

## Supporting Information

A schematic of the system used in this study is shown in Figure 1 below.

Figure 1. Constant-Volume Dense Film Permeation Apparatus.

Labview program to feed the membrane on the upstream. As the gas diffused through the membrane to the permeate side, the pressure was recorded on the downstream using the Labview program. The upstream pressure was maintained constant throughout the experiment and also recorded using Labview. A downstream pressure vs. time plot was then generated using the data collected. The slope of the plot was calculated after steady-state was reached (after 10-12x the time lag) and used to calculate the permeability coefficient using Equation 1. In the case of mixed gas, the permeate composition was obtained using a Varian 450-GC gas chromatograph and the selectivity was calculated using Equation 7. Since  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are highly condensable gases, all measurements were adjusted for fugacity as shown in Figure 2. These coefficients were determined using the ThermoSolver thermodynamic and engineering software package, where the Peng-Robinson equation of state was chosen for calculations; they were then inserted in Equation 7 to calculate the mixed gas selectivity. The feed pressure and retentate flow were maintained by keeping the stage cut below 1% using an ISCO syringe pump and a metering valve. The syringe pump was maintained at constant pressure and the gas was fed at the same rate as the retentate vented through the metering valve. The stage cut is the fraction of a feed mixture that is allowed to permeate through the membrane. A low stage cut was used to prevent concentration polarization on the upstream in order to maintain a constant driving force across the membrane during the experiment.

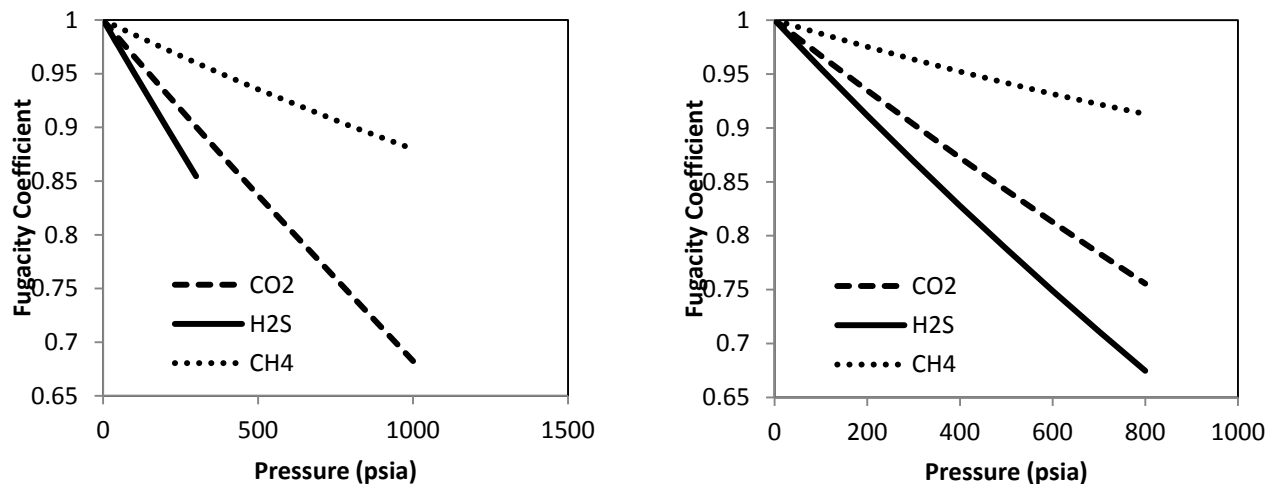


Figure 2. Fugacity coefficients of CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> for pure gas (left) and 20%/20%/60% CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> gas mixture (right).

## II. Reactor Selection and Other Reactions Procedures

A stainless-steel autoclave reactor was chosen because VTMS ( $b_p=123^\circ\text{C}$ ) is a gas at the temperature of the reaction. The pressure inside the reactor will be similar to the vapor pressure of VTMS at  $200^\circ\text{C}$ , which is not currently available in literature. The saturation pressure at  $25^\circ\text{C}$  is estimated at 16.4mmHg from Lookchem.

As mentioned in the manuscript, other reactions were carried with a similar procedure as the manuscript but with different silane and a catalyst. The reaction conditions of these different procedures are summarized in Table 1 along with some terminologies.

Table 1: Silane Modification of CA at Different (Suboptimal) Reaction Conditions

Terminology	Reaction Conditions	Reactant Ratio	Drying Conditions
GCV-Modified	1 day at $200^\circ\text{C}$	1:100 CA:VTMS	1 day at $150^\circ\text{C}$
GCV-DCP-Modified	1 day at $150^\circ\text{C}$	1:100:0.1 CA:VTMS:DCP	1 day at $150^\circ\text{C}$
GCT-Modified	1 day at $150^\circ\text{C}$	1:100 CA:TMS	1 day at $150^\circ\text{C}$

## III. FTIR Results of GCV-DCP-Modified and GCT-Modified CA

Even though the resulting GCV-DCP-Modified film was brittle, we characterized it using FTIR to understand this outcome. The IR spectra of neat CA and VTMS are shown on Figures 3 and 4 and their band assignments in Table 2 and 3, respectively. Some important features of the IR spectra of the GCV-DCP-Modified CA film (Figure 5) include: (1) a slight shift and a decrease in intensity in the –OH band in CA around  $3469\text{ cm}^{-1}$ , (2) a decrease in the band that occurs in neat VTMS at  $1410\text{ cm}^{-1}$ , a disappearance of the bands at  $1011$  and  $968\text{ cm}^{-1}$ , and the merging of the doublet at  $811$  and  $769\text{ cm}^{-1}$ . These bands were characteristic of the vinyl group present in the VTMS structure but, (3) the band at  $2842$  and  $1191\text{ cm}^{-1}$  characteristic of the  $\text{Si-OCH}_3$  was not changed significantly.

