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WASTE MINIMIZATION STRATEGY

FLEXIBLE POLYURETHANE FOAM MANUFACTURE

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INTRODUCTION

Since the discovery of the diisocyanate polyaddition process by German chemist Otto Bayer in 1937, polyurethane chemistry has matured into a sophisticated industry with applications in numerous industries (Table 1). By 1985, world manufacturing capacity for polyurethane foams had reached nearly five million metric tons located primarily in North America and Western Europe.[18]

FURNITURE	38%
TRANSPORTATION	29%
BEDDING	15%
CARPET UNDERLAY	12%
PACKAGING	2%
TEXTILES	2%
OTHER	2%

Table 1 - Flexible Polyurethane Foam Consumer Products

WATER	30%
WATER/CCl_3F	42%
WATER/CH_2Cl_2	28%

Table 2 - Use Of Blowing Agents In Soft Polyurethane Foam

In the 1960's to increase penetration into furniture component and bedding markets (displacement of latexes), polyurethane foam density was reduced (to increase softness) by the addition of auxiliary blowing agents to the formulations.3 The primary blowing process involves the reaction of an isocyanate with water to produce gaseous carbon dioxide which expands the foam network. The auxiliary foaming process involves no chemical reactions, but is merely a change of state of the auxiliary blowing agent (methylene chloride or chlorofluorocarbon). Volatilization of the auxiliary blowing agent from liquid to gas coincides with the primary evolution of CO_2 and urethane polymerization to provide a significant increase in the number and size of foam cells. The increase in cell size and number produces the low density desired for specific foam end uses. Furthermore, the heat of evaporation of the auxiliary blowing agent contributes to decreasing the temperature of the foaming polyurethane mass adding to plant safety from flash point accidents. Historically, chlorofluorocarbons (primarily CFC-11) were utilized to decrease foam density due to the low boiling points, thermal conductivity, relative insolubility, and chemical stability. In the past two decades, CFC's have been linked to global warming and depletion of stratospheric ozone; consequently, many foam manufacturers have substituted methylene chloride as the auxiliary blowing agent (Table 2). In addition to meeting market specifications for cushion softness and indentation, low density foams significantly impact profit margins by decreasing the amount of toluene diisocyanate (the most commonly used isocyanate) required in formulations and the amount of chemicals per cubic foot of product.

Global restrictions on the manufacture and emission of chlorofluorocarbons are rapidly propagating. As these regulations are enacted, the supply of current CFCs will tighten and the prices of CFCs are expected to dramatically increase. Additionally, air toxics legislation within various states may severely limit emissions of methylene chloride, a suspected carcinogen. Options available to foam manufacturers which limit air emissions while maintaining worker safety, product quality and profitability include:

- Eliminate the use of auxiliary blowing agents and only produce water (CO_2) blown foams. Several questions arise concerning the capability to make a wide range of low density foams. This limit directly affects corporate marketing potentials. Additionally, the negative cost impacts (higher raw material costs) to small and medium manufacturers would be significant.

- Substitute materials (such as HCFCs which supposedly have lower ozone-depletion and global warming potentials) as auxiliary blowing agents.[5,6,9] Near and long-term production capabilities of these materials along with consequent foam properties are mostly unknown. In addition, manufacturing plants will probably be under pressure to minimize any organic emissions.

- Utilize new chemical systems to eliminate auxiliary blowing agents. These new systems require modifications to existing formulations and even some of the recent innovations that have been commercially introduced do not appear to be viable for low density foams.

- Invest in latest-generation enclosed machinery for batch foam processing.[21] Although this option directly addresses air emissions, return on capital and production capabilities are very questionable. Control of product quality and consistency is generally more difficult in batch processes.

- Recover/recycle auxiliary blowing agents by modifying the current continuous process. Benefits include the maintenance of current chemical formulations, product qualities, worker safety, productivity, and profit margins. Recycling of auxiliary blowing agents would also offer a potential cost savings by reducing material costs.

The recovery of an auxiliary blowing agent is a complex issue coupled directly with another manufacturing requirement, the maintenance of safe plant working conditions in the presence of small quantities of isocyanates. Worker safety is presently maintained with adequate air flow to keep ambient isocyanate concentrations at acceptable limits (the maximum allowable indoor air concentration of TDI is 0.02 ppm). This air flow also lowers the auxiliary blowing agent concentrations to a range where recovery technologies are not economically feasible. The objectives of this research were to:

- quantify the dynamics of blowing agent loss in laboratory prepared foams using representative formulations,
- validate laboratory experimentation with analogous plant data, and
- examine innovative means to maintain safe worker conditions while simultaneously recovering the auxiliary blowing agent and minimizing air emissions.

Basic information on organic volatilization and concentration/recovery/recycle of fugitive emissions is transferable to other chemical process industries.

POLYURETHANE CHEMISTRY

The chemistry of polyurethane foam formation can be reduced to a few simple reactions. Concurrent competing processes are listed in Table 3. These reactions which all involve toluene diisocyanate (TDI) are exothermic and reversible. The fastest and most exothermic reactions involve reaction of TDI with primary hydroxyl groups (water and polyol). The reaction of TDI and water becomes irreversible as soon as the CO_2 escapes from the foam cells; all available water is consumed. A typical sequence of events in the foaming process in the manufacture of polyurethane foam is given in Table 4. The polyurethane foam process is carried out in the presence of a catalyst system to balance the isocyanate-water

1. foaming (blowing) reaction between water and TDI to produce an amine and CO_2 gas (only one functional group shown).

$$\mathrm{R\text{-}N=C=O} + \mathrm{H_2O} \rightarrow \mathrm{RNH_2} + \mathrm{CO_2}$$

immediately followed by the formation of a urea:

$$\mathrm{R\text{-}N=C=O} + \mathrm{R''NH_2} \rightarrow \mathrm{RNH\text{-}C(O)\text{-}NHR''}$$

2. primary chain forming (polymerization) reaction between a polyol and TDI to produce the urethane foam network.

$$\mathrm{R\text{-}N=C=O} + \mathrm{R'OH} \rightarrow \mathrm{RNH\text{-}C(O)\text{-}OR'}$$

3. secondary crosslinking reactions of the polymer products and TDI to strengthen the foam network (formation of biurets and allophanates).

$$\mathrm{R\text{-}N=C=O} + \mathrm{R'NH\text{-}C(O)\text{-}NHR''} \rightarrow \mathrm{RNH\text{-}C(O)\text{-}NR'\text{-}C(O)\text{-}NHR''}$$

$$\mathrm{R\text{-}N=C=O} + \mathrm{R'NH\text{-}C(O)\text{-}R''} \rightarrow \mathrm{RNH\text{-}C(O)\text{-}NR'\text{-}C(O)\text{-}OR''}$$

Table 3 - Competing Reactions

1. Ingredients at uniform temperatures are mixed, CO_2 is generated in the liquid phase as finely dispersed gas bubbles.
2. Gas evolution causes a rapid increase in volume as the exothermic generation of heat continues.
3. Vaporization (and boiling) of auxiliary blowing agent.
4. Bubbles increase in size and number, space between bubbles decreases forming a three-dimensional network of gas filled cells with thin membrane faces.
5. Membranes break and polymer network becomes self-supporting (blow off point; foam becomes open cell); volatiles under excess pressure escape, foam volume nears maximum.
6. Crosslinking reactions predominate with continued generation of heat and diffusive loss of residual volatiles.

