CHAPTER IV

ANALYSIS OF MEA AND ITS OXIDATIVE DEGRADATION PRODUCTS DURING CO_2 ABSORPTION FROM FLUE GASES: A COMPREHENSIVE STUDY OF GC-MS, HPLC-RID AND CE-DAD ANALYTICAL TECHNIQUES AND POSSIBLE OPTIMUM COMBINATIONS

4.1 Research Objectives

It has also been observed that most degradation studies often make use of a single technique to characterize the oxidative degradation of alkanolamines. Although the GC, especially GC-MS, has been a powerful and heavily used tool, its analysis can be limited to volatile products. Degradation products of high molecular weights might be potentially left undetected, resulting in incomplete information of their formation pathways. LC might overcome this problem and could be used as a confirmation technique. CE could also be used in the same manner as LC. In order to adequately gain information of alkanolamine degradation in terms of an alkanolamine decline as well as the distribution of its degradation products in the liquid phase for a formulation of a mechanism based kinetics, a combination of analytical techniques is required. A summary showing GC, LC, CE techniques, and less used FTIR and NMR spectroscopy previously used for analysis of alkanolamines and their degradation products is given in Table 4.1.

Table 4.1 Summary of analytical techniques previously used for analysis of alkanolamines and their degradation products

Analytical Technique	Reference	Operating Conditions				System Applied	Limitation/Shortcomings
		Column Type	Stationary Phase	Mobile Phase/ Electrolyte	Detector		
GC	Brydia and Persinger (1967)	Packed	5% Neopentylglycol succinate	He	TCD	Alkanolamine analysis	Tedious derivatization
	Piekos, Kobylczyk, and Grzybowski (1975)	Packed	3% OV-1, methyl polysiloxane	Ar and N_2	FID	Alkanolamine analysis	Tedious derivatization
	Saha, Jain, Dua (1977)	Packed	2,6-diphenyl-p-phnylene oxide	N_2	FID	Alkanolamine analysis	Low efficient packed column
	Kennard and Meisen (1983)	Packed	2,6-diphenyl-p-phnylene oxide	N_2	FID	CO_2-induced DEA degradation	Low efficient packed column
	Dawodu and Meisen (1991 and 1993)	Packed and capillary	2,6-diphenyl-p-phnylene oxide/ polyethylene glycol	N_2	FID/MS	COS-induced DEA degradation	Limited to COS-induced degradation
	Supap et al. (2001)	Capillary	Crosslinked polyethylene glycol	He	MS	O_2-induced MEA degradation	Peak overlaps
	Strazisar and Anderson (2003)	Capillary	14%-(cyanopropyl-phenyl)-methylpolysiloxane/nitrotetraphthalic acid-modified polyethylene glycol	He	MS/FTIR/AED	MEA degradation products in a flue gas treating plant samples	Caustic-modified samples tested the technique was not tested on actual degraded samples.
	Bello and Idem (2005)	Capillary	Crosslinked polyethylene glycol	He	MS	O2-induced MEA degradation	Peak overlaps
LC	Blanc, Grall, and Demarais (1982)	Ion exclusion	N/A	N/A	N/A	O_2-induced MEA/DEA/MDEA degradation	Lack of simutaneous MEA detection
	Kadnar and Rieder (1995)	Anion exchanger	IonPac AS10/AS9-SC	$Na_2B_4O_7$/NaHCO3/ NaOH	PED using mode of conductivity	Heat stable salts in MDEA plant samples	Need of extra suppression system, increasing cost
	Rooney, Dupart, and Bacon (1998)	Anion exchanger	Did not provide	Did not provide	Did not provide	O_2 and O_2-CO_2-induced various alkanolamine degradation	Lack of simutaneous MEA detection
	Kadnar and Rieder (1999)	Cation exchanger	Ionpac CS10/Ionpac CS12A	H_2SO_4	PED using mode of conductivity	Alkanolamine, mono, divalent cations	Need of extra suppression system, increasing cost
	Kaminski et al. (2002)	Cation exchanger	Nucleosil 100 - 5SA	KH_2PO_4	RID	Amines, products and wastewater in desuphurization process	Overlap of products when applied to oxidative degradation system
	Strazisar and Anderson (2003)	Cation exchanger	Ionpac CS14	Na_2CO_3/NaHCO3	Conductivity	Inorganic species in MEA used in a flue gas treating plant	Need of extra suppression system, increasing cost
CE	Altria et al. (1995)	Capillary	None	NaH_2PO_4	UV	Basic drugs	Not applied yet to alkanolamine and degradation products
	Altria, Bryant, and Hadgett, (1997)	Capillary	None	$Na_2B_4O_7.10H_2O$	UV	Acidic drugs	Not applied yet to alkanolamine and degradation products
	Pereira and Tavares (2004)	Capillary	None	Imidazole/HIBA/ 18-crown-6	DAD	Volatile corrosion inhibitors	Not applied yet to alkanolamine and degradation products
FT-IR	Chi and Rochelle (2002)	None	None	None	IR	Oxidative degradation of MEA	No compound separation
NMR	Talzi, and Ignashin (2002)	None	None	None	NMR	MEA plant samples	No compound separation
	Talzi (2004)	None	None	None	NMR	MEA plant samples	No compound separation

This table also shows the present limitations of these techniques. In this study, improved methods are being developed as well as exploring the best combinations of gas chromatographic, liquid chromatographic and capillary electrophoresis analytical techniques to completely characterize the oxidative degradation of two aqueous monoethanolamine systems, MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2. In the GC-MS technique, 3 different chromatographic columns of different stationary phase polarity were evaluated for separation, detection, identification, and quantification of MEA and its degradation products for both systems. On the other hand, in the HPLC technique, 2 different columns and 2 different mobile phases were evaluated for the same purpose. The capillary electrophoresis technique (CE) with selected electrolyte solutions was also explored. Some standards were used to identify degradation products using spiking techniques. The results for all the techniques are reported in this work in terms of compatibility of each analytical technique to separation of aqueous MEA and its oxidative degradation products as well as the best combinations of techniques to achieve this objective.

4.2 Results and Discussion

4.2.1 MEA Degradation at 393 K

4.2.1.1 GC-MS Analysis

The numbers of observed degradation products from both systems (i.e. MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2) for the 3 different GC columns having widely different polarities were different. The columns are HP-Innowax (high polarity), HP-35MS (intermediate polarity), and HP-5MS (non polar). Figures 4.1(a)-(c) show chromatograms obtained by HP-Innowax, HP-35MS, and HP-5MS, respectively for the MEA-H_2O-O_2 system while Figures 4.2(a)-(c) represent the respective columns for the MEA-H_2O-O_2-CO_2 system. Although not a primary goal of this study, the detected peaks were labeled and their identification was attempted, as shown in Table 4.2. Although some of the commonly found products (e.g. formic and acetic acids, and ammonia) as well as additional compounds (i.e. pyrimidine,

acetamide, 2-methylamino ethanol, acetaldehyde, and ethanol) were not shown in the chromatograms (except formic and acetic acids), they were detected and most of them verified in this work. These products either were not completely separated and so exhibited co-elutioned with the water peak or MEA peak or existed in low concentrations. The primary products also reacted further with themselves, MEA, or O_2 eventually resulting in stable final degradation products labeled in Figure 4.1(a)-(c) and 4.2(a)-(c), in which some have been consistently reported in the literature (Bello and Idem, 2005; Blanc, Grall, and Demarais, 1982; Chi and Rochelle, 2002; Hofmeyer, Scholten, and Lloyd, 1965; Rooney, Dupart, and Bacon, 1998; Starzisar, Anderson, and White, 2003; Talzi and Ignashin, 2002).
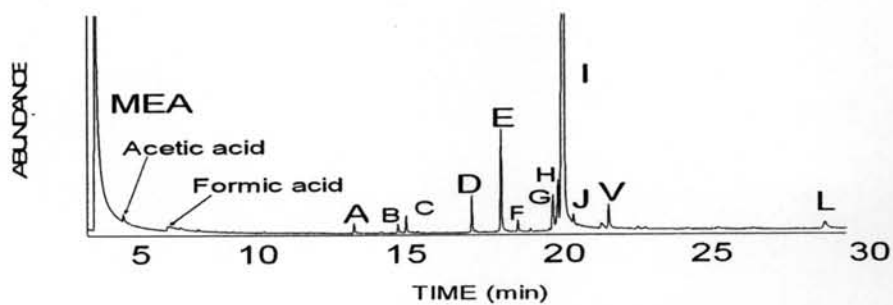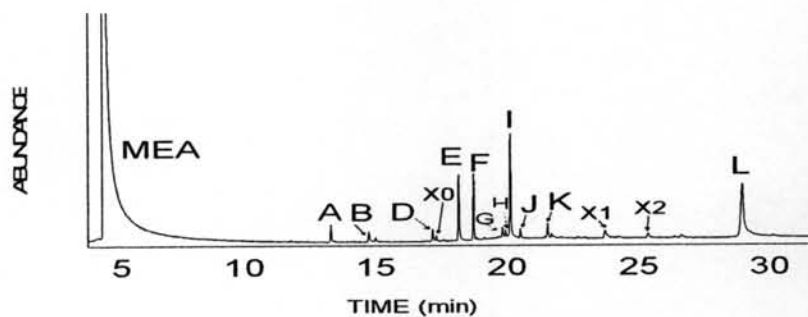
(a) HP-Innowax column-high polarity
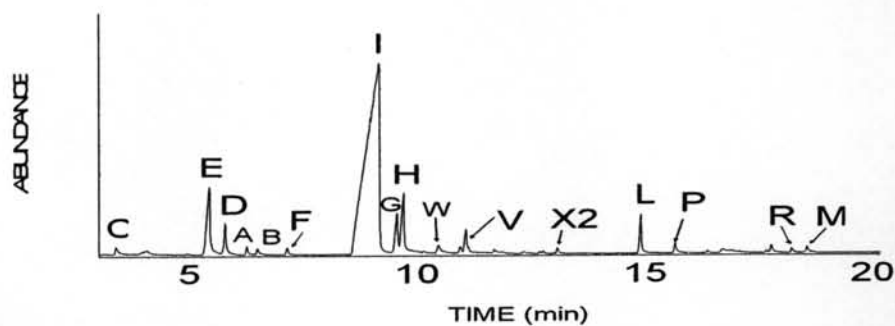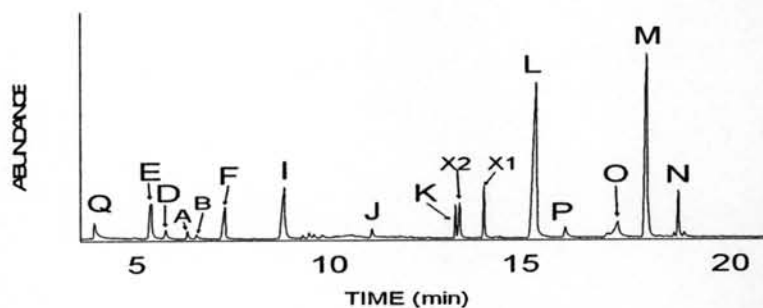

(b) HP-35MS column-intermediate polarity
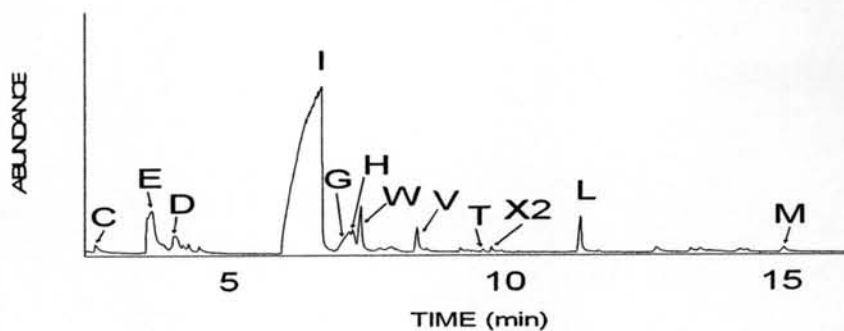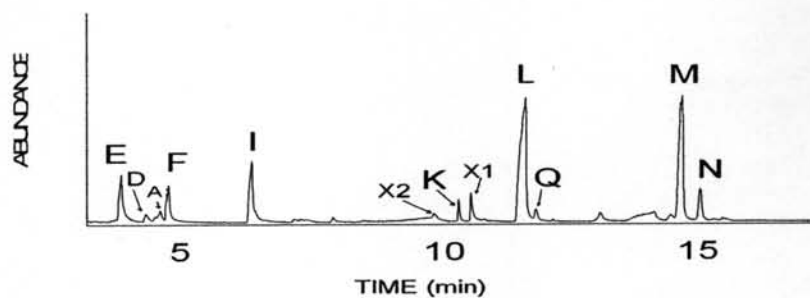

(c) HP-5MS column-non polarity

Figure 4.1 GC-MS chromatograms of degraded MEA solution in MEA-H_2O-O_2 system, 5.13 kmol/m^3 initial MEA concentration, 393 K, 250 kPa O_2 pressure, and 220 hour-reaction time: (a) HP-Innowax column-high polarity; (b) HP-35MS column-intermediate polarity; (c) HP-5MS column-non polarity.