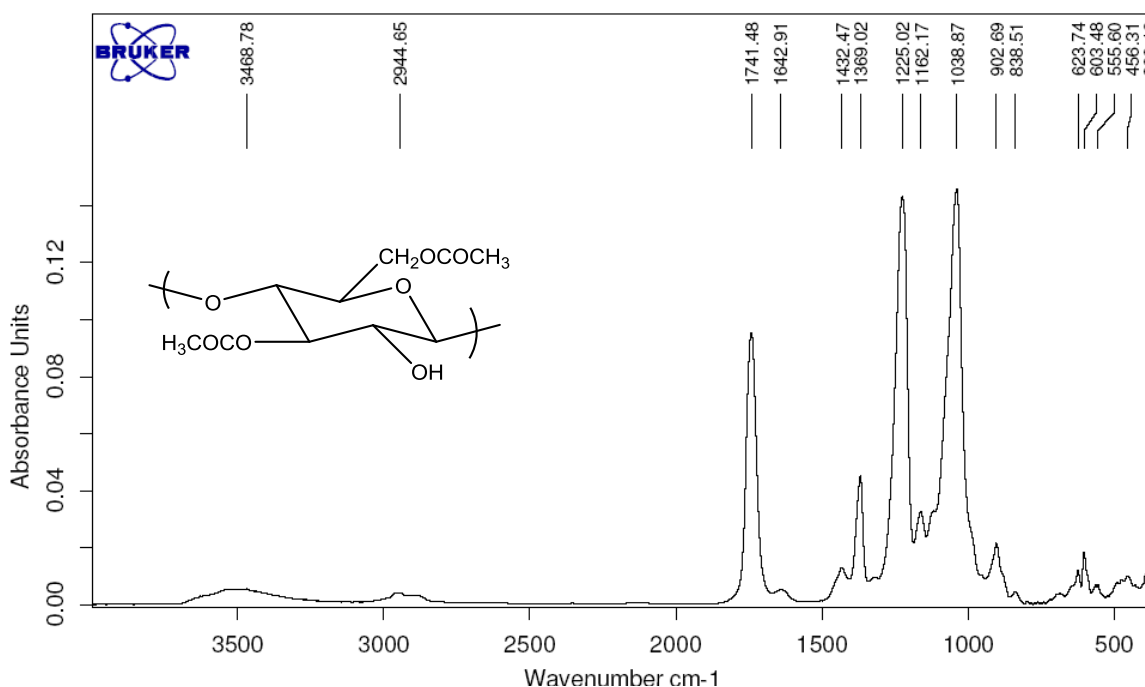


Figure 3. ATR-IR Spectrum of Neat CA Dense Film.

**Table 2.** FTIR Band Assignments of Neat CA Dense Film

Wavenumber ( $\text{cm}^{-1}$ )	Band Assignment
3469	-OH stretching (H-bonding)
2945	C-H stretching valence vibrations of –CH and –CH <sub>2</sub> groups

1741	C=O stretching of ester
1432	C-OH bending
1369	-CH <sub>3</sub> in plane bending ( -CH <sub>3</sub> group from acetate group)
1225	O-C-C stretching of acetyl group
1162	C-O-C antisymmetric bridge stretching
1039	Ether linkage connecting neighboring glucopyranose rings

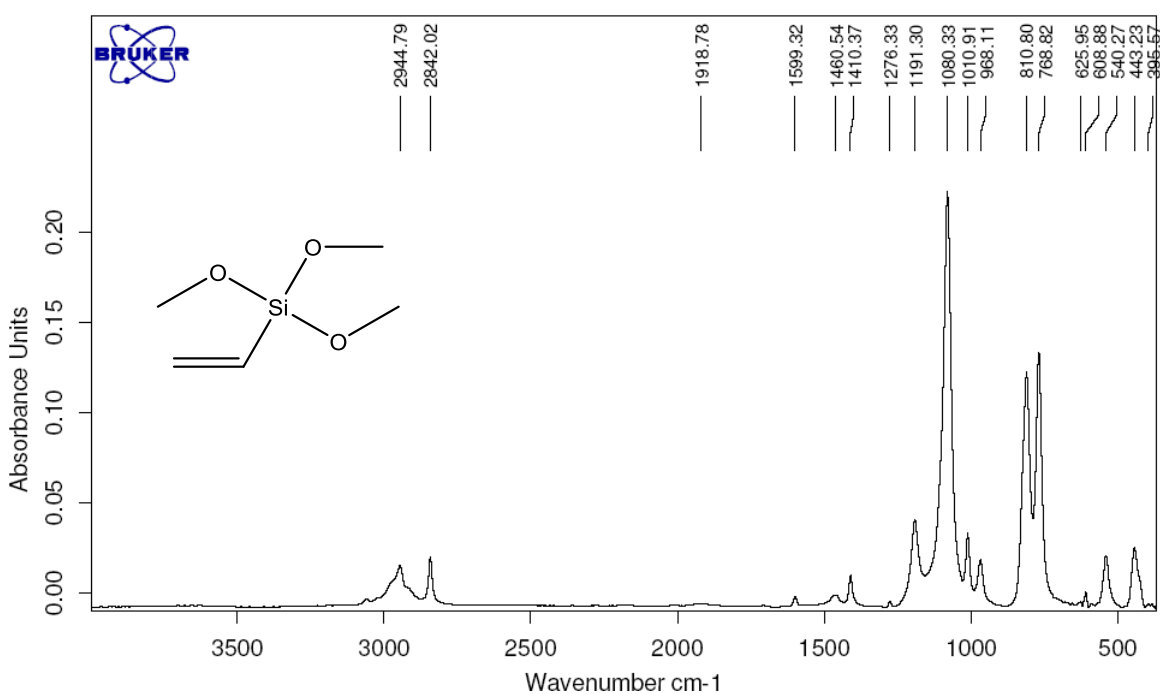


Figure 4. ATR-IR Spectrum of Neat VTMS Liquid.

**Table 3.** FTIR Band Assignments of Neat VTMS Liquid

Wavenumber (cm <sup>-1</sup> )	Band Assignment
2945	CH <sub>2</sub> asymmetric stretch
2842	CH symmetric stretch (Si-OCH <sub>3</sub> )
1599	C=C stretch
1410	CH <sub>2</sub> deformation (Si-CH=CH <sub>2</sub> )
1191	O-CH <sub>3</sub> rocking (Si-OCH <sub>3</sub> )

1080	Si-O-C stretch (Si-OCH <sub>3</sub> )
1011	Vinyl CH <sub>2</sub> twist (Si-CH=CH <sub>2</sub> )
968	Vinyl CH <sub>2</sub> wag (Si-CH=CH <sub>2</sub> )
811	=CH & =CH <sub>2</sub> (Si-CH=CH <sub>2</sub> )
769	=CH & =CH <sub>2</sub> (Si-CH=CH <sub>2</sub> )
540	Vinyl C-H bend
443	C-Si-O bend

To refer to some band intensities as decreasing or increasing, we carefully normalized all of the spectra used for comparison with respect to one another, and the same peak sensitivity setting was used for each spectrum for peak detection. Therefore, it is reasonable to say that some peak are not being detected or have decreased in intensity relative to the others. Observation 1 shows that –OH groups have reacted, and observation 3 showed that some bands that are characteristic of the vinyl groups are no longer detected except from the ones at 1410 and at 443 cm<sup>-1</sup>. As noted above, to better quantify the latter observation, we used a band ratio analysis. Since the band at 1410 cm<sup>-1</sup> is characteristic of the Si-CH=CH<sub>2</sub> bond and the band at 443 is characteristic of the C-Si-O bend in VTMS, we took their ratio in both VTMS and GCV-DCP-Modified CA for comparison.