Table 4 - Sequence Of Events

reaction (gas and amine formation) and the isocyanate-polyol reaction (urethane formation). Typically,a tertiary amine such as triethylene diamine or N-ethyl morpholine is utilized in combination with an organometallic catalyst such as dibutyltin laurate, stannous oleate, or stannous octoate. The favored tertiary amines are sterically unhindered and are excellent Lewis bases (availability of the free electron pair on the nitrogen). Formation of an intermediate quaternary amine is hypothesized to increase the rate of the isocyanate-water reaction. Organotin materials probably promote the isocyanate-polyol reaction by an oxidative addition/reductive elimination mechanism. Literature data further suggest a synergistic effect of the two catalyst components on the rate of urethane formation. Addition of a silicone-based surfactant to the formulation lowers surface tension and influences foam cell size. Furthermore, the surfactant stabilizes the cell network thus delaying the escape of volatiles until the polymeric foam is self-supporting.

ATMOSPHERIC EFFECTS OF CFCs

Due to the thermal insulation properties, volatility, and chemical inertness, chlorofluorocarbons have attained commercial significance in applications including blowing agents, refrigerants, cleaning solvents, aerosols, and sterilizing agents (Table 5).

REFRIGERATION/AC	33%
FOAM BLOWING	31%
CLEANING AGENTS	23%
OTHER	13%

Table 5 - U.S. Uses Of CFCs

These same physical properties result in the stability of CFCs in the atmosphere. Fully halogenated materials pass through the troposphere and in the stratosphere absorb ultraviolet radiation. The result is the formation of chlorine free radicals which catalytically react with ozone.[10] This depletion of stratospheric ozone allows additional ultraviolet radiation to pass to the earth surface and deleteriously affect animal and plant life. An increase in exposure to ultraviolet radiation has been correlated with an increased incidence of human skin cancer. Theoretical atmospheric models and the discovery of a seasonal thinning of the stratospheric ozone over Antarctica[23] led to an international agreement (Montreal Protocol, 1987[11]) to severely curtail the production and use of fully halogenated CFCs. Subsequently, additional scientific evidence has strengthened the model predictions and linked a 3% reduction (accounting for natural variability) in stratospheric ozone over North America and Europe in the past 15 years to CFC emissions. In conjunction with a depletion of stratospheric ozone and an increase in the penetration of ultraviolet radiation, CFCs contribute to the well publicized global warming or greenhouse effect. Some of the UV radiation that passes through the atmosphere is re-emitted from the earth surface at longer wavelengths. The absorption of this re-emitted radiation by stratospheric-resident CFCs traps solar energy (in the same fashion as CO_2) normally allowed to escape from earth atmosphere and contributes to global warming. In July, 1988, the first restrictions on the manufacture of fully halogenated CFCs went into effect with manufacturers' production frozen at 1986 levels (essentially a 15% cut). EPA and the Montreal Protocol mandate an additional 20% cut in 1993 and a further 30% cut in 1998. CFC prices have risen by approximately 25-35% in the past year and are projected to increase as much as five-fold.

PROGRAM BACKGROUND

The Research Center for Waste Minimization and Management located at North Carolina State University focusses on the research, development, engineering, and economic stages necessary to implement a reduction in industrial waste emissions.[13] After an iterative screening process, Center programs are selected based on the following criteria:

- the magnitude of emission falls within a reasonable range for technical and economically viable recovery or elimination,
- the industry commitment to considering a waste minimization scheme is evident, and
- there exist crucial unavailable information which the Center could generate by laboratory and pilot-scale studies or by detailed engineering analysis and design.

The manufacture of flexible polyurethane foam meets all of these criteria. A preliminary engineering evaluation was completed on the waste reduction potential within the flexible polyurethane foam industry.[14] That study concluded that substantial quantities of the auxiliary blowing agent (CH_2Cl_2 or CCl_3F) could potentially be recovered as a means of reducing air emissions. The two major obstacles to economic recovery were determined to be the tunnel ventilation rate which dilutes the concentration of the auxiliary blowing agent and the potential poisoning of activated carbon by small quantities of toluene diisocyanate. Following the engineering assessment, a series of experiments were designed and conducted to produce the missing critical information necessary to develop and implement a waste minimization strategy. This report documents the results of those experimental investigations.

EXPERIMENTAL OBJECTIVES

Prior experimentation has primarily dealt with the mechanistic chemistry applied to product development. Additionally, DuPont[4] (and other suppliers of halogenated hydrocarbons) and Unifoam[21] (equipment manufacturer) performed investigations on the emission of volatiles from polyurethane foams. Union Carbide[2] (also a supplier of raw materials to the industry) conducted an elegant study on the sequence of events and kinetics of the most important reactions in the foaming process.

Experimentation in the current study was focused on developing a basic quantitative understanding of the various processes involved in the manufacturing operation (specifically events occurring within the foaming tunnel, curing, and storage areas). Previously, these sequences were understood only qualitatively making the possibility of cost-effective recovery very low as evidenced by three decades of little change. The steady state plant process was successfully simulated using a laboratory batch preparation commonly utilized by the industry. The events which take place as the foam travels down the tunnel are represented in the laboratory-produced foam as a travel time. While the smaller scale introduces some limitations, it is apparent that similar events occurred in the plant situations and the essential processes were unchanged. To concentrate the research effort, only one type of auxiliary blowing agent, methylene chloride, was investigated over a range of foams. Conclusions on methylene chloride blown foams are transferable to CFC blown foams with the recognition that CFC emissions may be further shifted within the foaming tunnel due to a boiling point lower than methylene chloride. The specific objectives of the several experimental studies were as follows:

- Quantification of the rates of mass (volatiles) loss for a range of foams in an open system.
- Collection of volatiles in a closed system with determination of methylene chloride and CO_2 in various stages of the process (collection times related to times in and out of the foaming tunnel).
- Determination of the effect of vacuum application on the rate of mass loss in the curing and storage areas.
- Generation of interior foam temperature profiles throughout the process as a function of time.
- Collection of mass loss data at three foam manufacturing plants for comparison to and validation of laboratory data.

RAW MATERIALS

A formulation (courtesy of Hickory Springs Manufacturing Company) for a typical polyurethane foam applicable for furniture components was utilized for laboratory experiments (Table 6).

Weight	Compound	pph Polyol
250.00g	Poly-ethylene ether triol	100.00
10.00g	Water	4.00
30.00g	Methylene chloride	12.00
1.05g	C-205 amine catalyst	0.42
0.14g	TD-33 amine catalyst	0.06
3.62g	B-8021 silicone surfactant	1.45
1.90g	B-95 Stannous octoate catalyst	0.76
127.00g	Toluene diisocyanate	55.80

Table 6 - Typical Laboratory Batch Formulation

This formulation yields a product with a density of 1.0-1.2 lb/cu ft with an indentation load deflection (foam resilience or firmness) of 21 lb. (the force required to compress a 4" thick slab to 3"). Additional formulations were utilized which varied the amount of methylene chloride to investigate the effects of changes in the ratio of primary to auxiliary blowing agents. Formulations are modified in industry to adjust foam physical properties and meet a range of product specifications (density, tensile strength, elongation, indentation load deflection, flammability, etc.).