(a) HP-Innowax column-high polarity

(b) HP-35MS column-intermediate polarity

(a) HP-5MS column-non polarity

Figure 4.2 GC-MS chromatograms of degraded MEA solution in MEA-H_2O-O_2-CO_2 system, 5.03 kmol/m^3 initial MEA concentration, 393 K, 250 kPa O_2 pressure, 0.51 mole CO_2/mole MEA, and 216 h degradation time: (a) HP-Innowax column-high polarity; (b) HP-35MS column-polarity; (c) HP-5MS column-non polarity.

Degradation Product			Standard Verification	Reference
Peak Labeled	Compound	% Confidence		
Products labeled in this work				
A	1-Methy Azetidine	58		
B	dl-Homoserine Lactone	86		
C	Imidazole	80	X	
D	N-(2-Hydroxyethyl) Acetamide	83	X	Hofmeyer et al., 1965*; Starzisar et al., 2003
E	N-methyl Formamide	40		Hofmeyer et al., 1965*
F	1,3-Dioxane	46		
G	2-ethyl1H-Imidazole	25		
H	5-hydrazinocarbonyl-1H-Imidazole	53		
I	Uracil	35		
J	N-(2-Hydroxyethyl) Succinimide	72		Starzisar et al., 2003
K	1-Amino-4-Methylpiperazine	64		
L	2-Pyrolidinone	38		
M	1-methyl-4-Imidazole-5-carboxylic acid	50		
N	N-methylene Ethanamine	25		
O	5-Aminovaleric Acid	59		
P	dl-Aspatic acid	72		
Q	2-((2-Aminoethyl))Amino) Ethanol	92		
R	Ethylamine	43		
T	4,5-Dimethyl Oxazole	64		
V	18-crown-6	47	X	
W	Ethyl urea	38		
X0	N-Glycylglycine	59		
X1	Dimethyl Hydrazone-2-Propanone	72		
X2	1-(2-Hydroxyethyl)-2-Imidazolidinone	86	X	Starzisar et al., 2003; Talzi et al., 2002
Additional products found in this work[#]				
	Ammonia	30		Hofmeyer et al., 1965; Chi et al., 2002; Rooney et al., 1998
	Formic acid	86	X	Blanc et al., 1982; Rooney et al., 1998
	Acetic acid	80	X	Blanc et al., 1982; Rooney et al., 1998
	Pyrimidine	86	X	
	Acetamide	70	X	
	2-methylamino-Ethanol	75	X	Bello and Idem, 2005
	Acetaldehyde	65		Rooney et al., 1998
	Ethanol	80		
Some of the previously reported products (not included in this work)				
	Oxalic acid			Hofmeyer et al., 1965; Chi et al., 2002; Rooney et al., 1998
	Glycolic acid			Hofmeyer et al., 1965; Chi et al., 2002; Rooney et al., 1998
	Bicine			Howard and Sargent, 2001

* Reported in terms of general amides
[#] These products did not appear in the chormatogram either due to incompletely coelution and low concentration except formic and acetic acids.

In addition, Table 4.2 also gives the percent identification confidence of the labeled peaks. Some were verified with standards as indicated earlier. The existence of imidazole and N-(2-hydroxyethyl) acetamide were confirmed. As indicated earlier, 18-crown-6 was also confirmed even though it had a low percent match, which was caused by incomplete separation from other products resulting in mixed mass fragmentation patterns. Using similar explanation, the remaining labeled peaks having low percent confidences, although not verified, are possibly to exist in the MEA oxidation systems. Certainly, for a future work, verification has to be carried out to confirm their existence.

For both degradation systems, the peaks were well separated with good shape and little tailing for the Innowax and HP-35MS columns. On the other hand, the non-polar column, HP-5MS, produced peaks with significant overlap, poor shape as well as some tailing. This implies that most of the MEA degradation products are polar, and thus, were able to match the high and intermediate polar stationary phases. The superior outcomes of the Innowax and HP-35MS respectively having high and intermediate polarities in terms of clean peak separation as compared to the non-polar HP-5MS could also result in easy relative quantitative analysis of these degradation products since peak areas are mostly used to determine their concentrations.

The degradation products distribution was evaluated as a function of degradation time for the 3 columns by constructing degradation time curves for the labeled peaks shown in Figure 4.1 and 4.2 for each column and degradation system. Figures 4.3(a)-(c) and 4.4(a)-(c) demonstrate the distribution of the degradation products against the degradation time corresponding to the peaks in Figure 4.1 and 4.2 for the MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 systems.
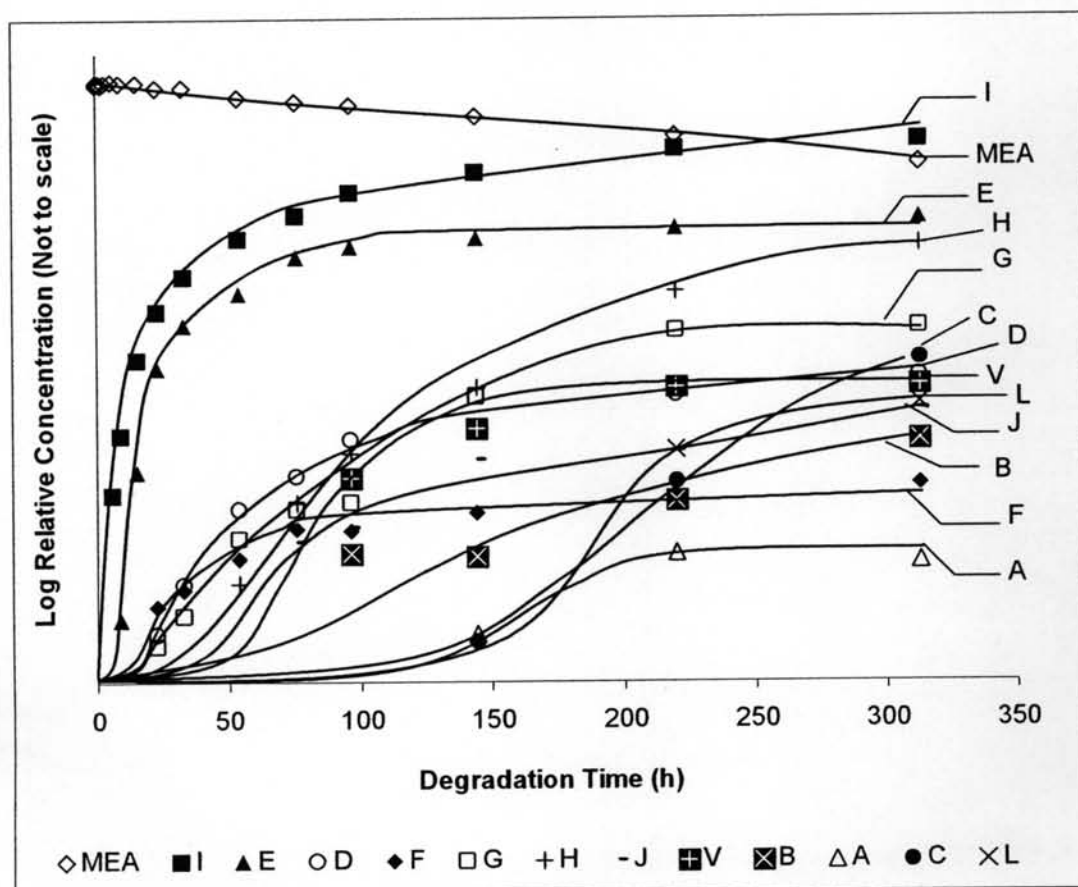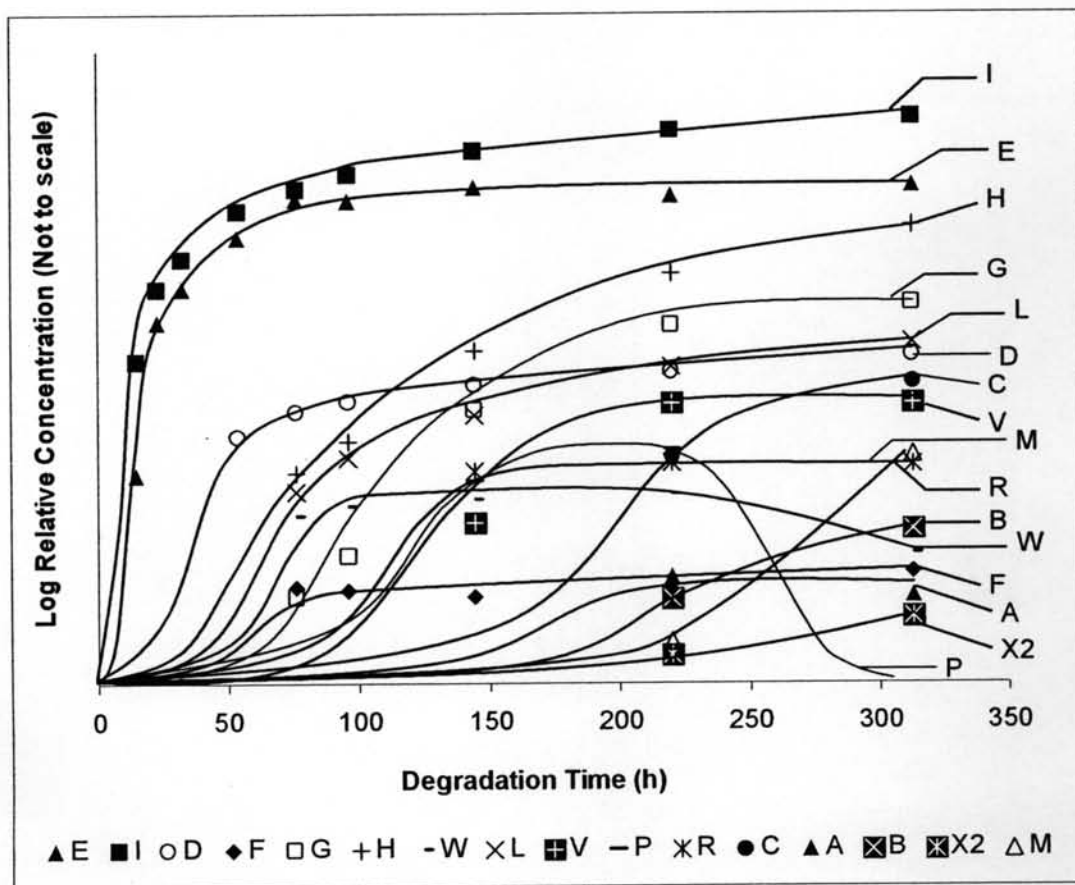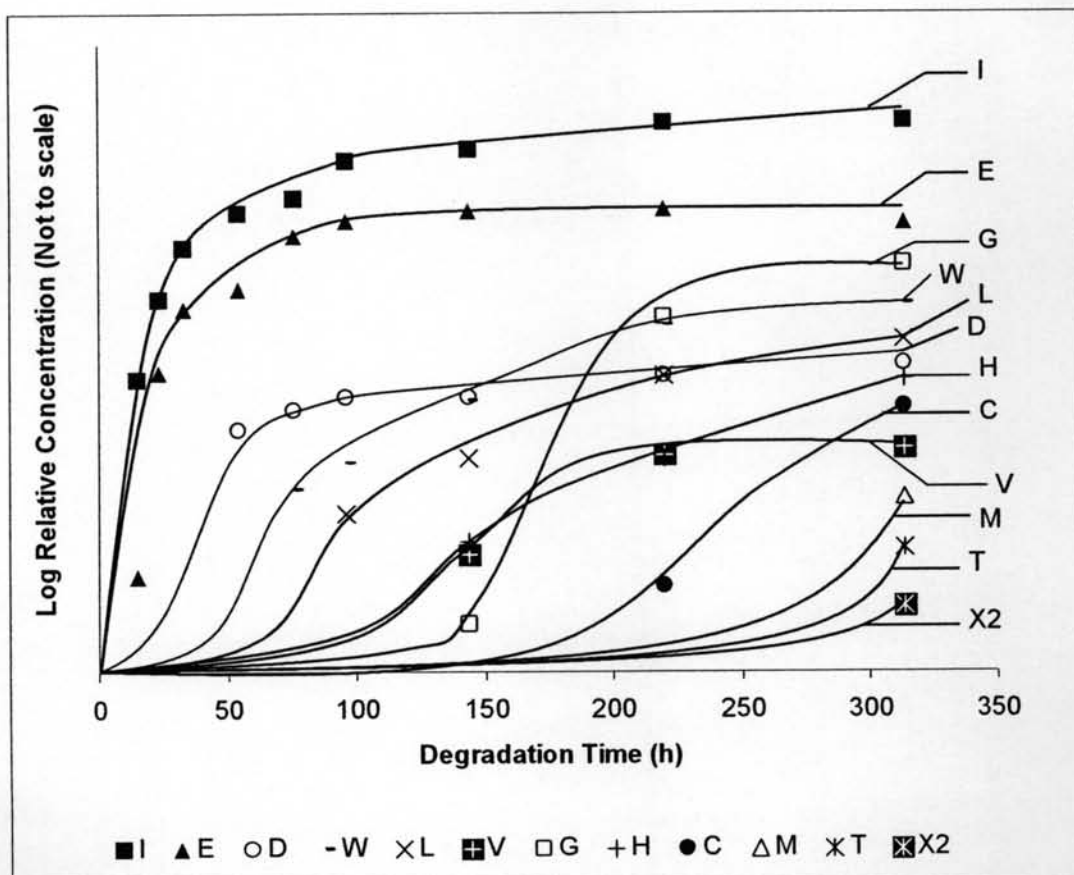
Figure 4.3 (a) GC-MS degradation product distribution of MEA-H_2O-O_2 system at 393 K: HP-Innowax column-high polarity.