$$\left[ \frac{Si-CH=CH_2|_{at\ 1410cm^{-1}}}{C-Si-O|_{at\ 443cm^{-1}}} \right]_{in\ Neat\ VTMS} = 0.529 \quad and \quad \left[ \frac{Si-CH=CH_2|_{at\ 1411cm^{-1}}}{C-Si-O|_{at\ 443cm^{-1}}} \right]_{in\ GCV-DCP-Modified\ CA} = 0.105$$

This analysis shows that roughly 80% of the vinyl groups have reacted in the presence of the DCP catalyst. Similarly, the neat VTMS liquid has three bands that corresponds to the Si-OCH<sub>3</sub> group: 2842, 1191, and 1080 cm<sup>-1</sup>. Therefore, we could also take the ratio of any two of those peaks and compare it to the ratio of the same peaks in the GCV-DCP-Modified film. In this case,

we used the bands at 1191 and 2842  $\text{cm}^{-1}$  since the band at 1080  $\text{cm}^{-1}$  merged with the one at 1039  $\text{cm}^{-1}$  in neat CA and was therefore not useful.

$$\left[ \frac{Si-OCH_3 \text{ at } 1191 \text{ cm}^{-1}}{Si-OCH_3 \text{ at } 2842 \text{ cm}^{-1}} \right]_{\text{in Neat VTMS}} = 1.25 \quad \text{and} \quad \left[ \frac{Si-OCH_3 \text{ at } 1189 \text{ cm}^{-1}}{Si-OCH_3 \text{ at } 2840 \text{ cm}^{-1}} \right]_{\text{in GCV-DCP-Modified CA}} = 0.94$$

The ratio of those methoxy peaks have decreased by roughly 25% from the neat CA, indicating less of those groups have reacted compared to the vinyl groups. In conclusion, in the GCV-DCP-modification, the predominant reaction occurs with the vinyl groups.

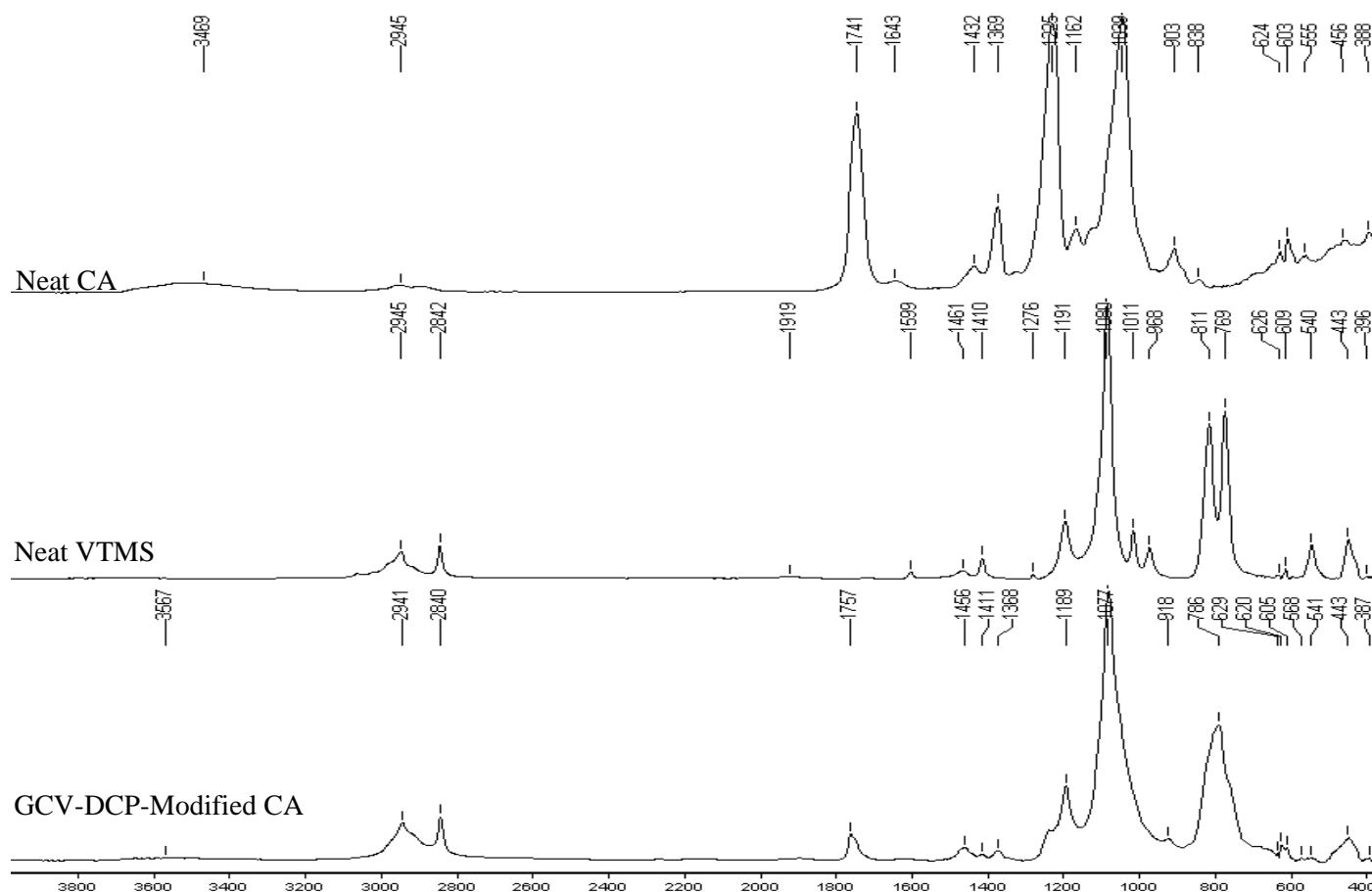


Figure 5. ATR-IR Spectra of CA (top), VTMS (middle), and GCV-DCP-Modified CA (bottom).