MASS LOSS EXPERIMENTS

FOAM PREPARATION

Laboratory foams were prepared using conventional techniques developed within the polyurethane industry. All formulation ingredients were weighed in tared beakers or syringes and added to a tared vessel in the order listed in Table 6; timing was started with the addition of toluene diisocyanate. After stirring (using a tared mechanical stirrer) the chemical mixture for approximately 12 seconds, the foaming liquid was rapidly transferred to a tared polyethylene (0.002" thickness) lined cardboard cakebox (12" x 12" x 6") sitting on an electronic balance. Pouring a completely mixed and foaming mixture onto a solid surface (cardboard) can be likened to the plant situation where a mixing head discharges onto a flat conveyor system. Typically, balance readings would stabilize at t = 0.5 minutes and mass readings would be collected periodically for 24 hours. The stirrer and mixing vessel were also weighed at 24 hours (when all volatiles have been lost) to account for transfer losses by back-calculation.

MASS BALANCE ON FOAM EXPERIMENTS

The total mass of the original ingredients is known, but the chemical reactions are so rapid that some mass loss occurs before the foam can be poured and the mold placed on a balance. Therefore, a convenient method of obtaining a mass balance of the foam process is to use the final mass of set foam. This final mass is the sum of the mass of foam in the mold, the mass of foam remaining in the mixing vessel, and the mass of foam remaining on the mechanical stirrer. The total mass of volatiles lost is determined by subtracting the final mass of set foam (total solids) from the original mass of ingredients.

Mass of set foam = Foam in mold + Foam in mixing vessel + Foam on stirrer
Mass of volatiles = Mass of original ingredients - Mass of set foam

The total mass of cured foam (aged for 24 hours) in the mold and remaining in the mixing vessel were determined for each run. The residual foam mass on the stirrer was weighed in a separate series of experiments and a constant factor of 2g was used in the mass balance calculations.[16]

Data presented in Table 7 shows good reproducibility of the percentage of material (93%) transferred to the mold. The total mass solids is slightly less than the theoretical value; therefore , the total mass of calculated is slightly greater than the theoretical amount. This small difference appears larger than the experimental error or an estimate of atmospheric moisture accidentally introduced with the ingredients or adsorbed on the walls of the vessels. The higher than expected volatiles (and lower than expected solids) may result from loss of the amine catalysts (1.2g) and volatilization of excess toluene diisocyanate. Overall, the mass balance experimental data are consistent with calculated values.

Analogous mass balance calculations were performed on each foam using the exact weights of ingredients and residual materials on the stirrer and reaction vessel. These data were utilized to determine the actual total amount of foam poured in the mold and the mass of theoretical volatiles available for loss.

As an example of a mass balance calculation, assume that a hypothetical foam was prepared using the standard formulation given in Table 6, i.e.,

Total mass of ingredients = 423.71g
Mass of $CO2$ generated = 24.42g
Total volatiles = 54.42g
Total solids = 369.29g

Assume that after 24 hours, the added weight on the stirrer was 2.10g and the added weight in the mixing vessel was 22.45g.

Original mass lost on stirrer = (Wt. gain on stirrer) x (Mass of Ingredients/Mass of Solids)
= (2.10g) x (423.71g/369.29g) = 2.41g

THEORETICAL AMOUNTS OF SOLIDS AND VOLATILES

Mass of CO_2 generated = (mass of H_2O/MW of H_2O) x (1 mole CO_2/1 mole H_2O) x (MW of CO_2)
= (10.00 g/18.02 g/m) x (44.01 g/m) = 24.42g

Mass of volatiles = Mass of CH_2Cl_2 + Mass of CO_2 generated
= 30.00g + 24.42g = 54.42g

Mass of solids = Mass of ingredients - Mass of volatiles
= 423.71g - 54.42g = 369.29g

Delta = Measured Solids - Theoretical Solids

RUN #	FOAM IN BOX	FOAM OTHER	TOTAL SOLIDS	DELTA	GASES LOST	FOAM IN BOX
1	334.00g	28.50g	362.50g	-6.79g	61.19g	92.14%
2	339.10g	22.80g	361.90g	-7.39g	61.79g	93.70%
3	343.40g	27.70g	371.10g	+1.81g	52.59g	92.54%
4	343.60g	22.00g	365.60g	-3.69g	58.09g	93.98%
5	345.60g	22.80g	368.40g	-0.89g	55.29g	93.81%
6	348.30g	23.06g	371.36g	+2.07g	52.33g	93.79%
7	337.50g	27.30g	364.80g	-4.49g	58.89g	92.52%
8	331.90g	37.10g	369.00g	-0.29g	54.69g	89.95%
9	333.50g	27.20g	360.70g	-8.59g	62.99g	92.46%
10	348.30g	23.06g	371.36g	+2.07g	52.33g	93.79%
11	337.90g	34.20g	372.10g	+2.81g	51.60g	90.81%
12	338.00g	27.45g	365.45g	-3.84g	58.25g	92.49%
13	346.30g	24.15g	370.45g	+1.16g	53.25g	93.48%
AVG	340.57g	26.72g	367.29g	-2.00g	56.40g	92.73%
STD DEV	5.47g	4.43g	3.85g	3.85g	3.85g	1.19%

Table 7 - Mass Loss Experiments

Original mass lost in mixing vessel = (Wt. gain of vessel) x (Mass of Ingredients/Mass of Solids)
= (22.45g) x (423.71g/369.29g) = 25.76g

Total Transfer Loss = Original mass lost on stirrer + Original mass lost in mixing vessel
= 2.41g + 25.76g = 28.17g

Total Mass transferred to cakebox = Mass of Ingredients - Total Transfer Loss
= 423.71g - 28.17g = 395.54g

Total volatiles available for loss = Total Mass in Cakebox x (Mass of Volatiles/Mass of Ingredients)
= (395.54g) x (54.42g/423.71g) = 50.80g

Total foam produced in box = Total Mass in Cakebox x (Mass of Solids/Mass of Ingredients)
= (395.54g) x (369.29g/423.71g) = 344.69g

RESULTS/DISCUSSION

Experimentation covered a series of foams prepared with a range of auxiliary (methylene chloride) to primary (water) blowing agent concentrations (0:1, 1:1, 3:1, 4:1); formulations were the same as listed in Table 6 with variations only in the amount of methylene chloride (0 - 40 g). Average mass loss data are presented in Tables 8-11 and Figures 1-12.

Foams prepared in the laboratory exhibited a cream time (formation of microscopic bubbles as the mixture turns very white) of between 5-7 seconds (estimated by a change in sound of the mechanical stirrer). In the plant, cream times are visibly observed and occur at approximately 8 seconds. Laboratory foam mixtures started to expand prior to pouring, blow off (visible escape of gases through the top of the foam) occurs between 1.5 and 2.5 minutes after mixing. At the time of blowoff, the foam was set and had reached a maximum height of approximately six inches.