Figure 4.3 (b) GC-MS degradation product distribution of MEA-H$_2$O-O$_2$ system at 393 K: HP-35MS column-intermediate polarity.

Figure 4.3 (c) GC-MS degradation product distribution of MEA-H$_2$O-O$_2$ system at 393 K: HP-5MS column-non polarity.
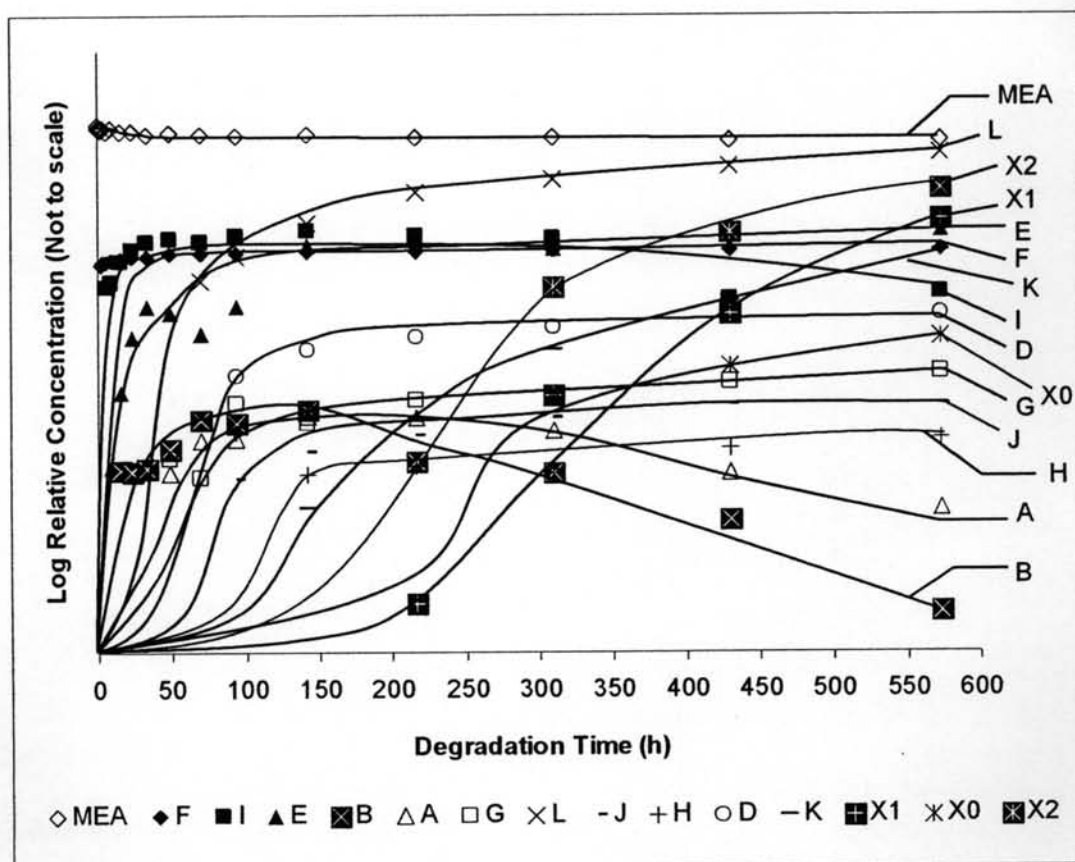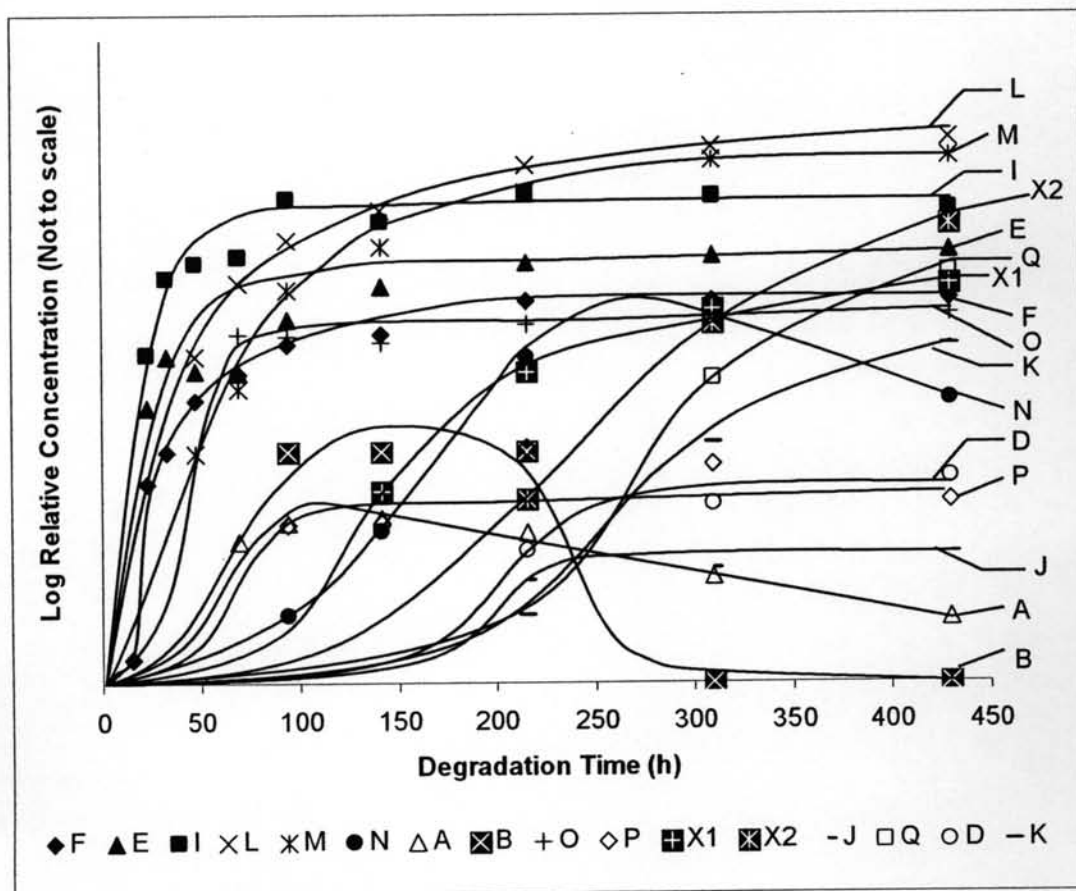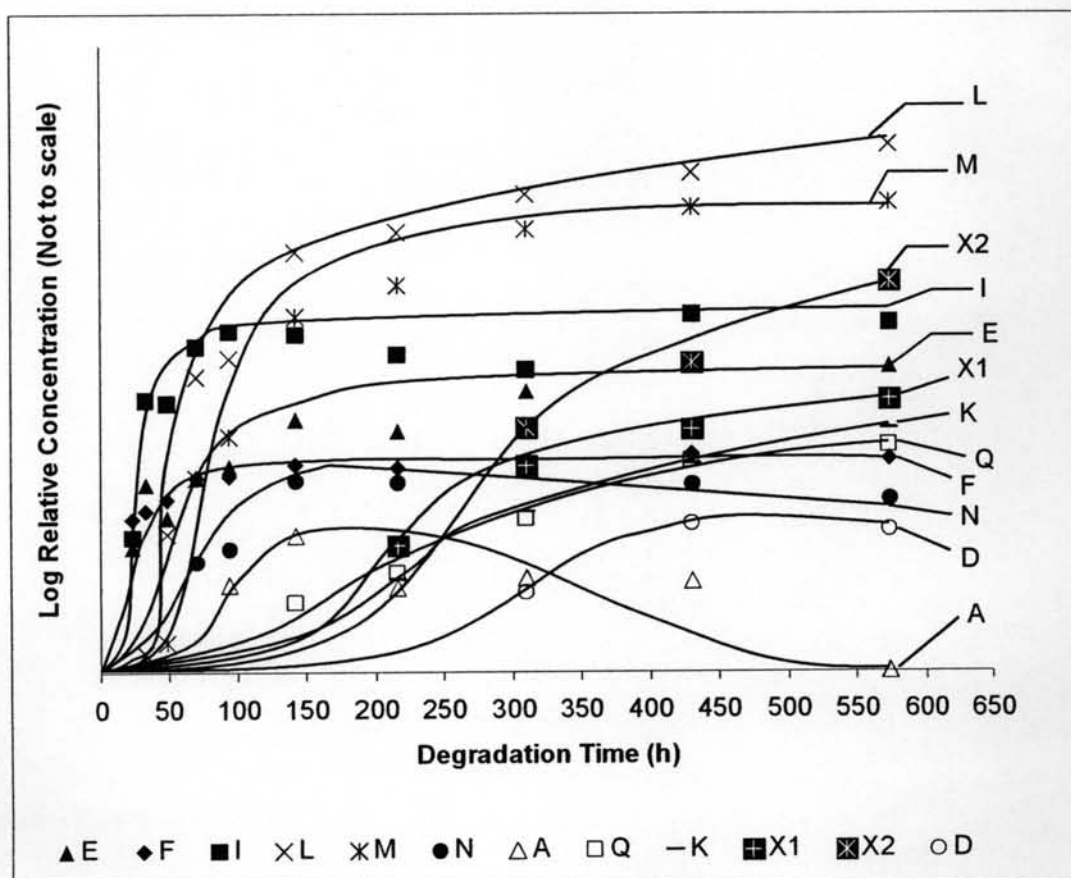
Figure 4.4 (a) GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-Innowax column-high polarity.