The brittleness that was observed with this DCP modified film may have been caused by the reaction of the vinyl group which we originally hoped would add flexibility to the polymer to offset rigidification from the ultimate silanols crosslinking. In any case the GCT-Modification with the conditions of Table 1 led to a brittle and cloudy film of limited utility. The difference between the VTMS and TMS lies in the replacement of the vinyl group in VTMS with hydrogen. By looking at the FTIR spectra of the resulting GCT-Modified membrane on Figure 6, we see: (1) the Si-OCH<sub>3</sub> bands at 2844, 1193, and 1085 cm<sup>-1</sup> present in neat TMS are no longer detected, indicating that those methoxy groups reacted, (2) the band assigned to the Si-H group in TMS at 2199 cm<sup>-1</sup> has reduced significantly. The three spectra were also normalized and the same peak sensitivity was used. By using a similar band ratio analysis as above, we were able to further characterize those observations. The ratio of the Si-OCH<sub>3</sub> bands could not be taken as done in the previous case because they were not detected in the case.

$$\left[ \frac{Si-H|_{at\ 2199cm^{-1}}}{Si-H|_{at\ 872cm^{-1}}} \right]_{in\ Neat\ TMS} = 0.206 \quad and \quad \left[ \frac{Si-H|_{at\ 2220cm^{-1}}}{Si-H|_{at\ 831cm^{-1}}} \right]_{in\ GCT-Modified\ CA} = 0.043$$

In this case, a ~80% of the Si-H groups have reacted. The opening of the vinyl group and the resulting brittleness of the film in the GCV-DCP-Modified film and their absence in GCT-Modified, which resulted in a brittle film as well support the fact the vinyl groups are needed for the optimum polymer to remain flexible for practical membranes. It may, of course, be possible to replace the vinyl groups with a simple ethyl group; however, this is beyond the scope of this study.



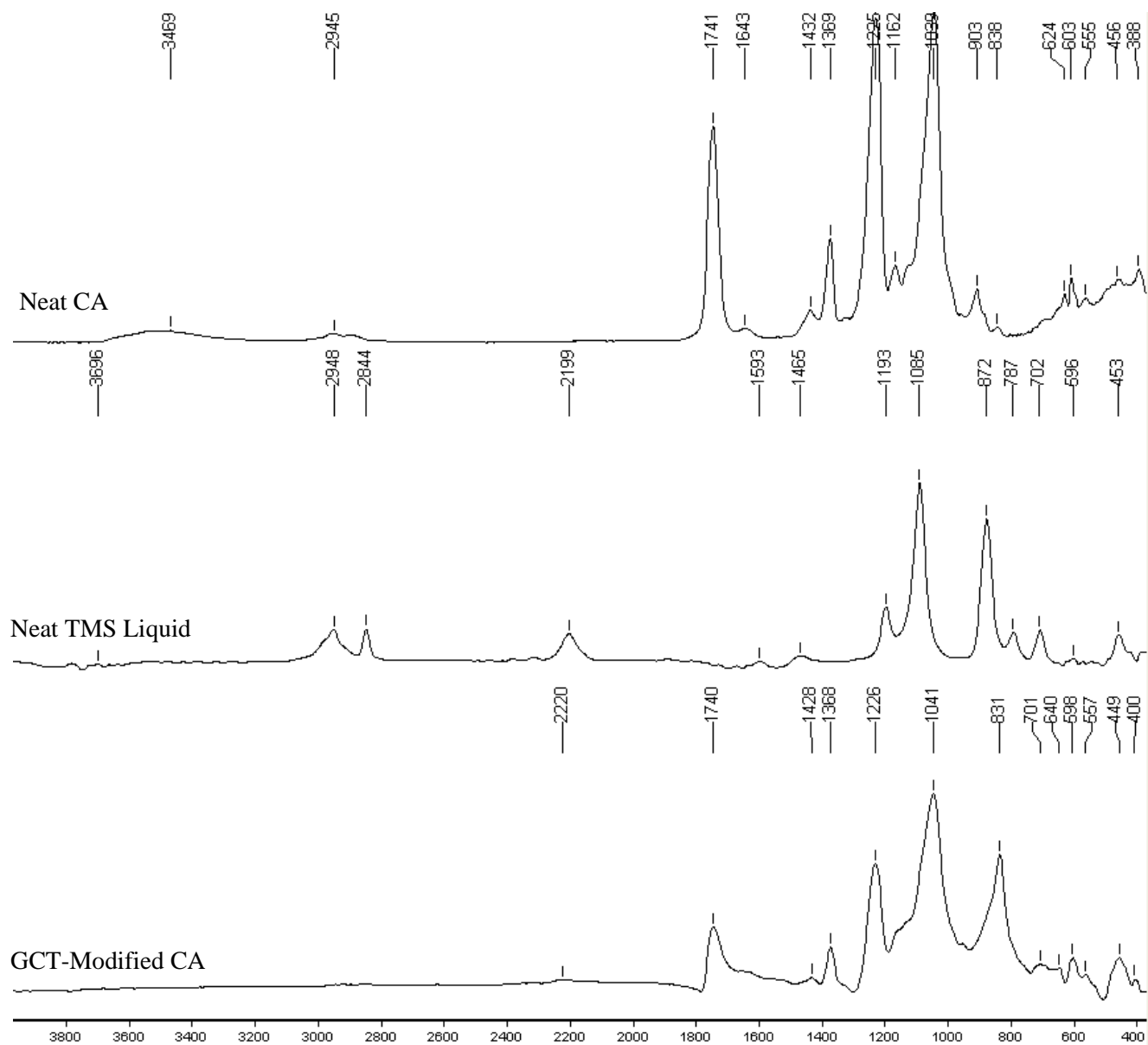


Figure 6. ATR-IR Spectra of CA (top), TMS liquid (middle), and GCT-Modified CA (bottom).

#### IV. NMR Spectra of GCV-DCP-Modified CA

The  $^{13}\text{C}$  NMR spectrum of the GCV-DCP-Modified CA on Figure 7 shows some differences as expected from FTIR analysis. We note that the  $-\text{OCH}_3$  signal around 50 ppm is now the highest of all the other signals which wasn't the case for the GCV-Modified CA, which shows, as discussed earlier, that less methoxy groups react with DCP added compared to when none is used. In addition, the signal corresponding to the vinyl carbons is weaker compared to the signal of GCV-Modified CA. This additional characterization further shows that the use of the DCP caused an uncontrolled reaction and it made the film brittle and thus not useful for this purpose.