The laboratory data are characterized by an initial rapid loss of approximately 60-70% of the available volatiles in 10 minutes; the residual volatiles are then slowly lost over 24 hours. These two regimes of mass loss are logarithmically proportional to the elapsed time and represent a complex mechanism of volatilization. Simplistically, the first regime of mass loss is hypothesized to relate to the kinetically fast reaction between the diisocyanate and water generating CO_2 and heat. The heat generated by the competing reactions increases the temperature of the foaming mass and the liberation of CH_2Cl_2 is initiated. The rapid loss of volatiles occurs from the surface of the rapidly expanding multiphase foam and from the block interior as the foam becomes an open cell structure (blow-off point). The second regime of mass loss appears to be a slow diffusion of volatiles through a open cell foam mass as crosslinking reactions continue.

As the amount of methylene chloride is increased in the formulation (at constant water content), the mass loss rates increase. When the data are normalized on a percent of total volatiles lost, the time dependent mass loss rates and total mass loss over the first 10 minutes for 1:1, 3:1, and 4:1 formulations appear independent of the amount of auxiliary blowing agent present in the formulation. After 10 minutes, the normalized 3:1 and 4:1 data continue to coincide. Conversely, the mass loss rate for the 1:1 formulation noticeably slows after 10 minutes and looks similar in shape to the analogous water-blown (0:1) foam data. The reason for this behavior is unknown but may relate to a density effect.

These observations support a rapid chemical rate of formation and loss of CO_2 followed by a temperature and diffusion dependent loss rate of CH_2Cl_2. The rise in foam temperature would be expected to be independent of CH_2Cl_2 content while from industry experience, foam density is inversely proportional (non-linear) to CH_2Cl_2 content (foam density decreases with higher levels of auxiliary blowing agents).

The laboratory experiments are potentially different from the full scale plant operation with respect to the dissipation of heat from a foam block. Laboratory foams were prepared in an insulated cakebox and mass losses were recorded. The two phases of volatile loss were again observed; however, the initial rates of mass loss were greater for the insulated versus the uninsulated foams. This observation implies that the temperature profile of the insulated foam mass is shifted toward earlier times and possibly to a higher temperature maxima than an uninsulated foam; consequently, volatile loss (especially CH2Cl2) would also be shifted to earlier times. Internal foam temperature measurements are discussed in a later section.

The key observations from this section of experimentation include:

> Mass loss data are consistent when normalized for the amount of auxiliary blowing agent present in the formulation.
>
> Mass loss profiles are characterized by two regimes (probably different mechanisms).

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	9.77	19.54	9.77	40.00	80.10	40.00
0.75	3.21	12.83	12.97	13.12	52.50	53.13
1.00	2.52	10.09	15.50	10.33	41.32	63.46
1.25	1.49	5.98	16.99	6.12	24.47	69.58
1.50	1.14	4.54	18.13	4.65	18.61	74.23
1.75	0.84	3.34	18.95	3.39	13.55	77.61
2.00	0.89	3.55	19.84	3.62	14.48	81.24
2.50	0.72	1.45	20.56	2.96	5.93	84.20
3.00	0.26	0.51	20.82	1.05	2.10	85.25
4.00	0.20	0.20	21.02	0.83	0.83	86.08
5.00	0.47	0.47	21.49	1.92	1.92	88.00
6.00	0.05	0.05	21.54	0.21	0.21	88.21
7.00	0.10	0.10	21.64	0.42	0.42	88.63
8.00	0.16	0.16	21.80	0.65	0.65	89.28
9.00	0.21	0.21	22.01	0.86	0.86	90.14
10.00	0.06	0.06	22.07	0.23	0.23	90.37

