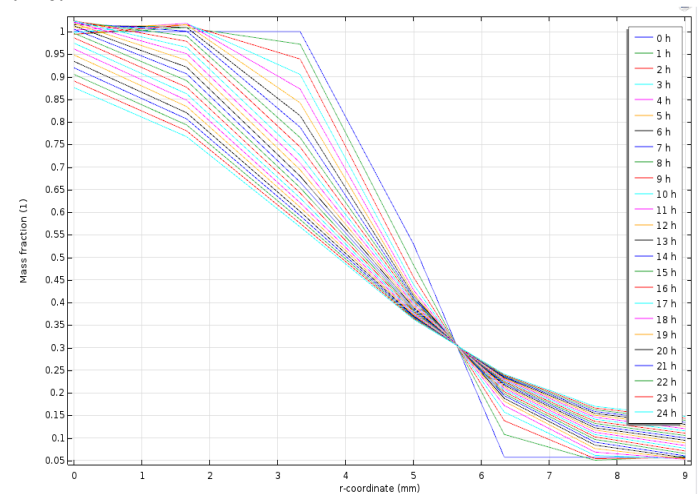


Fig. 7 A Weight Fraction of MEK vs. r(mm) at z=L/2

A cut point was taken at a radius of 5mm (inside wall of PVC) and L/2(middle of pipe) in order to estimate the change in the weight fraction of the solvent filled tube, shown in Figure 8. Since the initial mass of MEK in the pipe is known, the simulated weight fraction can be used to estimate the cumulative permeation versus time. This allows the simulated data to be compared to the experimental data in Bromwich and Parikh⁽¹⁾.

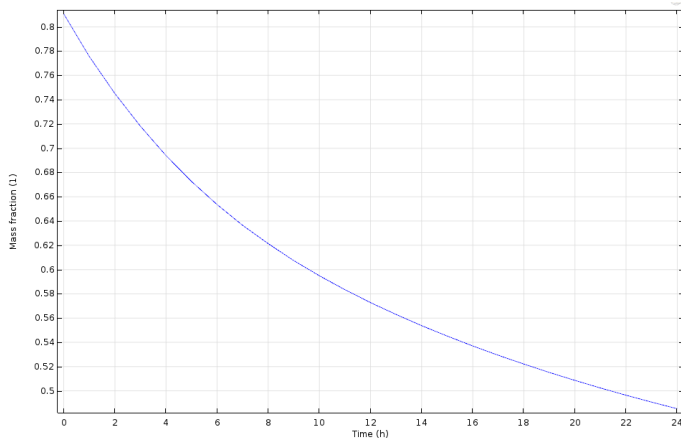


Fig. 8 B Weight Fraction of MEK vs. Time (hr) at $r=4$ mm and $z=L/2$

Once the path to collect the cumulative permeation versus time data from the COMSOL model was determined, the temperature and D_p was corrected for each temperature case and the MEK was set to the case temperature. A temperature dependent D_p was attempted for the model but an error in the simulation caused the model to not run fully. Therefore the project was completed by using the various constant D_p values for each temperature that were calculated by the lag times. The weight fraction versus time data for the point at a radius of 5 mm and a length of $L/2$ was collected from COMSOL. The initial mass of MEK in the pipe was calculated by the known volume of the pipe and the density of MEK. The weight fraction versus time was then converted into the mass divided by the length versus time for the internal volume. Using the change in mass over time for the internal area, the external area's change in mass was calculated. The results for the 19 and 30 °C cases are shown in Figure 9 for both the COMSOL model's results and the experimental results from Bromwich and Parikh⁽¹⁾.