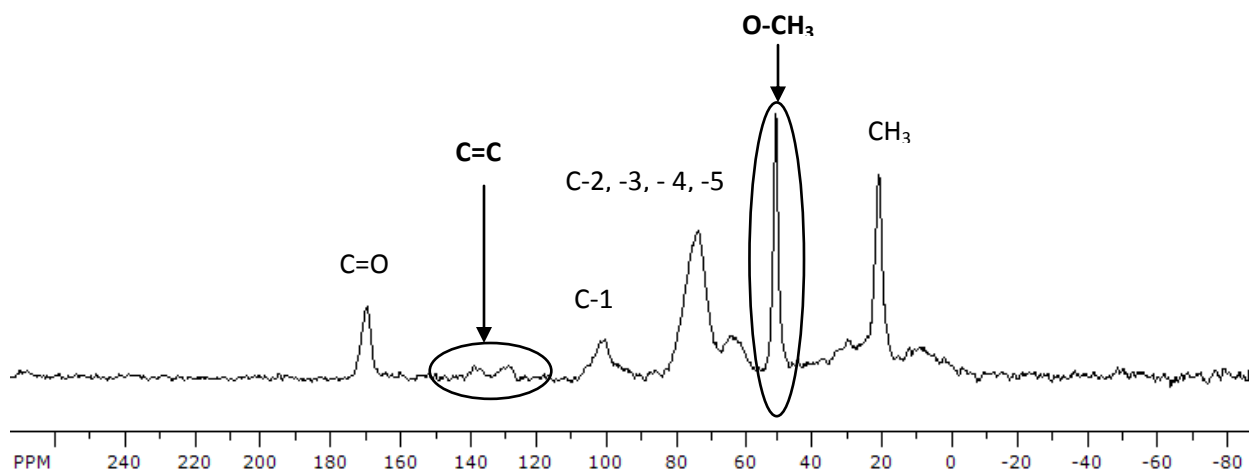


Figure 7.  $^{13}\text{C}$  Solid State NMR of GCV-DCP-Modified CA dense film membrane.

In the  $^{29}\text{Si}$  NMR spectrum of GCV-DCP-Modified CA on Figure 8, we note that as a few the vinyl groups reacted, a new signal characteristic of the ETMO (ethyltrimethoxysilane) appeared but with much lower intensity. However, as shown in FTIR results, ~80% of the vinyl groups have reacted in the GCV-DCP-Modified CA, which explains the much lower signal around -58 ppm in Figure 8 compared to a much higher signal around -43 ppm.

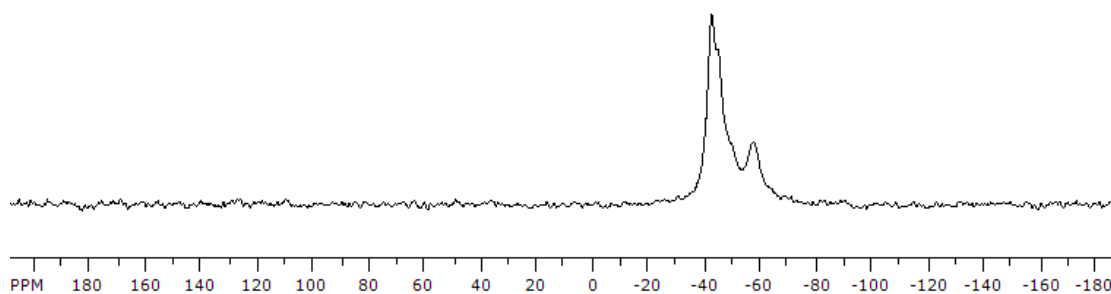


Figure 8.  $^{29}\text{Si}$  Solid State NMR of GCV-DCP-Modified CA Film.

## V. DSC Curve of GCV-Modified CA Powder

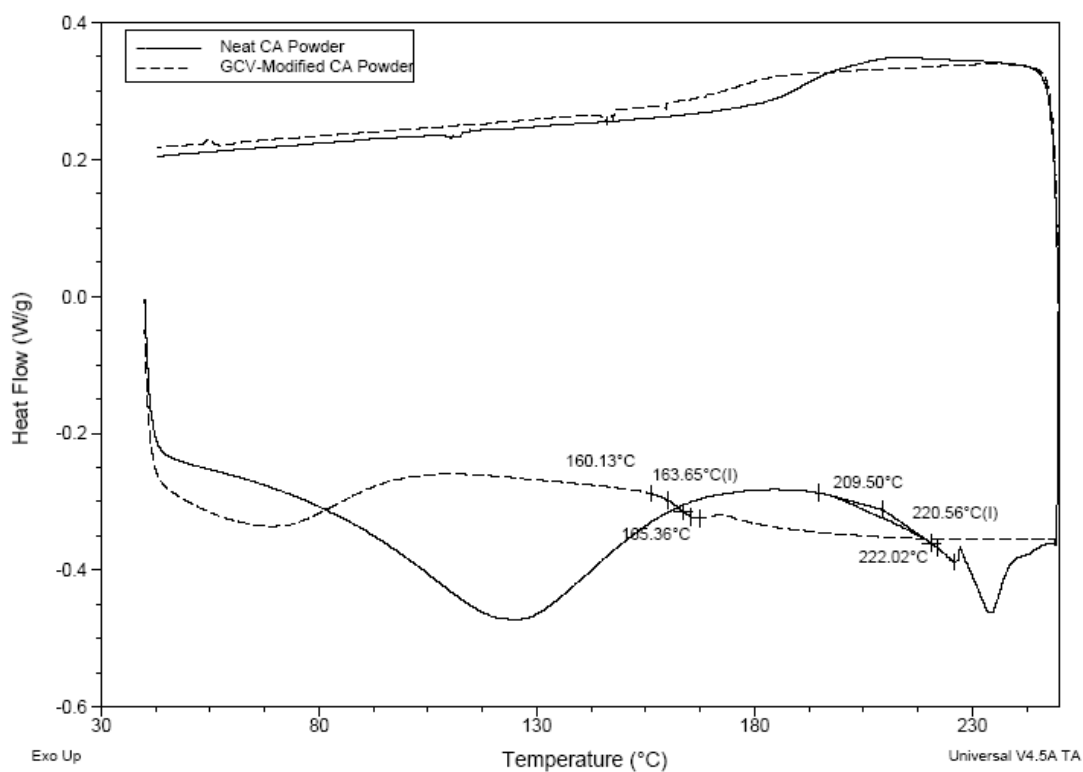


Figure 9. DSC curve of the Neat CA and GCV-Modified CA powder.