Table 8 - Average Mass Loss Data - 0:1 CH_2Cl_2 : H_2O

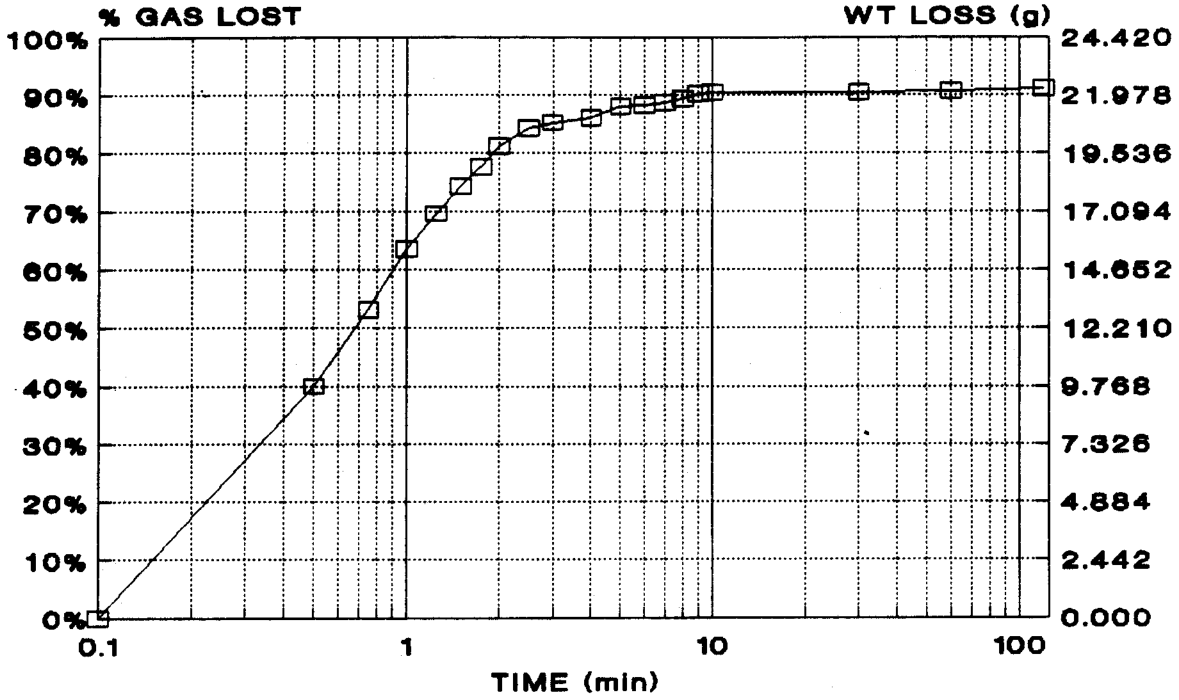

Figure 1 - Mass Loss Profile - 0 : 1 CH_2Cl_2: H_2O

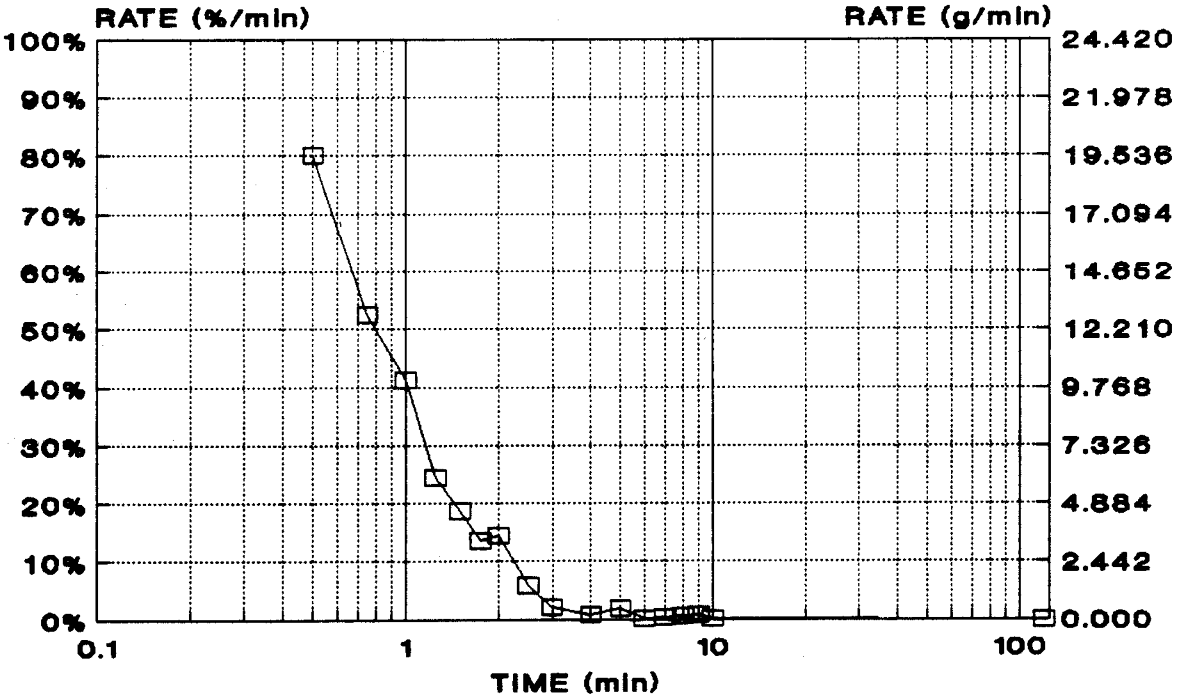

Figure 2 - Rate of Mass Loss - 0 : 1 CH_2Cl_2: H_2O

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	2.84	5.67	2.84	8.24	16.48	8.24
0.75	2.54	10.15	5.37	7.37	29.47	15.61
1.00	2.91	11.63	8.28	8.45	33.82	24.06
1.25	2.92	11.66	11.20	8.47	33.88	32.53
1.50	3.77	15.09	14.97	10.96	43.83	43.49
1.75	2.11	8.45	17.08	6.14	24.57	49.63
2.00	1.58	6.31	18.66	4.58	18.31	54.21
2.25	0.97	3.90	19.63	2.83	11.31	57.03
2.50	1.03	4.12	20.66	2.99	11.96	60.02
2.75	0.38	1.53	21.04	1.11	4.43	61.13
3.00	0.97	3.88	22.01	2.82	11.29	63.95
4.00	1.09	1.09	23.10	3.16	3.16	67.11
5.00	0.17	0.17	23.26	0.48	0.48	67.59
6.00	0.28	0.28	23.54	0.80	0.80	68.38
7.00	0.11	0.11	23.65	0.32	0.32	68.70
8.00	0.17	0.17	23.81	0.48	0.48	69.18
9.00	0.06	0.06	23.87	0.16	0.16	69.34
10.00	0.00	0.00	23.87	0.00	0.00	69.34
15.00	0.06	0.01	23.92	0.16	0.03	69.50
20.00	0.04	0.01	23.96	0.12	0.02	69.62
30.00	0.10	0.01	24.06	0.28	0.03	69.90
60.00	0.26	0.01	24.32	0.76	0.02	70.66
120.00	0.51	0.01	24.83	1.49	0.02	72.15