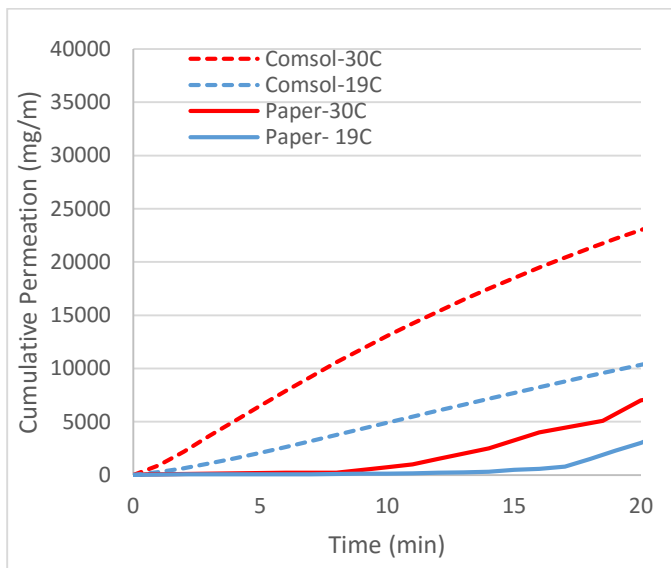


Fig 9. Comparison of Cumulative Permeation Versus Time for 19°C and 30°C

The 19 and 30 °C COMSOL data shows the same overall trend as the experimental data. However, a large offset is seen for the model. The model is better at predicting the cumulative permeation over long times compared to the initial transfer. In addition, the model shows a larger predicted cumulative permeation for all times compared to the experimental data. This over prediction could be due to the assumption that the Biot number was infinity and that the permeant was not accumulating on the surface of the pipe. The assumption of a Biot number of infinity maximizes the diffusion gradient and gives the worst case scenario. Figure 10 shows the COMSOL model's results and the experimental results from Bromwich and Parikh⁽¹⁾ for the 40 and 50 °C cases.

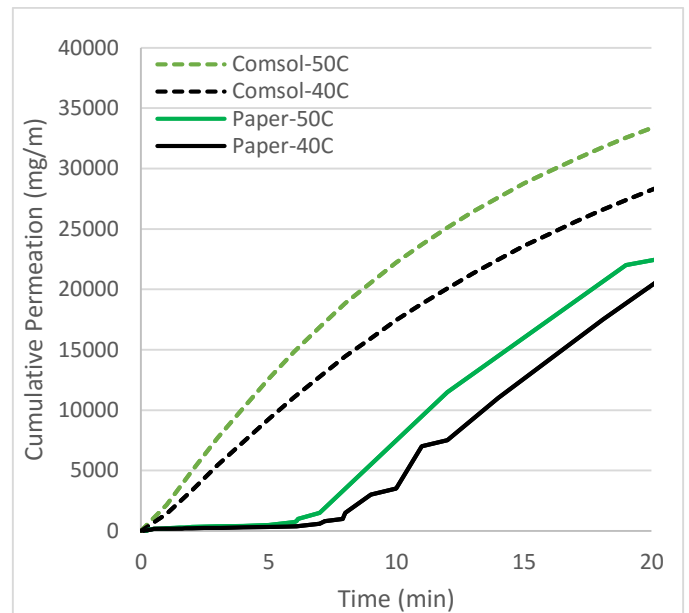


Fig 10. Comparison of Cumulative Permeation Versus Time for 19°C and 30°C

The results for the 40 and 50 °C cases still show an overall offset but the offset is less than the 19 and 30 °C cases. This makes sense because as the MEK is heated the mass transfer coefficient of it in the air also increase. Therefore, as the temperature of the MEK increase the experimental data is more like the COMSOL model's assumption that the Biot number is infinity. The results from the 60 and 70 °C cases are shown in Figure 11. Again the COMSOL model data shows a higher cumulative permeation result for all time. The offset of the COMSOL model data versus the experimental data is less than the offset seen in the lower temperature cases. This again shows that as temperature increase the Biot number increases and the approximation that the Biot number is infinity is a better assumption.

All the experimental results from Bromwich and Parikh⁽¹⁾ are plotted with all the COMSOL results and are shown in Figure 12. When comparing the full set the overall prediction of the model is good. The simulation model predicts a higher cumulative permeation than the experimental data in all temperature cases. The offset of the experimental and

simulation data decreases as the temperature decreases since the assumptions made in the model are a better fit to reality.