Figure 4.4 (b) GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-35MS column-intermediate polarity.

Figure 4.4 (c) GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-5MS column-non polarity.

Due to the wide differences in the extents of formation of these degradation products, the peak areas were converted to log values so that the products eluted from the same GC column could be plotted clearly in the same graph. As a result, the y-axis only represents arbitrary quantities on a log scale, and hence, only serves for qualitative evaluation for trends as a function of degradation time. Thus, only the trends of degradation product formation are intended for presentation in both Figure 4.3 and 4.4. This procedure was also later applied to the analysis of HPLC-RID and CE-DAD.

As illustrated in Figure 4.3(a) – (c) and 4.4(a) – (c), the number of detected degradation products are in the order of HP-35MS (16) > HP-Innowax (12) = HP-5MS (12) for the MEA-H_2O-O_2 system and HP-35MS (16) > HP-Innowax (14) > HP-5MS (12) for the MEA-H_2O-O_2-CO_2 system. The number of detected intermediates products also observed were in the order HP-35MS (2; i.e. peak W and P) >> HP-Innowax (none) = HP-5MS (none) for the MEA-H_2O-O_2 system and HP-35MS (3; i.e. peak A, B, and N) > HP-Innowax (2; i.e. peak A and B) = HP-5MS (2; i.e. peak A and N) for the MEA-H_2O-O_2-CO_2 system. In both degradation systems, HP-35MS clearly revealed the most information on degradation products as well as the intermediates. This is crucial for the development of degradation mechanisms. This is attributed to the intermediate polarity of its stationary phase being a compromise between the respective high and non-polar phases of HP-Innowax and HP-5MS. This means that if most of the products have widely different polarities, the optimum number of products that could be detected in a single column would be obtained by using the column with intermediate polarity (e.g. HP-35MS). Also, most of the products separated with HP-Innowax and HP-5MS could also be separated with HP-35MS. Despite the fact that HP-35MS was superior to the rest of the columns in terms of the total number of degradation products that can be clearly separated, one shortcoming was that the MEA peak separated with an abnormal shape, and was also too close to the water peak, thereby causing an overlap of the MEA peak with water peak (note that MEA peak is not shown in the Figure). As a result, quantitative measurement of MEA became difficult. The use of HP-5MS results in a similar problem as HP-35MS. In contrast,

HP-Innowax separated MEA from water with an acceptable peak shape, even though some tailing was still exhibited except in Figure 4.3(a) and 4.4(a) where a decline in quality was observed.

The foregoing results show that in order to quantitatively analyze the oxidative degradation of MEA in the presence or absence of CO_2, columns of high polarity and intermediate polarity (i.e. HP-Innowax and HP-35MS respectively) have to be used in combination for analysis if both the MEA concentration and the degradation products concentrations need to be followed. On the other hand, if only the degradation products are of interest, then the column with the intermediate polarity (HP-35MS) is adequate. A non-polar column (HP-5MS) is not suitable in all cases.

Attempts were made to characterize and compare the oxidative degradation of MEA in the presence and in the absence of CO_2 by using information extracted from the product distribution obtained from earlier results. Figure 4.3(b) and Figure 4.4(b) were used for this comparison due to the excellent performance of the HP-35MS column as described earlier. In Figure 4.3(b) for the O_2 alone environment, apart from 2 intermediate products (W and P) which disappeared, 6 other products (A, E, G, F, R, and V) seemed to stabilize as final products after reaching certain reaction times (about 300 h of degradation time). The concentrations of the remaining 8 products (B, C, D, H, I, L, M, and X2) continued to increase even after 300 h of degradation time. This indicates that the increasing concentrations of these 8 products may be attributed to the decline in the concentrations of W and P. On the other hand, the concentration of MEA still decreased even beyond the 300 h of degradation time showing that it was also responsible for the continued increase of the concentrations of B, C, D, H, I, L, M, and X2. Therefore, these products could possibly be formed by reactions of MEA-O_2, MEA-intermediates, O_2-intermediates and intermediates-intermediates. For the O_2-CO_2 system shown in Figure 4.4(b), a total of 8 components (D, E, F, I, J, M, O, and P) were sufficiently stable as final products whereas only 5 (K, L, Q, X1, and X2) of the compounds continued to increase even after 450 h of degradation time. MEA decreased up to a degradation time of 300 h beyond which it stabilized with degradation time. These results show

that for the O_2-CO_2 system, MEA was not responsible for the continued increase of the concentration of K, L, Q, X1, and X2, thus, their presence could arise only from O_2-intermediates and intermediates-intermediates reactions. The presence of CO_2 seemed to induce the formation of stable products and hinder further transformation, thus minimizing the chances of MEA to further react with those products, thereby reducing the extent of degradation. This could also be used to explain why a decrease in MEA concentration with degradation time was less steep in the O_2-CO_2 degradation system than that in the O_2 alone system as shown in Figures 4.3(a) and 4.4(a).

4.2.1.2 HPLC-RID Analysis

The initial trials were to evaluate the compatibility of nucleosil and shodex YK-421 columns with the two mobile phases used for this study (potassium dihydrogen phosphate, and a mixture of L-tartaric acid, 2, 6-pyridinecarboxylic acid and boric acid). Degraded MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 samples as well as fresh aqueous MEA solutions were chosen for the tests. Figure 4.5(a) and (b) illustrate the chromatograms for MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 respectively obtained by nucleosil column with potassium dihydrogen phosphate as the mobile phase. The figures show that the buffer produced an excellent separation of MEA and its degradation products for both systems. The total analysis time was about 35 min. Most products eluted approximately after 10 min of the MEA peak. A mixture of L-tartaric acid, 2, 6-pyridinecarboxylic acid, and boric acid was also used with the same column for which even with fresh solution, MEA was eluted with a poor peak shape and excessive tailing as shown in Figure 4.5(c). This indicates incompatibility of the column with the mobile phase. We therefore decided not to carry out any further runs of MEA degraded samples with this arrangement.
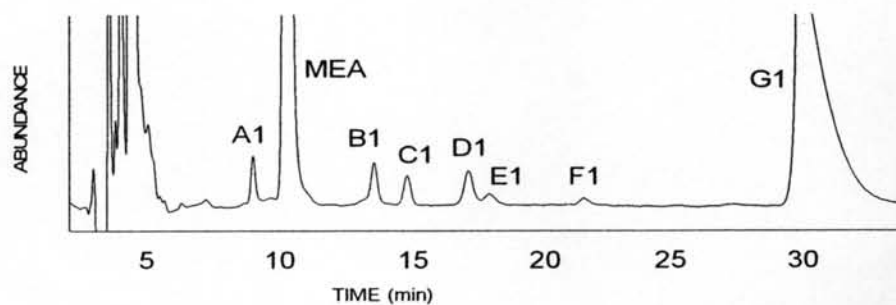
(a) mobile phase of 0.05 kmol/m³ potassium dihydrogen phosphate: MEA-H₂O-O₂ system
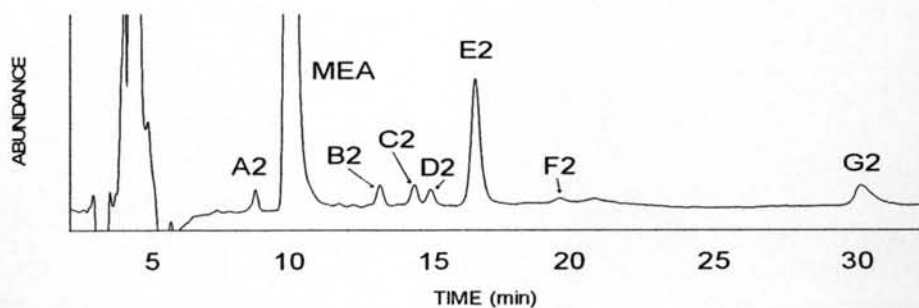
(b) mobile phase of 0.05 kmol/m³ potassium dihydrogen phosphate: MEA-H₂O-O₂-CO₂ system,
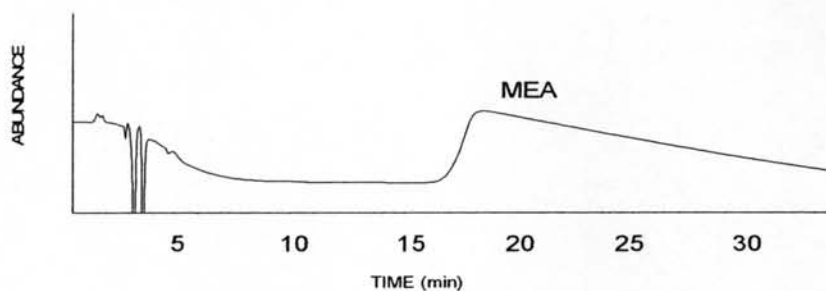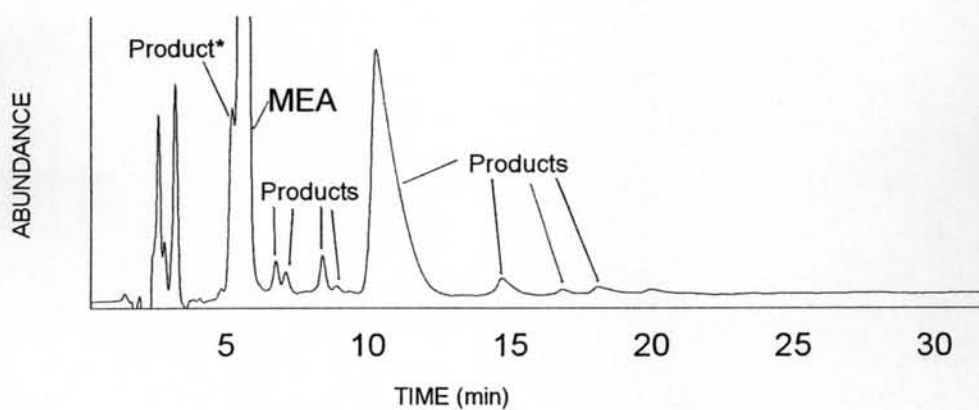

(c) mobile phase of mixture of 0.005 kmol/m³ L-tartaric acid, 0.001 kmol/m³ 2, 6-pyridinecarboxylic acid, and 0.024 kmol/m³ boric acid: fresh MEA solution.

Figure 4.5 HPLC-RID chromatograms using nucleosil column at 393 K.
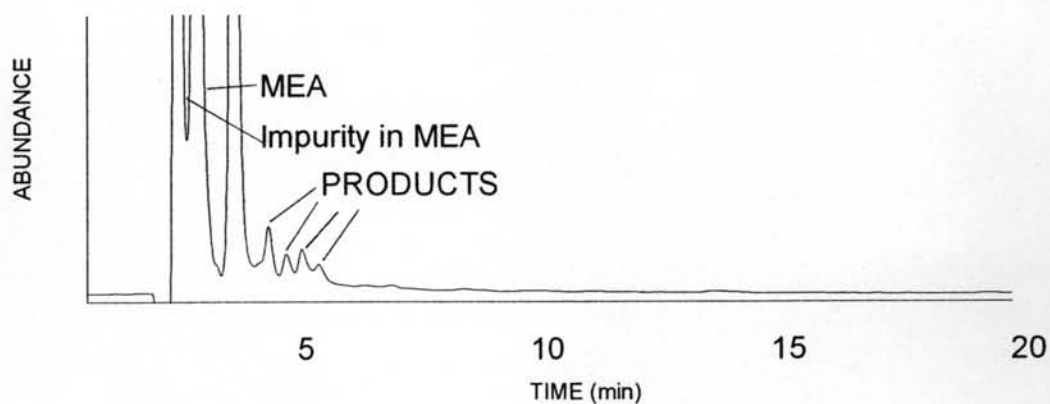
(a) mobile phase of 0.05 kmol/m^3 potassium dihydrogen phosphate

(b) mobile phase of mixture of 0.005 kmol/m^3 L-tartaric acid, 0.001 kmol/m^3 2, 6-pyridinecarboxylic acid, and 0.024 kmol/m^3 boric acid.