Table 9 - Average Mass Loss Data - 1 : 1 CH_2Cl_2 : H_2O

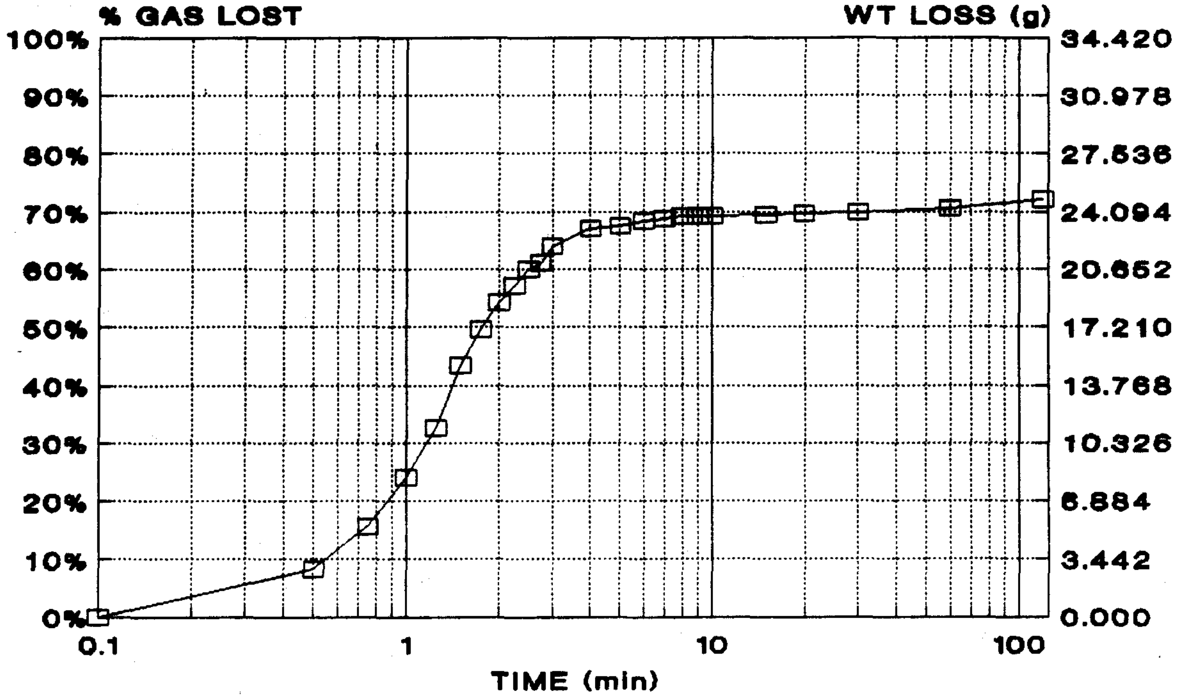

Figure 3 - Mass Loss Profile - 1 : 1 CH_2Cl_2: H_2O

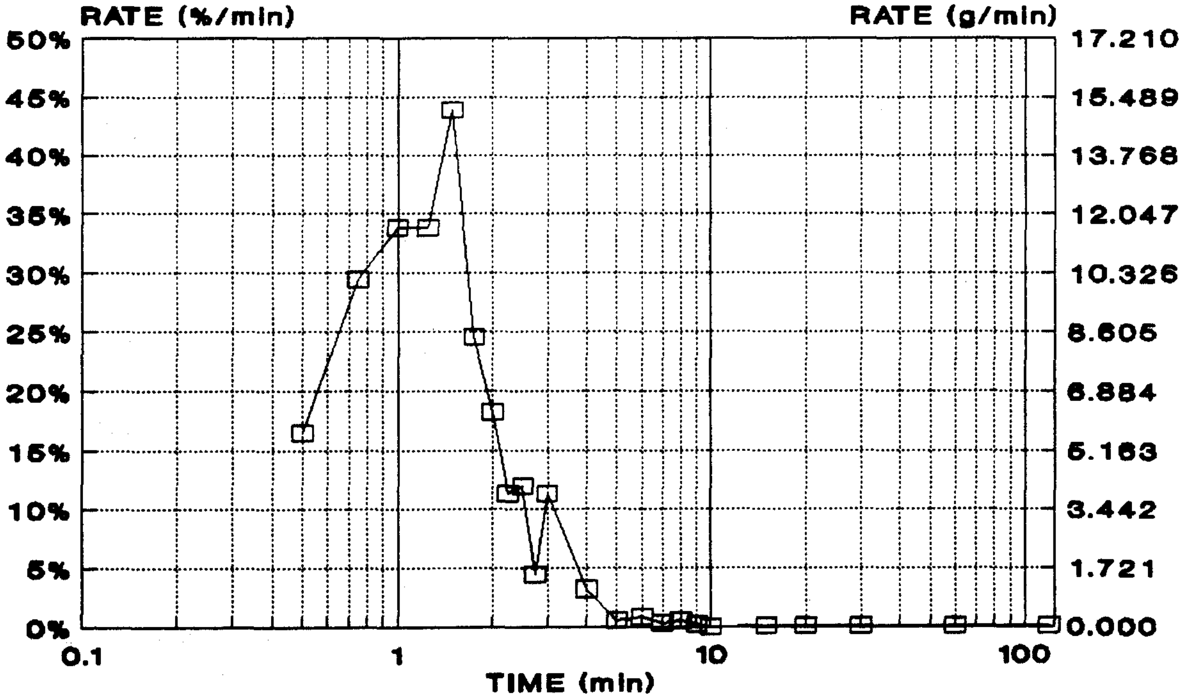

Figure 4 - Rate of Mass Loss - 1 : 1 CH_2Cl_2: H_2O

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	9.13	18.25	9.13	16.77	33.54	16.77
0.75	3.85	15.39	12.97	7.07	28.28	23.84
1.00	2.04	8.14	15.01	3.74	14.96	27.58
1.25	3.49	13.95	18.50	6.41	25.62	33.99
1.50	3.60	14.39	22.09	6.61	26.44	40.60
1.75	1.95	7.81	24.05	3.59	14.38	44.19
2.00	2.79	11.15	26.84	5.12	20.50	49.32
2.25	1.96	7.84	28.79	3.60	14.40	52.91
2.50	1.42	5.68	30.22	2.61	10.44	55.53
2.75	1.24	4.94	31.45	2.27	9.10	57.80
3.00	1.86	7.42	33.31	3.41	13.65	61.21
4.00	2.03	2.03	35.34	3.73	3.73	64.94
5.00	1.41	1.41	36.75	2.59	2.59	67.53
6.00	0.60	0.60	37.35	1.11	1.11	68.64
7.00	0.60	0.60	37.95	1.10	1.10	69.73
8.00	0.54	0.54	38.50	1.00	1.00	70.74
9.00	0.22	0.22	38.71	0.40	0.40	71.14
10.00	0.33	0.33	39.04	0.60	0.60	71.74
15.00	0.97	0.19	40.02	1.79	0.36	73.53
20.00	0.87	0.17	40.89	1.59	0.32	75.13
25.00	0.54	0.11	41.43	1.00	0.20	76.13
30.00	0.48	0.10	41.91	0.89	0.18	77.01
35.00	0.49	0.10	42.40	0.90	0.18	77.91
40.00	0.27	0.05	42.67	0.50	0.10	78.41
45.00	0.54	0.11	43.21	0.99	0.20	79.40
50.00	0.11	0.02	43.32	0.21	0.04	79.61
55.00	0.27	0.05	43.59	0.49	0.10	80.10
60.00	0.27	0.05	43.86	0.50	0.10	80.60
70.00	0.60	0.06	44.46	1.10	0.11	81.70
80.00	0.33	0.03	44.79	0.60	0.06	82.30
90.00	0.71	0.07	45.49	1.30	0.13	83.59
100.00	0.49	0.05	45.98	0.90	0.09	84.49
110.00	0.39	0.04	46.37	0.71	0.07	85.20
120.00	0.33	0.03	46.69	0.60	0.06	85.80