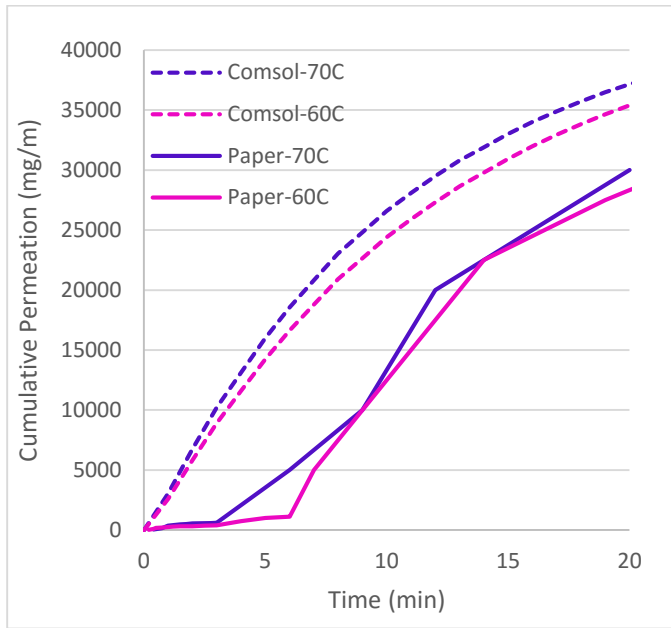


Fig 11. Comparison of Cumulative Permeation Versus Time for 19°C and 30°C

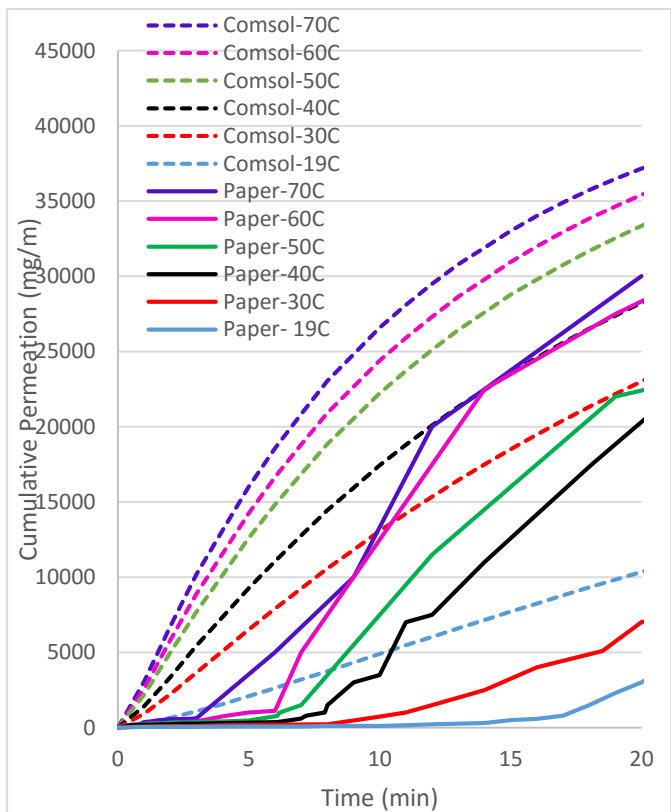


Fig 12. Comparison of Cumulative Permeation Versus Time for 19°C and 30°C

V. CONCLUSION

Although the experimental paper studied the effects of various steady state, above ambient temperatures, the model

proposed tries to investigate the effects of a non-isothermal environment on the diffusion through the tube wall using model simulation by COMSOL. Overall the model is able to predict the experimental cumulative permeation for the system. However, the model predicts higher cumulative permeation values for all temperatures at the various times. The offset is postulated to be caused by the assumption in the model that the permeant is being removed fully from the outside wall of the PVC pipe by a stream of air flowing across it. This assumption is consistent with assuming that the Biot number is infinitely large and that the external diffusion resistance is negligible. Thereby, maximizing the diffusion gradient and allowing the model to determine the worst case scenario. The fact that the offset decreases with an increase in the MEK temperature is consistent with the proposed explanation that the Biot number of the experiment is not actually at infinity.

In addition, the proposed simulation model is better at fitting the experimental data over long time compared with at a short time. This may mean that the diffusion coefficient may change, possible due to the low molecular weight species in the PVC migrating out along with the MEK. To examine this, further experimental results would need to be collected and more data points should be generated at short times to give a better estimation of the diffusion coefficient.

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