**Figure 4.6** HPLC-RID chromatograms of MEA-H$_2$O-O$_2$ system at 393 K using shodex YK-421.

Figure 4.6(a) represents the chromatogram for the MEA-H_2O-O_2 system produced by shodex YK-421 using potassium dihydrogen phosphate as the mobile phase. Although, the phosphate buffer could separate MEA from most of the products within a short time, the overlap of MEA with its impurity caused an error in MEA quantification. The separation of the products eluting after MEA was also incomplete. A mixture of L-tartaric acid, 2, 6-pyridinecarboxylic acid, and boric acid was also run with this same column. This is shown in Figure 4.6(b) which shows that the separation of degradation products was improved, but, still it suffered from a minor overlap of a couple of compounds. Co-elution of MEA and one of the degradation products labeled as product* was also present.

Attempts were also made to improve separation in shodex YK-421 column, by reducing the flow rates of both mobile phases from 1 to 0.5 ml/min. It was observed that a decrease in the flow rate seemed to shift all components almost equally to the right without improving separation efficiency. Analysis time also increased, especially for the tri-component mobile phase in which it was almost as long as those run by nucleosil column with phosphate buffer. Although, the length of column might affect separation performance, an increase of column length for YK-421 might not be economical since the approximate cost of shodex YK-421 of 125 mm length is already 4 times than that of nucleosil column. As a result, nucleosil column with a phosphate mobile phase was selected for further tests on the distribution of degradation products with degradation time.

For the accurate analysis of the distribution of degradation product, evaluation was made only with the well-separated components labeled in Figure 4.7(a) and (b). These figures demonstrate the distribution of degradation products versus degradation times in MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 systems, respectively. The plots correspond to peaks shown in Figure 4.5(a) and (b).
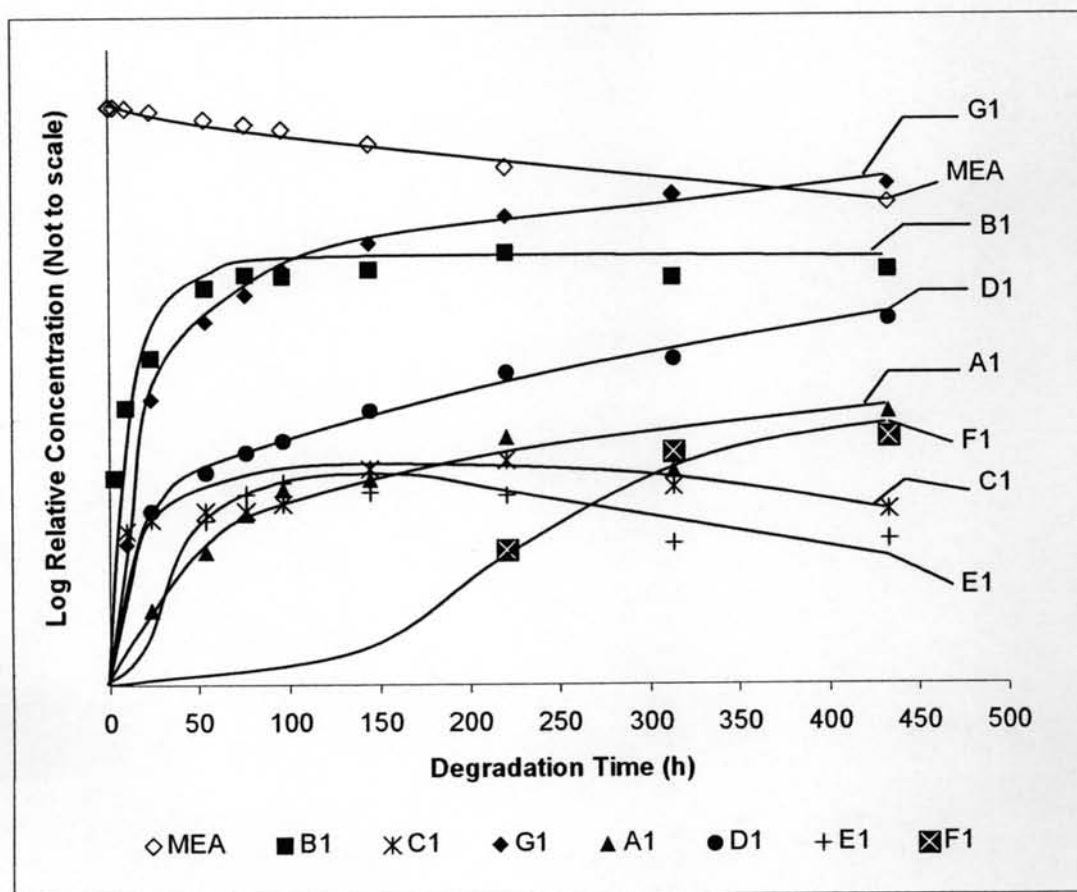
Figure 4.7 (a) HPLC-RID degradation product distribution at 393 K using
nucleosil column and phosphate mobile phase: MEA-H_2O-O_2.
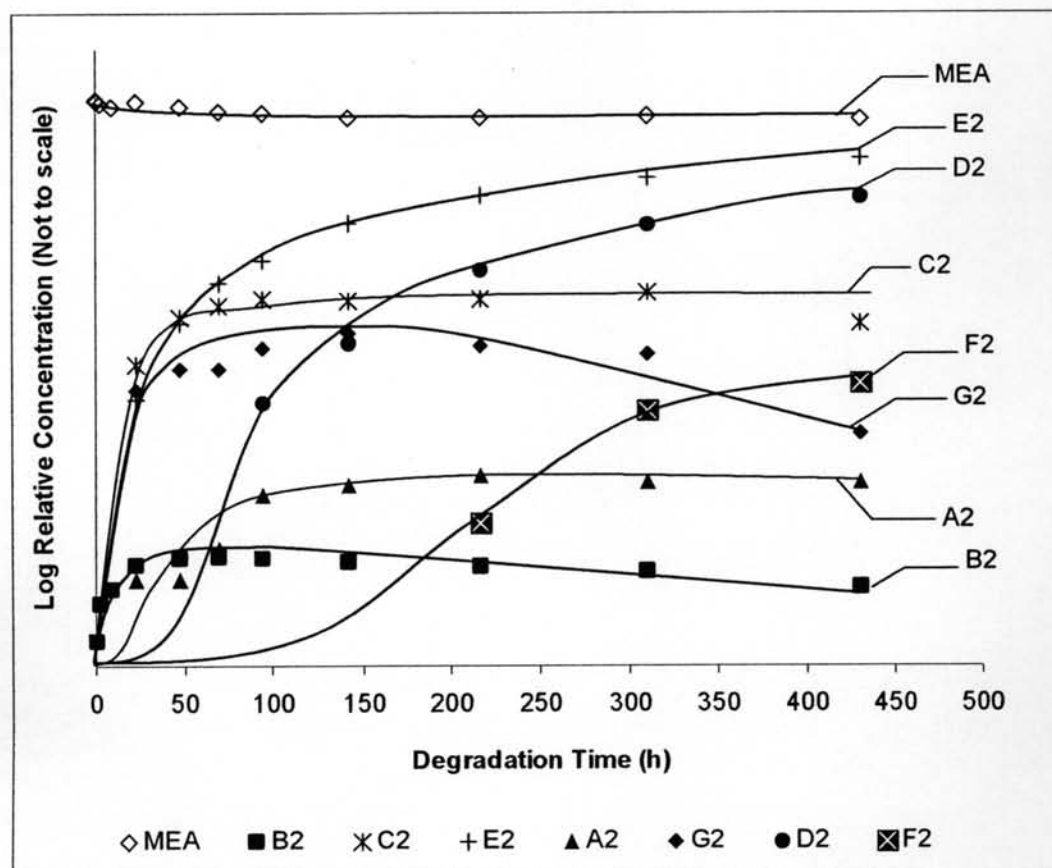
Figure 4.7 (b) HPLC-RID degradation product distribution at 393 K using nucleosil column and phosphate mobile phase: MEA-H_2O-O_2-CO_2.

In Figure 4.7(a), a couple of intermediate products labeled as C1 and E1were clearly observed as their concentration increased to maxima before declining then after. Two intermediates of B2 and G2 were also observed to reach maxima and then declined for the O_2-CO_2 system as shown in Figure 4.7(b). Also, only product B1 in the O_2 alone environment, increased to a maximum and tended to stabilize. On the other hand, in the O_2-CO_2 reaction system, only 2 of the products (marked as A2 and C2) tended to stabilize. The remaining detected products for both systems are those in which their concentrations still increased even after 450 h. In the O_2 system, MEA was still decreasing showing that MEA and the intermediates contributed to the increasing concentration of products with time. On the other hand, in the O_2-CO_2 system, MEA stabilized showing that it is the intermediates that contributed to the increasing concentration of some of products with degradation time. These outcomes were consistent with those obtained by GC-MS analysis in which CO_2 was observed to influence the formation of stable products. This also suggests the validity of both techniques for degradation analysis of MEA and O_2 in the presence or absence of CO_2.

Although this was not a primary objective, attempts were made to identify the products using the spiking technique. Only 3 standards (imidazole, 2-methylamino ethanol, and 18-crown-6) were used. A typical example of product identification for the MEA-H_2O-O_2 system using standard imidazole is shown in Figure 4.8(a). Chromatograms of pure standard imidazole, 220 h degraded MEA solution, and 220 h degraded MEA solution spiked with standard imidazole have been overlayed for ease of comparison. Not only was the standard imidazole eluted about the same location of peak F1, but the peak also increased in size in the spiked sample. Therefore, peak F1 could be identified as imidazole. Figure 4.8(b) shows a similar result for the MEA-H_2O-O_2-CO_2 system in which peak F2 was also identified as imidazole. This outcome is consistent with the GC-MS analysis in which imidazole was also detected and identified. Peak C1 and C2 were matched with standard 2-methylamino ethanol using the same approach. 18-crown-6 was not detected by the ion-exchange technique due to inability in acquiring a charge.