Table 10 - Average Mass Loss Data - 3 : 1 $CH_2Cl_2 : H_2O$

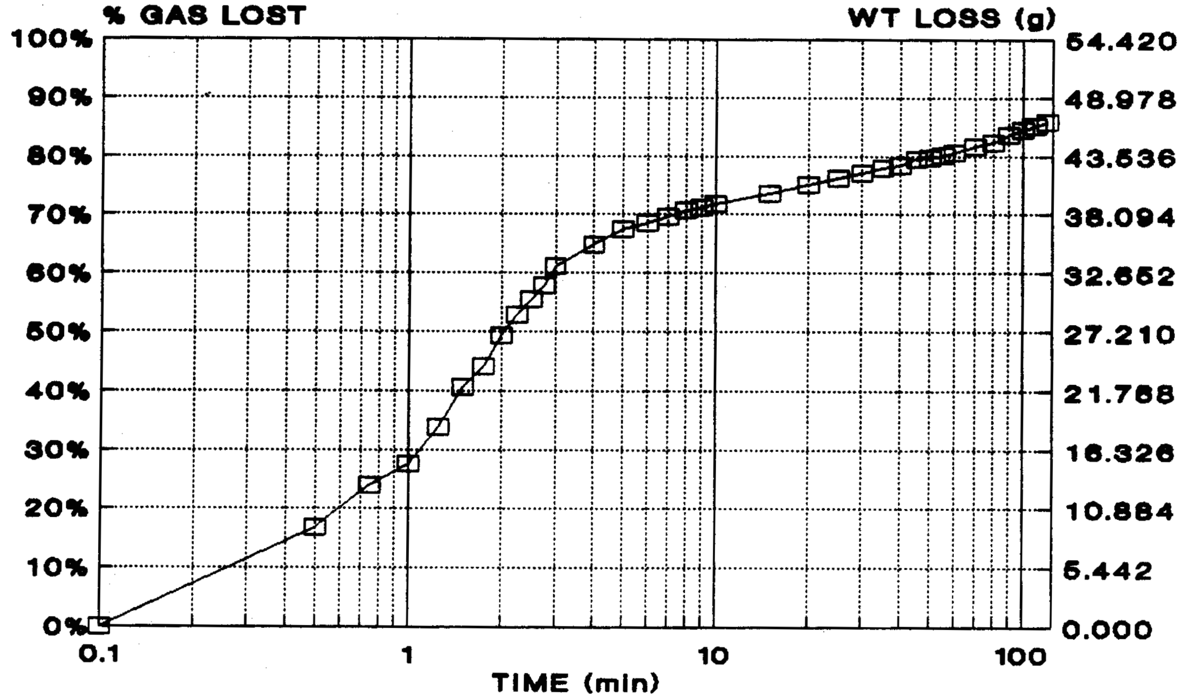

Figure 5 - Mass Loss Profile - 3 : 1 CH_2Cl_2: H_2O

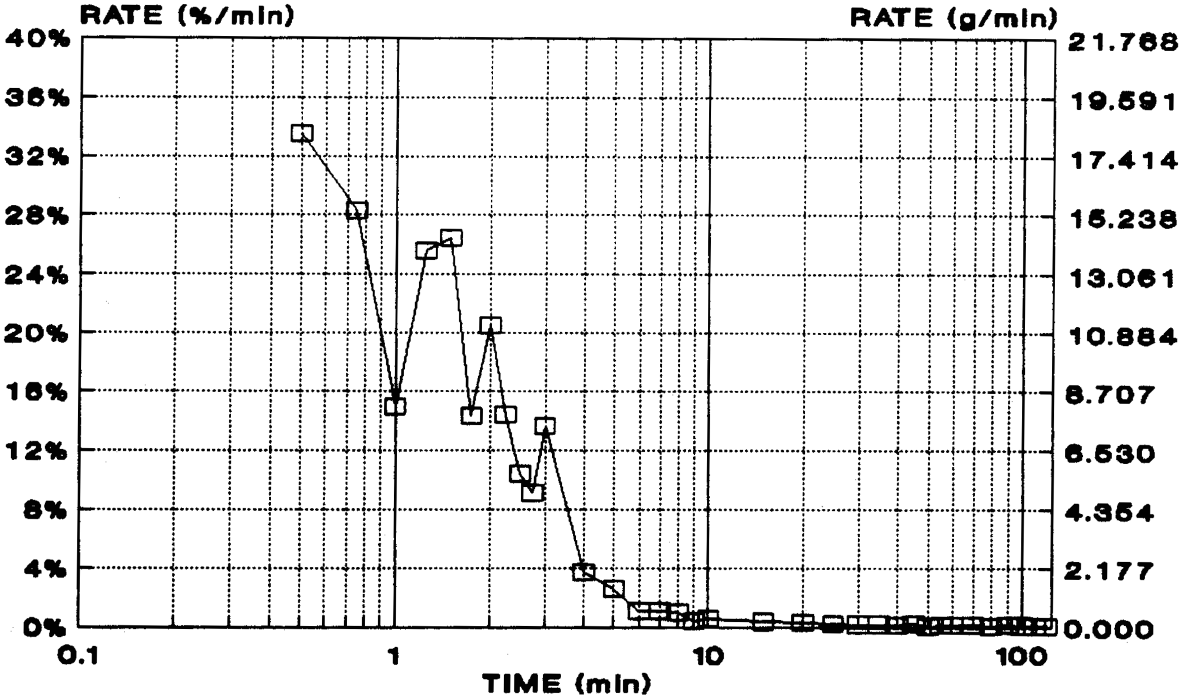

Figure 6 - Rate of Mass Loss - 3 : 1 CH_2Cl_2: H_2O

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	8.65	17.30	8.65	13.43	26.86	13.43
0.75	3.90	15.59	12.56	6.05	24.21	19.49
1.00	3.16	12.65	15.71	4.91	19.62	24.39
1.25	3.21	12.83	18.92	4.98	19.92	29.37
1.50	3.26	13.04	22.18	5.06	20.25	34.43
1.75	3.85	15.38	26.03	5.97	23.89	40.41
2.00	3.00	11.98	29.02	4.65	18.58	45.05
2.25	2.46	9.84	31.48	3.82	15.26	48.87
2.50	1.87	7.47	33.35	2.90	11.61	51.77
2.75	2.19	8.76	35.54	3.40	13.61	55.17
3.00	1.33	5.33	36.88	2.07	8.29	57.25
4.00	3.68	3.68	40.56	5.72	5.72	62.96
5.00	1.66	1.66	42.21	2.57	2.57	65.53
6.00	0.86	0.86	43.07	1.33	1.33	66.86
7.00	0.86	0.86	43.92	1.33	1.33	68.18
8.00	0.70	0.70	44.62	1.08	1.08	69.26
9.00	0.43	0.43	45.04	0.66	0.66	69.92
10.00	0.37	0.37	45.42	0.58	0.58	70.50
15.00	1.55	0.31	46.97	2.40	0.48	72.91
20.00	1.02	0.20	47.99	1.58	0.32	74.49
25.00	0.70	0.14	48.68	1.08	0.22	75.56
30.00	0.59	0.12	49.26	0.91	0.18	76.47
35.00	0.32	0.06	49.58	0.50	0.10	76.97
40.00	0.59	0.12	50.17	0.91	0.18	77.88
45.00	0.43	0.09	50.60	0.66	0.13	78.55
50.00	0.43	0.09	51.03	0.66	0.13	79.21
55.00	0.05	0.01	51.08	0.08	0.02	79.29
60.00	0.37	0.07	51.46	0.58	0.12	79.88
70.00	0.53	0.05	51.99	0.83	0.08	80.71
80.00	0.64	0.64	52.63	1.00	0.10	81.70
90.00	0.59	0.06	53.22	0.91	0.09	82.61
100.00	0.48	0.05	53.70	0.75	0.08	83.36
110.00	0.48	0.05	54.18	0.75	0.08	84.11
120.00	0.70	0.07	54.87	1.08	0.11	85.18