## VI. DMA Spectrum of GCV-Modified CA (Duplicate Scan)

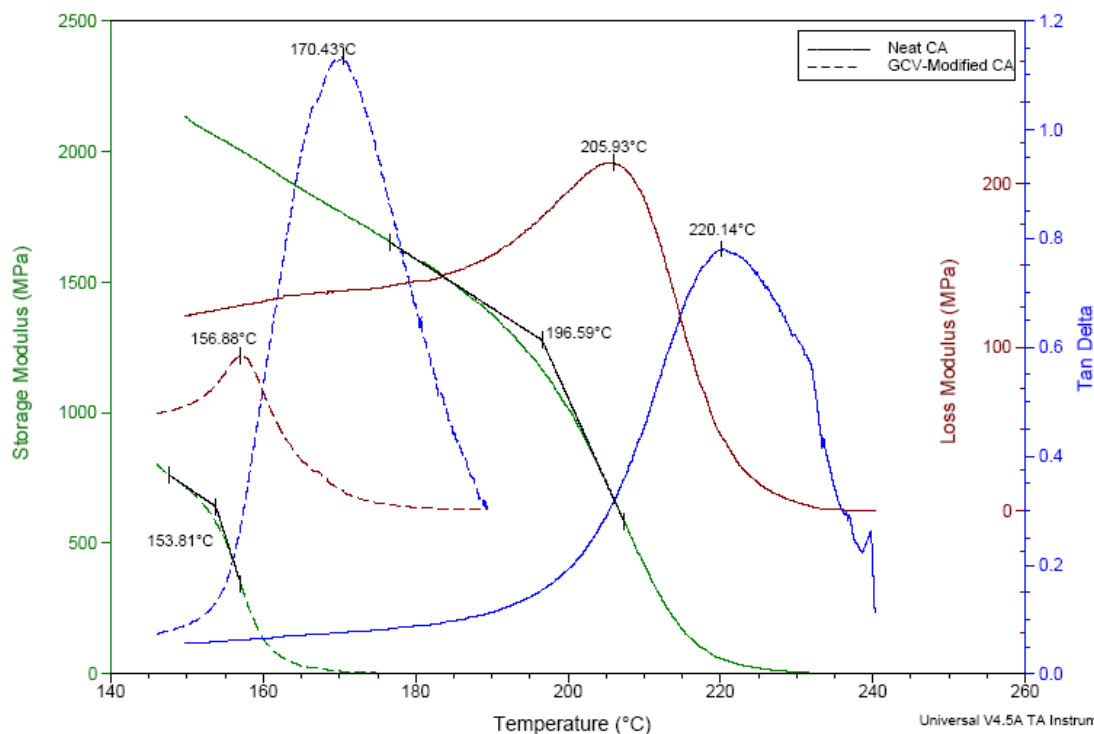


Figure 10. Dynamic Mechanical spectrum of neat CA and GCV-Modified CA dense film membrane at 3 Hz (duplicate scan).

## VII. GC-MS Analysis of GCV-Modified CA Reaction Liquid Residue

The instrument used in for GC-MS measurements was a Micromass AutoSpec M, and the GC was an Agilent 6890 with an Agilent 6890 autosampler. The GC column was a J&W DB 5MS, 30m x 0.25mm, with a 0.25 $\mu$ m film thickness. One  $\mu$ L of the sample solution was injected at a split ratio of 50:1, and the carrier gas was helium. The initial column temperature was 30°C, and after a 1-minute hold, the temperature was ramped to 300°C at 15°C/min, with a 6-minute hold at 300°C. As hypothesized in Scheme 1 of the manuscript, methanol is a byproduct of the reaction in step 1 and this method was used to confirm the presence of methanol in the reaction liquid residue, since VTMS was used in excess. Figure 11a shows the total ion chromatogram (TIC) of neat VTMS liquid and Figure 11b shows the extracted ion chromatogram (XIC) for

only the 31 ion in neat VTMS liquid, which is a marker for methanol. Figure 12a and 12b shows the TIC chromatograph of the GCV-Modified CA and the XIC chromatograms of the 31 ion, respectively. The mass spectrum of the GC peaks at 1.60 mins and 1.58 mins (which is when the methanol elutes) in the neat VTMS liquid and GCV-Modified liquid residue is shown in Figure 12. This technique is qualitative as it only shows that methanol evolves as the byproduct of the reaction. Even though the VTMS used in this study was sure sealed, a trace amount of methanol was still detected in the neat liquid as shown in Figure 11. However, the magnitude of the peak in the GCV-Modified CA liquid residue is much higher than that of the neat VTMS, indicating that methanol is evolved.

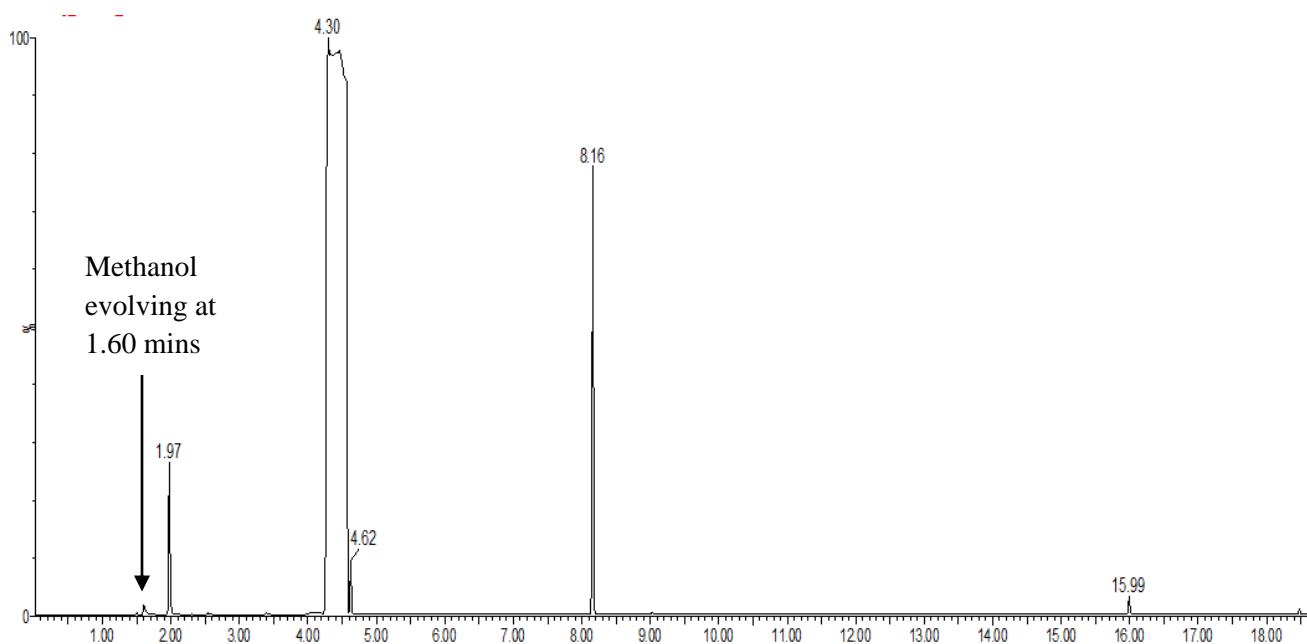


Figure 11a. Total ion chromatogram (TIC) analysis of neat VTMS liquid.