Verification by mass spectrometric technique is suggested to confirm the existence of these degradation products.
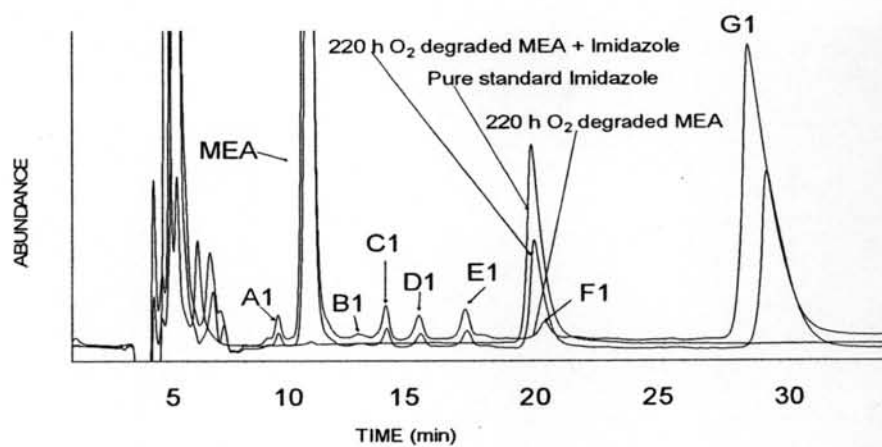

(a) MEA-H_2O-O_2
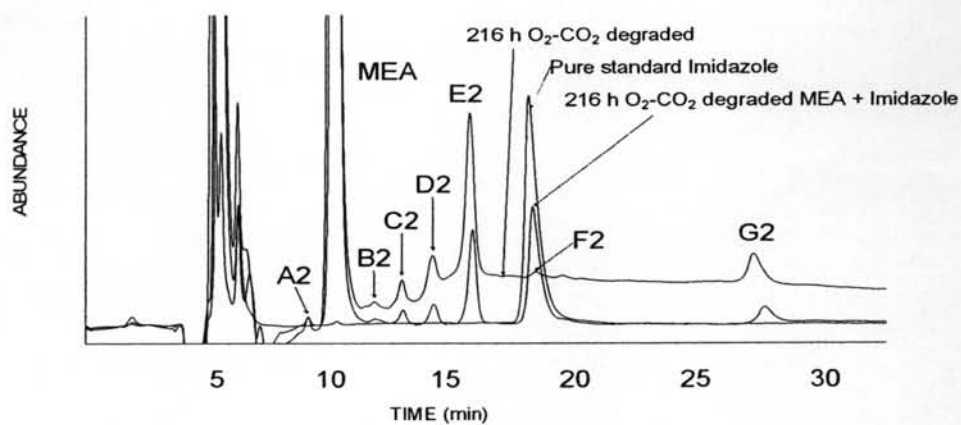
(b) MEA-H_2O-O_2-CO_2

Figure 4.8 Identification using standard imidazole.

4.2.1.3 CE-DAD Analysis

Three types of electrolytes were selected mainly to target the separation of MEA, basic degradation products and acidic degradation products. Figure 4.9 shows the chromatogram of fresh MEA solution using a combination of imidazole, 18-crown-6, and HIBA as the electrolyte. Although, a well-separated, symmetric MEA peak could be obtained, sample preparation was tedious and time consuming, and thus, made the method unattractive from our perspective. MEA samples had to be diluted up to 4,000 times as compared to 5 and 40 times by GC and HPLC techniques, respectively. Dilution serves to maintain MEA linearity and also prevents column overload. The dilution causes inconvenience if used in CO_2 capture process in which MEA concentration can be as high as 5 $kmol/m^3$. Although, the technique was quite simple, high dilution imposes an analytical difficulty that can possibly cause quantitative error.
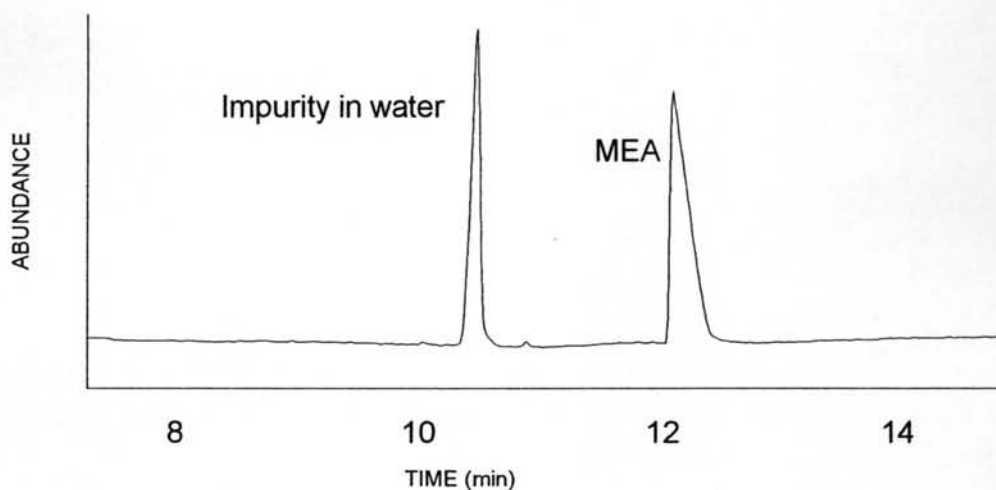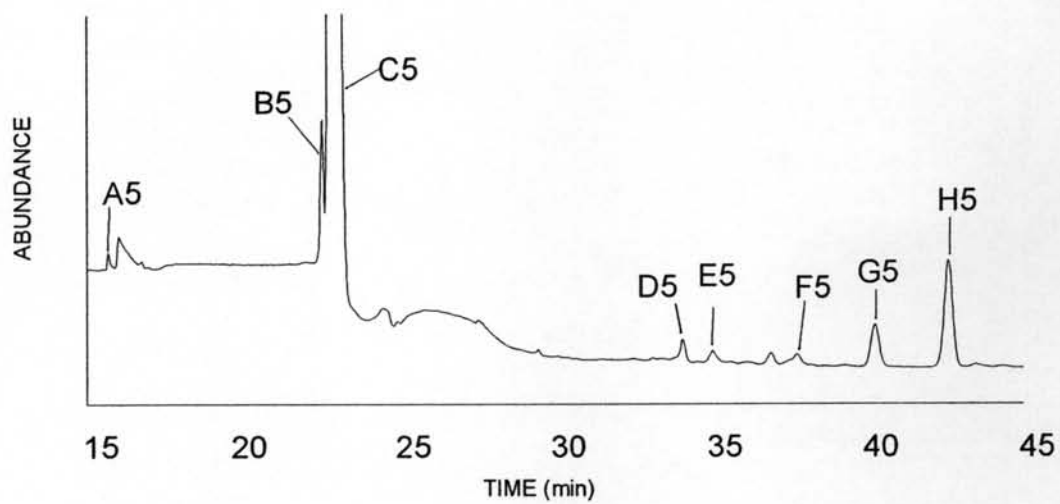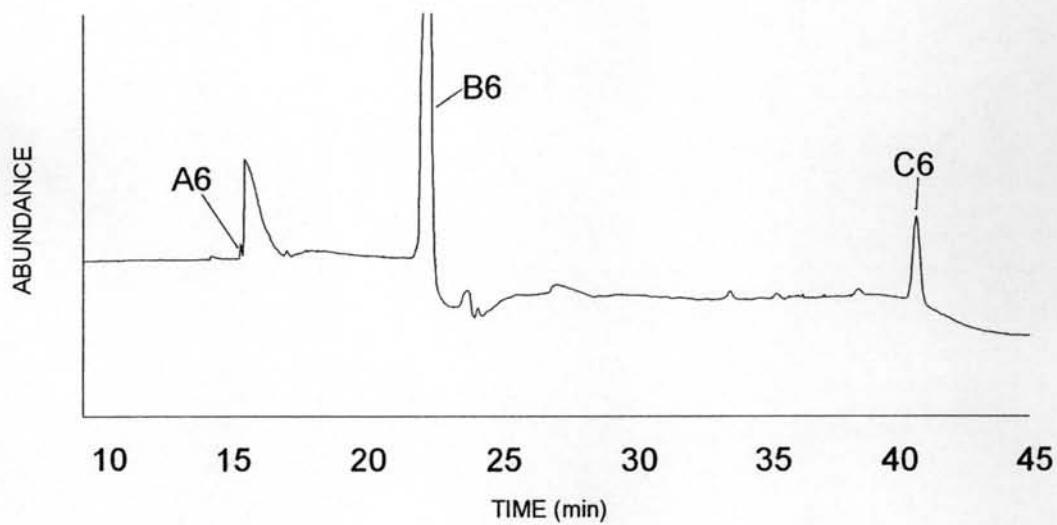

Figure 4.9 CE chromatogram of fresh MEA solution using combination of imidazole, 18-crown-6, and HIBA electrolyte.

Despite the incompatibility in MEA quantification, CE was capable of detecting some degradation products using KH_2PO_4 and $Na_2B_4O_7.10H_2O$ electrolytes. Phosphate solution was employed for analysis of basic products capable of being protonated under the pH of 2.6. Figure 4.10(a) and (b) illustrate typical chromatograms of degraded MEA solution at approximately 200 h of degradation time in the O_2 and O_2-CO_2 systems. The number of detected products in the O_2 alone system was approximately twice as many as that in the O_2-CO_2 system confirming the higher severity of degradation in the former system. On the other hand, the borate electrolyte was used for analysis of acidic compounds in which ionization could take place under the influence of the electrolyte alkalinity. Figure 4.11(a) and (b) show chromatograms of degraded MEA samples obtained at approximately 400 h of degradation time in the absence and presence of CO_2. MEA-H_2O-O_2 again generated more acidic products than those of the system with CO_2.

Trends from Figure 4.12(a) and (b) were matched with corresponding peaks in Figure 4.10(a) and (b) to check the product distribution. Approximately, the concentrations of 40% of the total basic products detected in the MEA-H_2O-O_2-CO_2 system continued to increase as a function of time up to 150 h of degradation time, but leveled off after then. In the case of the MEA-H_2O-O_2 system, the concentrations of only 23% behaved in a similar way. A similar trend was also exhibited in the case of acidic products shown in Figure 4.13(a) and (b), plotted corresponding to labeled peaks in Figure 4.11(a) and (b). Again, these results were consistent with those of the GC and HPLC techniques in which the presence of CO_2 resulted in a higher number of stable compounds thus, limiting further MEA degradation.
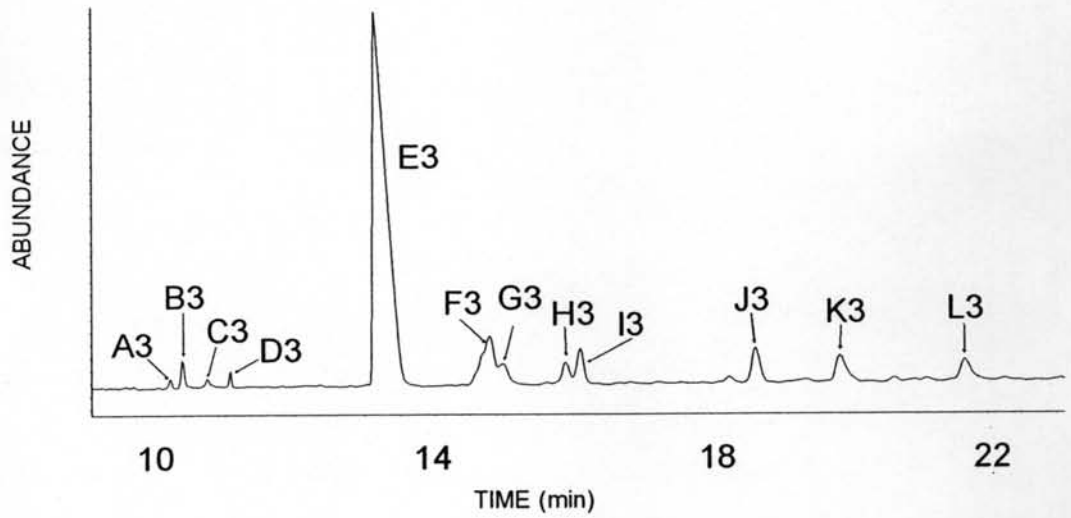
(a) MEA-H_2O-O_2
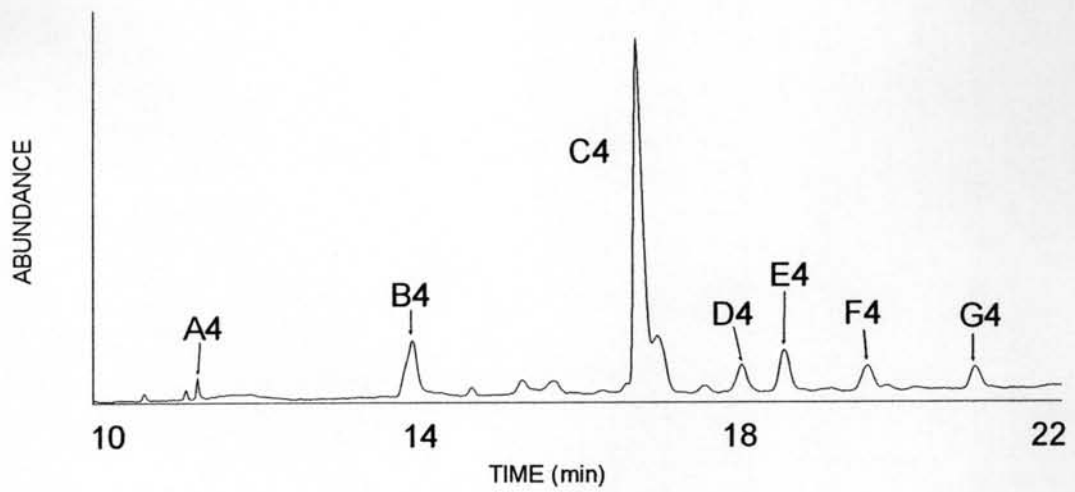
(b) MEA-H_2O-O_2-CO_2

Figure 4.10 Typical CE chromatograms for analysis of basic products of degraded MEA solution at approximately 200 h.

(a) MEA-H$_2$O-O$_2$

(b) MEA-H$_2$O-O$_2$-CO$_2$

Figure 4.11 Typical CE chromatograms for analysis of acidic products of degraded MEA solution at approximately 400 h.
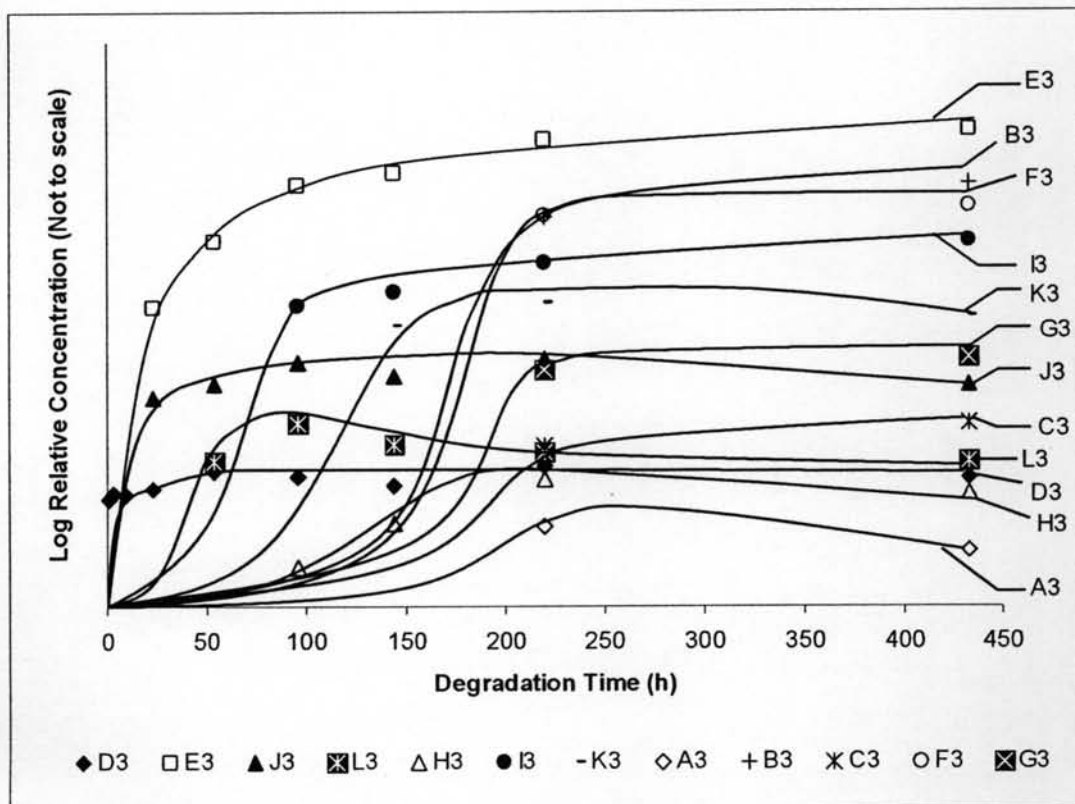
Figure 4.12(a) CE-DAD basic degradation product distribution: MEA-H$_2$O-O$_2$.
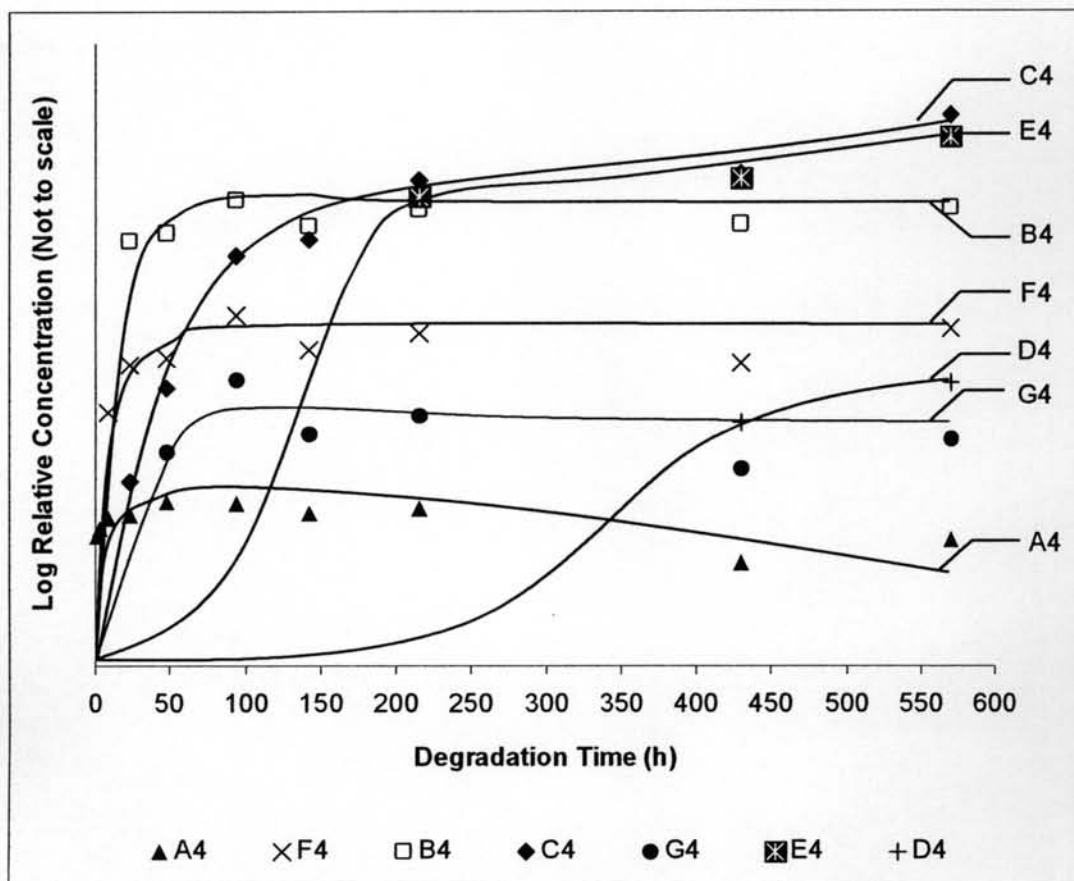
Figure 4.12(b) CE-DAD basic degradation product distribution:MEA-H_2O-O_2-CO_2.
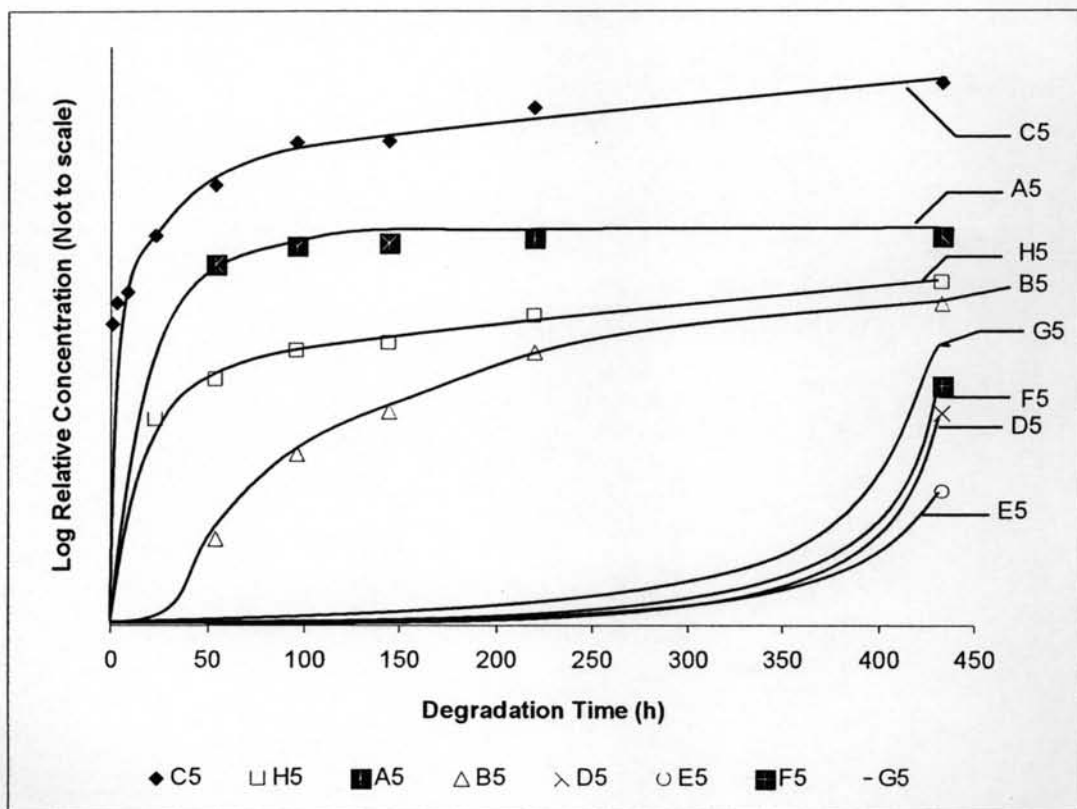
Figure 4.13(a) CE-DAD acidic degradation product distribution: MEA-H_2O-O_2.
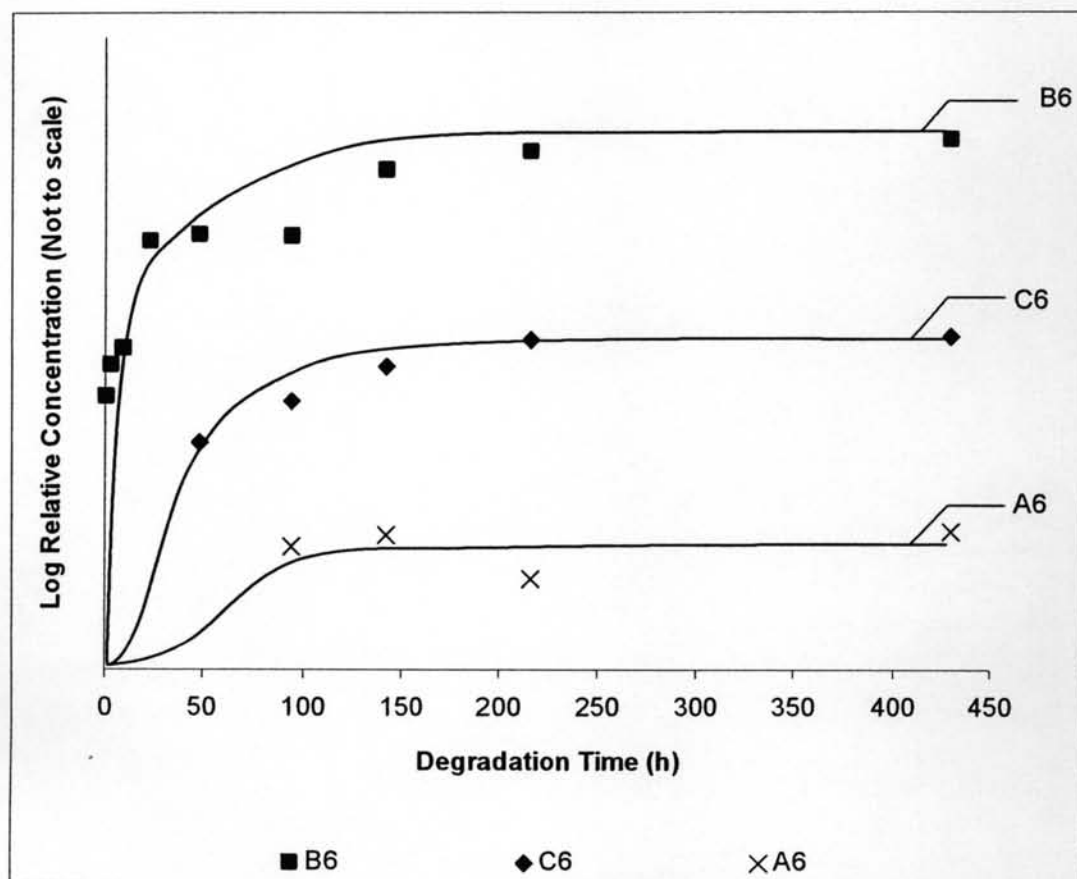
Figure 4.13(b) CE-DAD acidic degradation product distribution: MEA-H_2O-O_2-
CO_2.