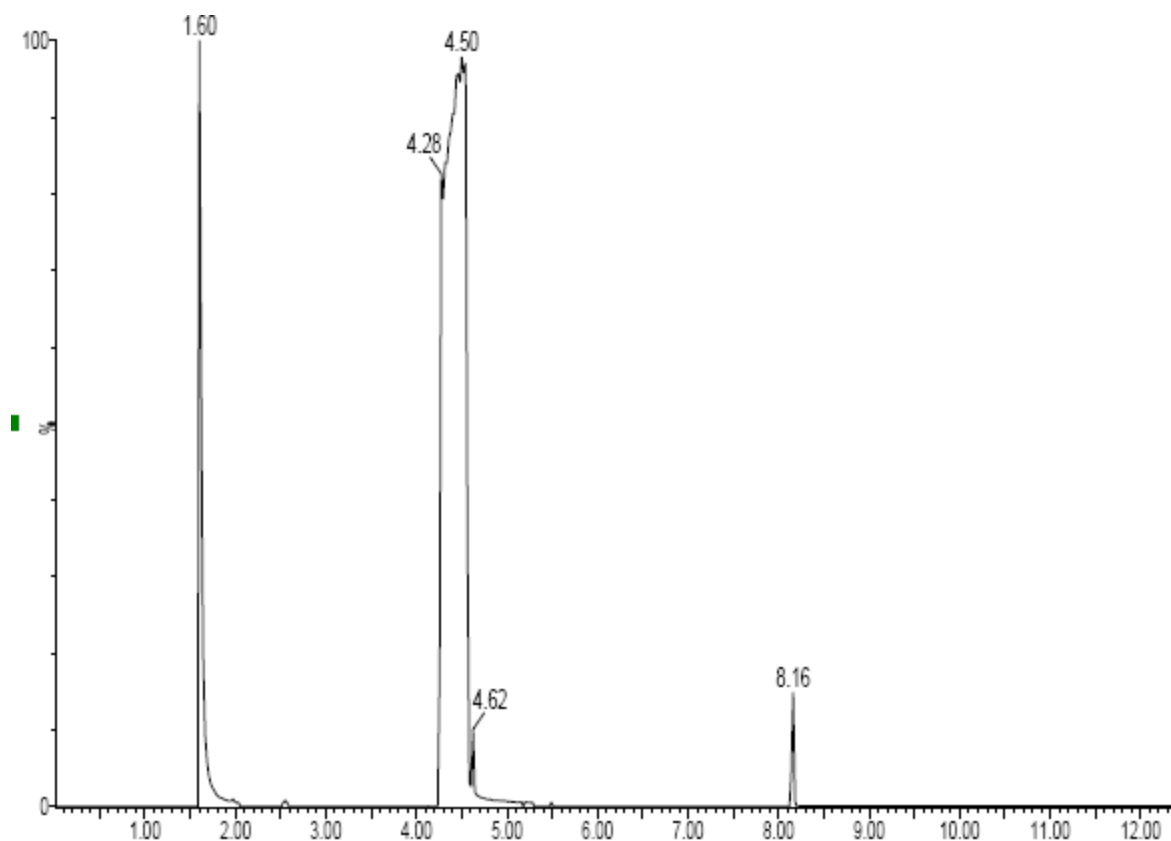


Figure 11b. Extracted ion chromatogram (XIC) for the 31 ion in neat VTMS liquid.

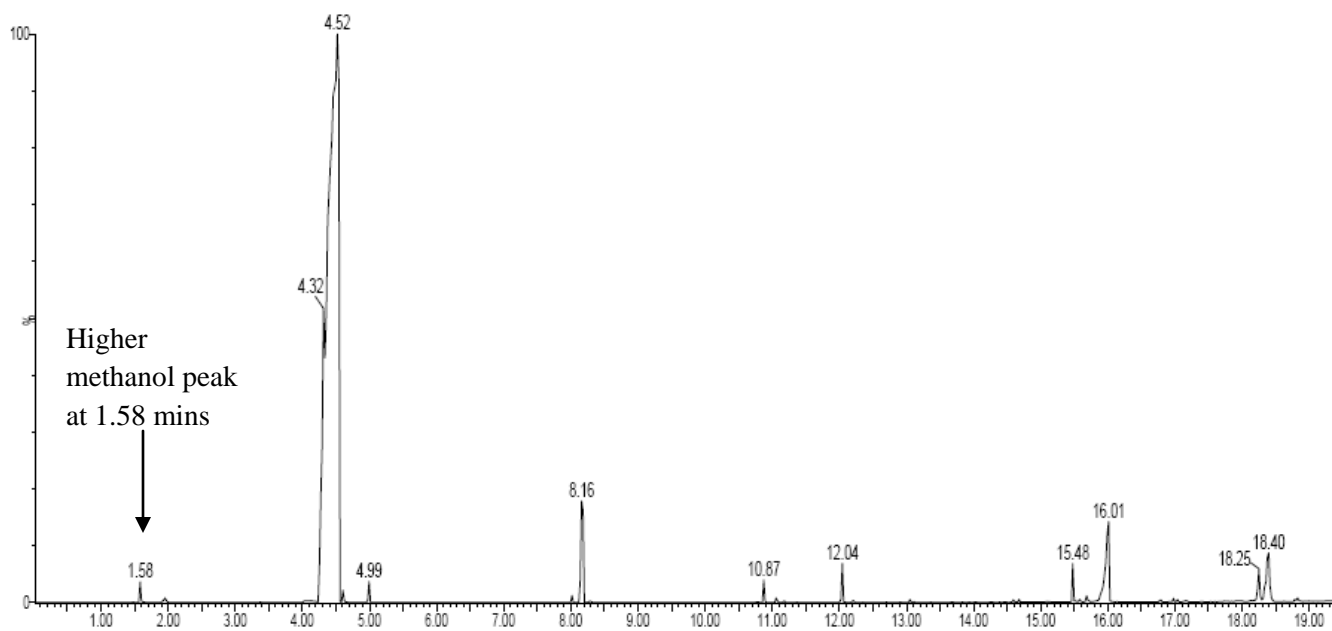


Figure 12a. Total ion chromatogram (TIC) analysis of GCV-Modified liquid residue.