Identification of products was done similarly to the case for the HPLC-RID analysis. Imidazole could be identified for the MEA-H_2O-O_2 system labeled as peak B3 in Figure 4.10(a). MEA-H_2O-O_2-CO_2 also produced imidazole but its concentration was too small to be recognized by the technique. Therefore it was not labeled in Figure 4.10(b). However, its peak could be observed to be located as the second peak from the left of peak A4.

4.2.2 MEA Degradation at 328 K

The degradation of the MEA-H_2O-O_2 system was conducted at the absorption temperature of 328 K, and was also evaluated by GC-MS and HPLC-RID. In terms of the degradation products, a product labeled " I " in a previous GC-MS analysis at 393 K was only detected after 500 h of the degradation time in the GC-MS technique. On the other hand, no degradation product was observed in HPLC-RID technique. The quality of the MEA peak as a function of the degradation time was also determined and plotted as shown in Figure 4.14. To evaluate the HPLC-RID and GC-MS techniques for data consistency, MEA measurement using the GC-MS technique with HP-Innowax column was also added in the same figure as that for HPLC-RID. No significant change of MEA concentration was observed by both techniques. These confirm a much less degradation in the absorber region of the CO_2 capture plant. Thus, temperature plays a significant role and can be used to determine whether or not O_2 induced degradation will be significant in the absorber.
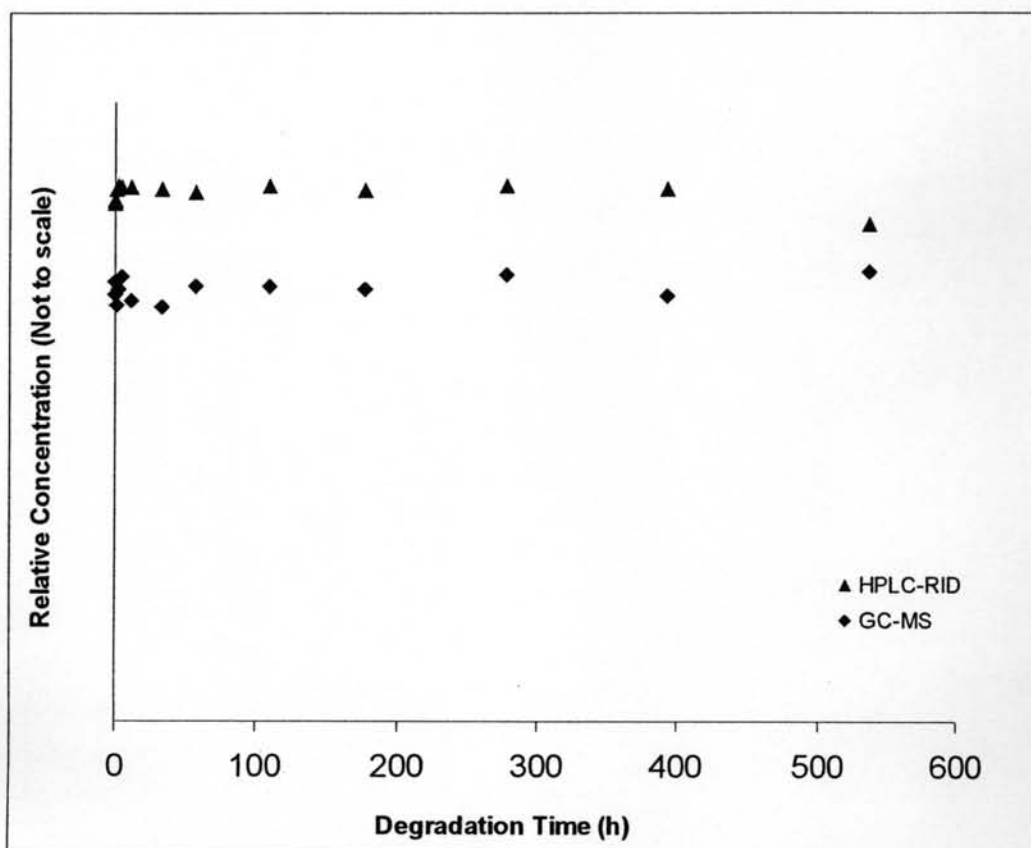
Figure 4.14 MEA concentration as a function of degradation time at 328 K using GC-MS and HPLC-RID techniques.

4.3 Comparison of GC-MS, HPLC-RID and CE-DAD

The best condition for each technique was picked for comparison. Table 4.3 presents a summary of this comparison for the 3 techniques for analysis of MEA oxidative degradation. GC-MS presented the most sensitive technique by detecting the most number of products (16 components) for both systems studied. Perhaps, this can be attributed to the fact that GC-MS required no component manipulation during the analysis. Vaporization is the major characteristic needed of the sample. Thus, the components in the sample are likely to enter the analytical unit as originally present in the liquid samples. Unlike the GC-MS technique, in the HPLC and CE, components must be converted into detectable forms either by protonation or ionization under a certain pH prior to the analysis. Therefore, compounds to be detected by these techniques were limited to those favoring protonation or ionization. HPLC-RID however, was capable of capturing the most degradation intermediates calculated to be 29% for both degradation systems whereas CE-DAD for basic intermediate products and GC-MS for all intermediates performed equally. Acidic products analyzed by CE-DAD did not show any reaction intermediate for both degradation systems. HPLC-RID was the only technique capable of simultaneous detection of MEA and MEA degradation products within a single analysis. GC-MS and CE-DAD needed additional column and electrolyte, respectively, for MEA detection. The analysis time for component separation was in the order of GC-MS < CE-DAD for basic products < HPLC-RID < CE-DAD for acidic products.

Table 4.3 is rotated in the right margin:

Table 4.3 Comparative details of GC-MS, HPLC-RID, and CE-DAD techniques for analysis of MEA oxidative degradation

Compared Parameter	Analytical Technique							
	GC-MS		HPLC-RID		CE-DAD			
Column	HP-35MS		Nucleosil 100-5 SA		Standard Bare Fused-Silica			
Product Type	Nuetral		Protonated		Basic (Protonated)		Acidic (Ionized)	
Mobile Phase	Helium		KH_2PO_4 pH 2.6		KH_2PO_4 pH 2.6		$Na_2B_4O_7.10H_2O$	
Degradation System	MEA-H₂O-O₂	MEA-H₂O-O₂-CO₂	MEA-H₂O-O₂	MEA-H₂O-O₂-CO₂	MEA-H₂O-O₂	MEA-H₂O-O₂-CO₂	MEA-H₂O-O₂	MEA-H₂O-O₂-CO₂
Degradation Product								
* Total product detected	16	16	7	7	12	7	8	3
* % Intermediate revealed	13%	19%	29%	29%	17%	14%	0	0
MEA Detection[1]	No	No	Yes	Yes	No	No	No	No
Sample Preparation								
* Dilution level	1 in 5	1 in 5	1 in 40	1 in 40	1 in 500	1 in 500	1 in 500	1 in 500
* Filtration	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Mobile Phase Preparation	None		Yes		Yes		Yes	
Analysis Time	20 min		35 min		25 min		45 min	
Column Cost[2]	~ $700		~ $360		~ $60		~ $60	

[1] MEA detection by GC-MS could be done on HP-Innowax. MEA could also be detected by CE-DAD with mobile phase of imidazole, 18-crown-6, and HIBA.

[2] Fund is in Canadian dollar.

In terms of sample and mobile phase preparation, GC-MS was the least tedious technique requiring the lowest dilution without filtration. Preparation of mobile phase was not needed. On the other hand, CE required the highest dilution which was as high as 4,000 times for MEA analysis and 500 times for analysis of basic and acidic degradation products, as compared to only 40 times for HPLC-RID. Prior to the analysis, both the HPLC and CE analytical techniques needed sample filtration and multi-step mobile phase preparation such as pH adjustment and degassing. A few advantages of CE-DAD technique could be drawn. The column cost of CE-DAD was approximately \$60 in which the GC and HPLC columns were about 12 and 6 times more expensive. If compared to HPLC-RID technique, CE-DAD consumed much less sample and mobile phase, this could lead to a higher cost saving.

Even though, each technique showed advantages and disadvantages over one another, a common ground still existed. For MEA oxidative degradation in the absence or presence of CO_2 characterized by GC-MS, HPLC-RID and CE-DAD, similar trends in regards to product distribution, decline of MEA and role-played by CO_2 were observed. This consistency indicates the validity of the 3 techniques showing their capabilities as analytical tools to characterize MEA oxidative degradation. In addition, each of the techniques could be used to confirm the outcomes from the other techniques.

4.4 Conclusions

1. A GC column of intermediate polarity of HP-35MS performed the best for analysis of degradation products of MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 degradation systems in terms of component separation, number of total products and intermediates detected. This column was found to be adequate if analysis of only the degradation products was required. A high polarity column (HP-Innowax) had to be used in combination if information on MEA decline was needed. The non-polar HP-5MS column was not suitable in all cases.

2.   The HPLC-RID technique using a combination of the cation exchanger Nucleosil 100-5 SA column and 0.05 $kmol/m^3$ KH_2PO_4 mobile phase was superior to the rest of the systems studied. MEA and products could be simultaneously analyzed in this single column in a single run.

3.   Due to high concentration of MEA used in CO_2 capture process, CE-DAD using an electrolyte consisting of a mixture of imidazole, 18-crown-6 and HIBA which required heavy dilution was not suitable for MEA analysis. However, some basic and acidic products could be analyzed through the use of KH_2PO_4 and $Na_2B_4O_7.10H_2O$ electrolytes, respectively.

4.   In addition to GC-MS, the spiking technique using standards could be used as a method for the identification of the degradation products separated by HPLC-RID and CE-DAD. Imidazole was detected and identified by all techniques, thus confirming its existence.

5.   GC-MS was found to be the most sensitive technique detecting the most products within the least time. In addition, it required the least amount of work in terms of sample preparation.

6.   The presence of CO_2 was found to induce more stable products. Therefore, further degradation by reaction with MEA was reduced. Thus, rate of MEA degradation was seen to be lower than that of the O_2 alone system.

7.   Consistency was obtained in all techniques in terms of product distribution, decline of MEA and role-played by CO_2 thus indicating their validity. Confirmation of the results could be accomplished through the use of a combination of GC-MS, HPLC-RID and CE-DAD.