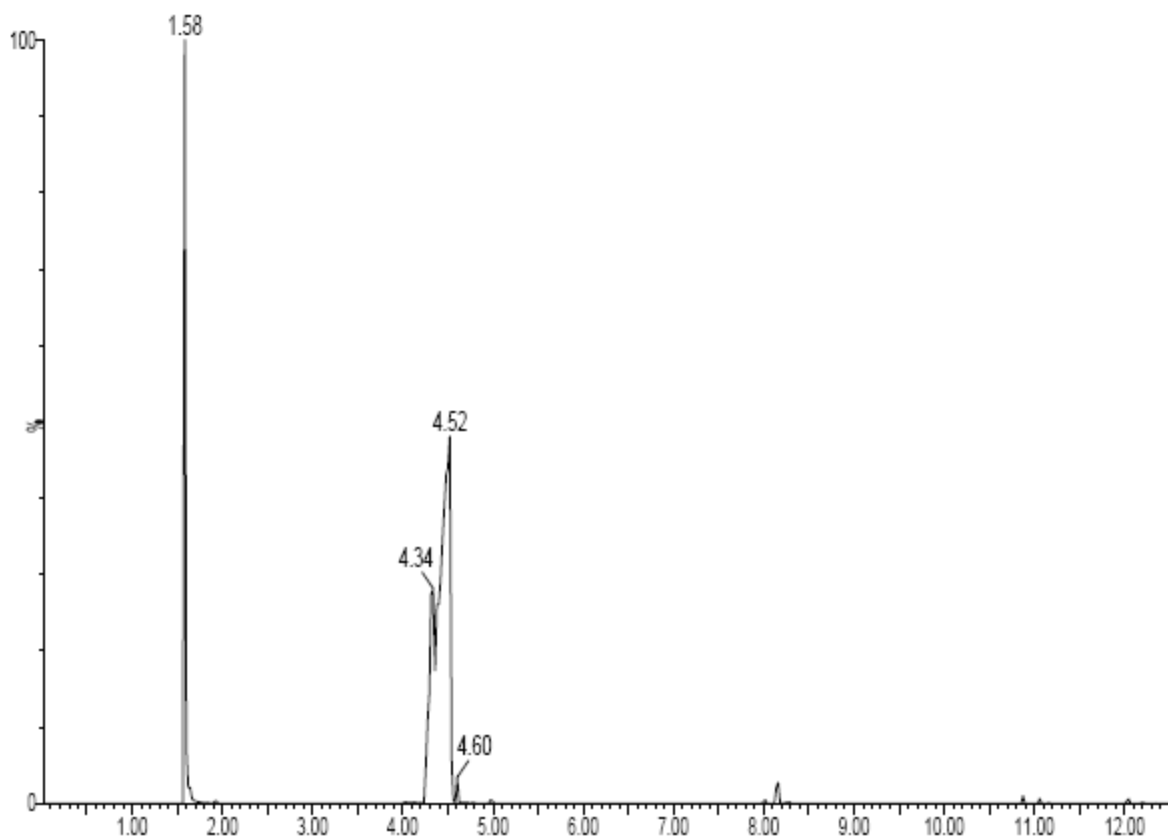


Figure 12b. Extracted ion chromatogram (XIC) for the 31 ion in GCV-Modified liquid residue.

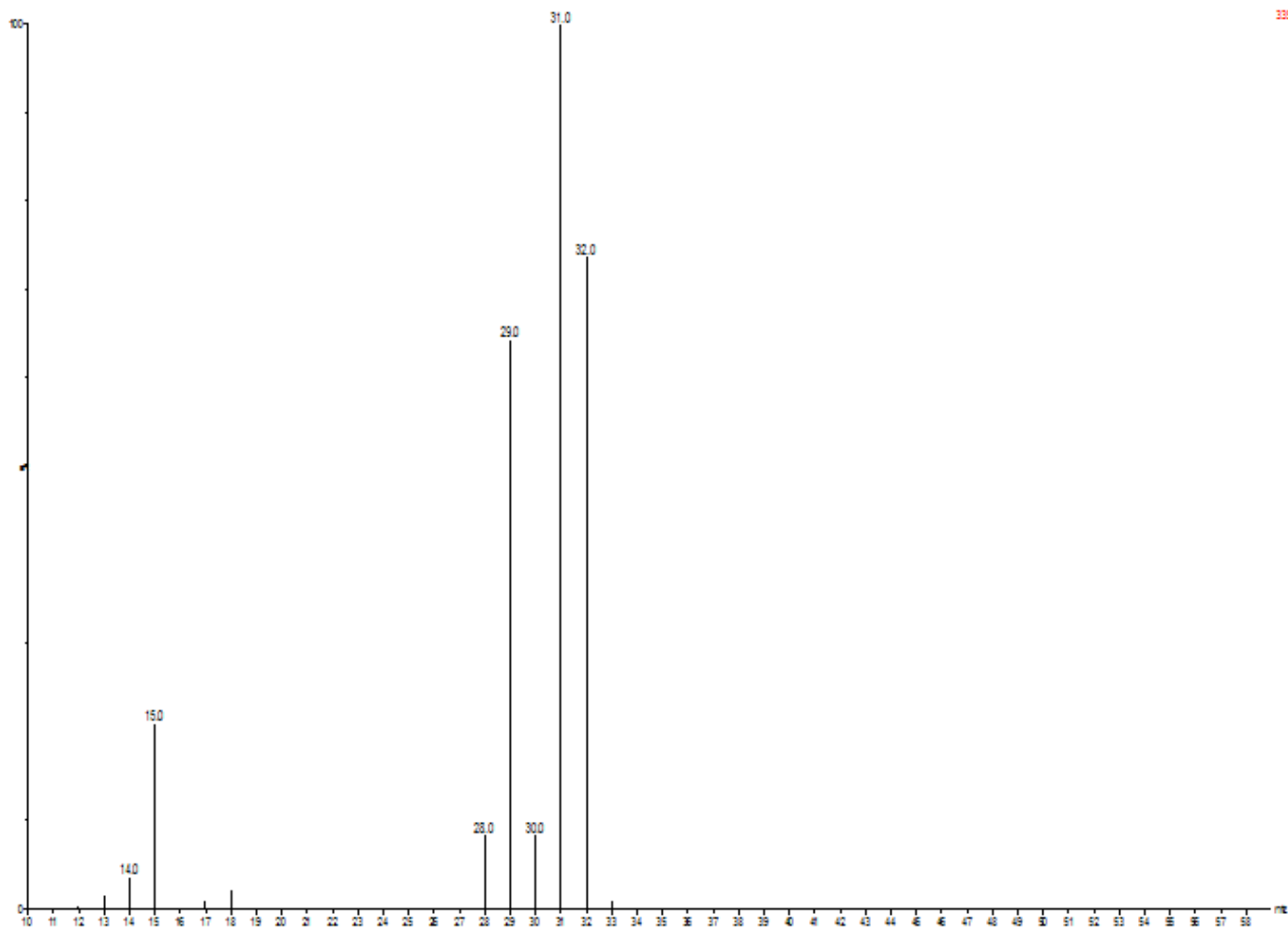


Figure 23. Mass spectrum of the GC peaks at 1.60 and 1.58 mins (methanol) in neat VTMS liquid and GCV-Modified liquid residue.