Table 11 - Average Mass Loss Data - 4 : 1 CH_2Cl_2 : H_2O

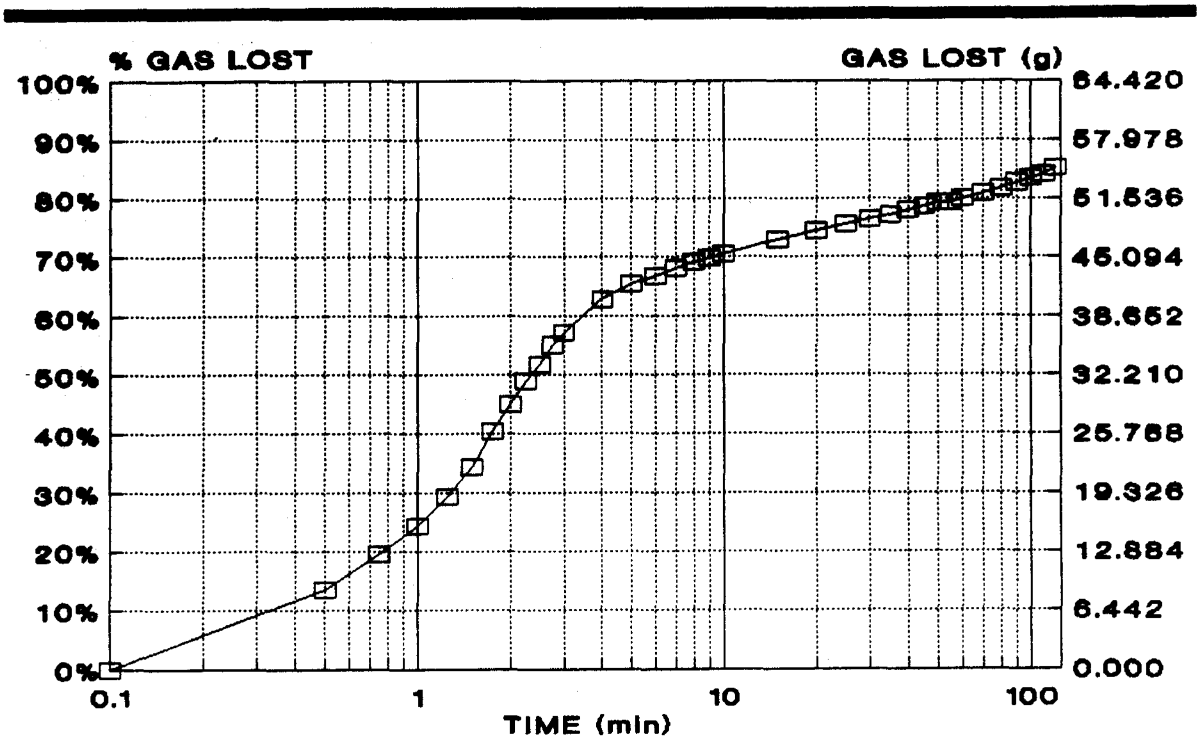

Figure 7 - Mass Loss Profile - 4 : 1 CH_2Cl_2: H_2O

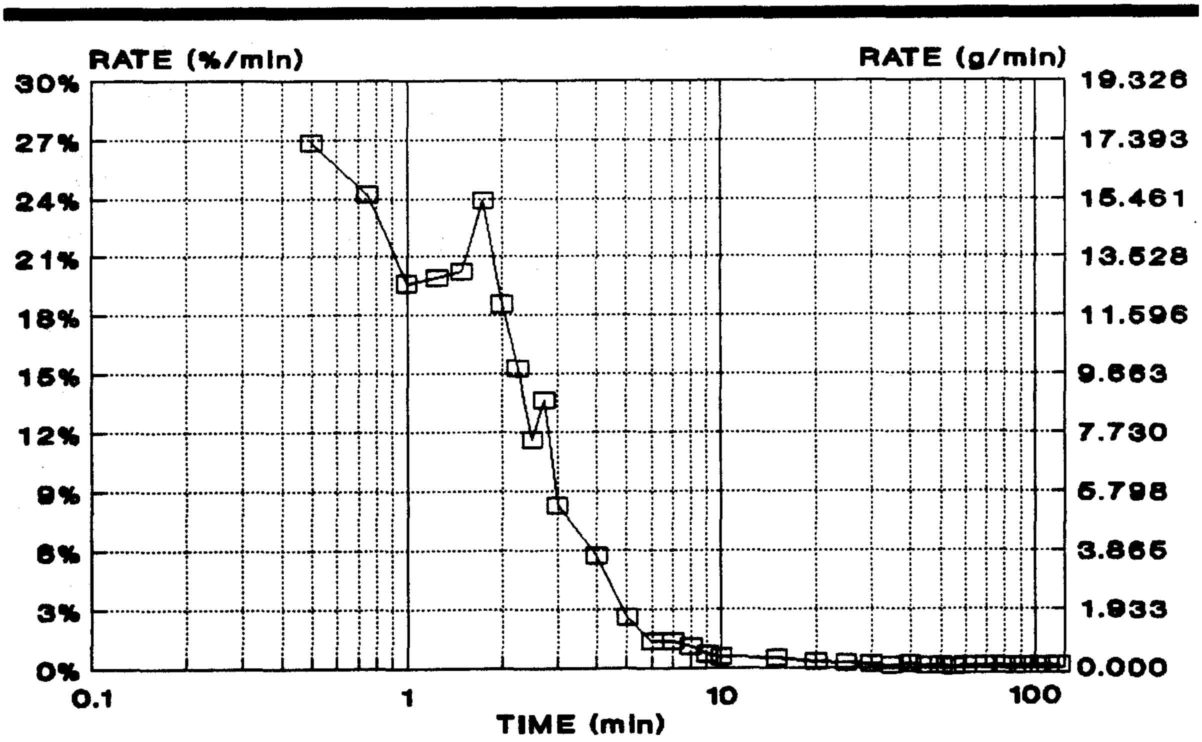

Figure 8 - Rate of Mass Loss - 4 : 1 CH_2Cl_2: H_2O

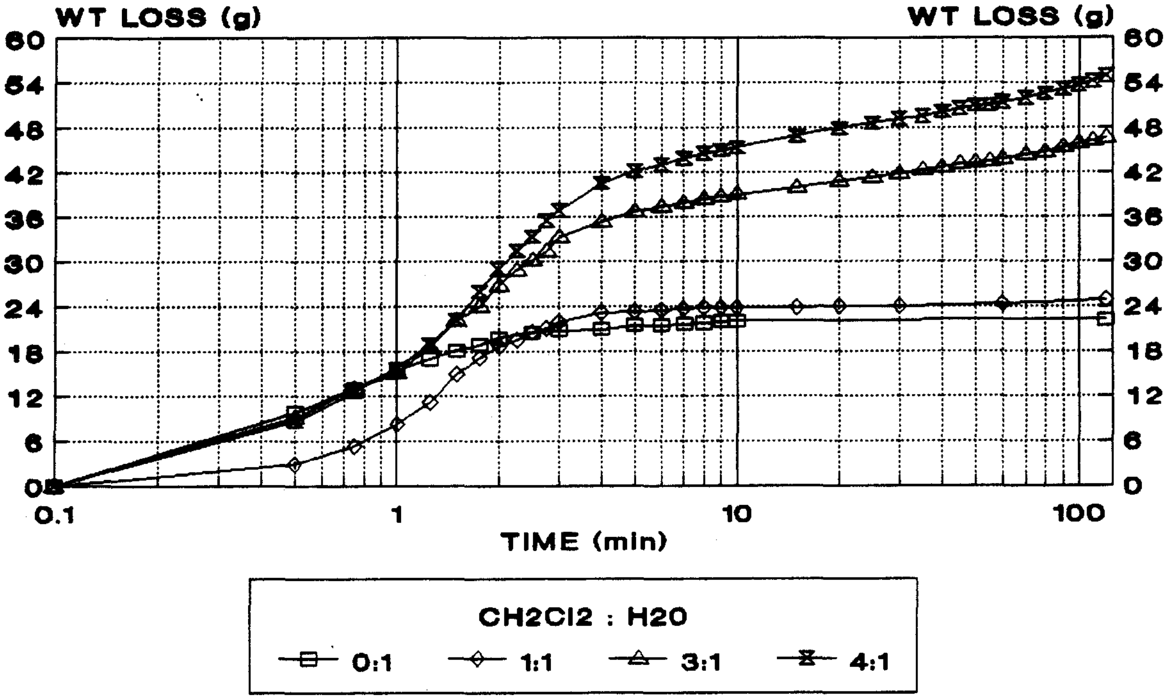

Figure 9 - Mass Loss Profiles - Laboratory Foams

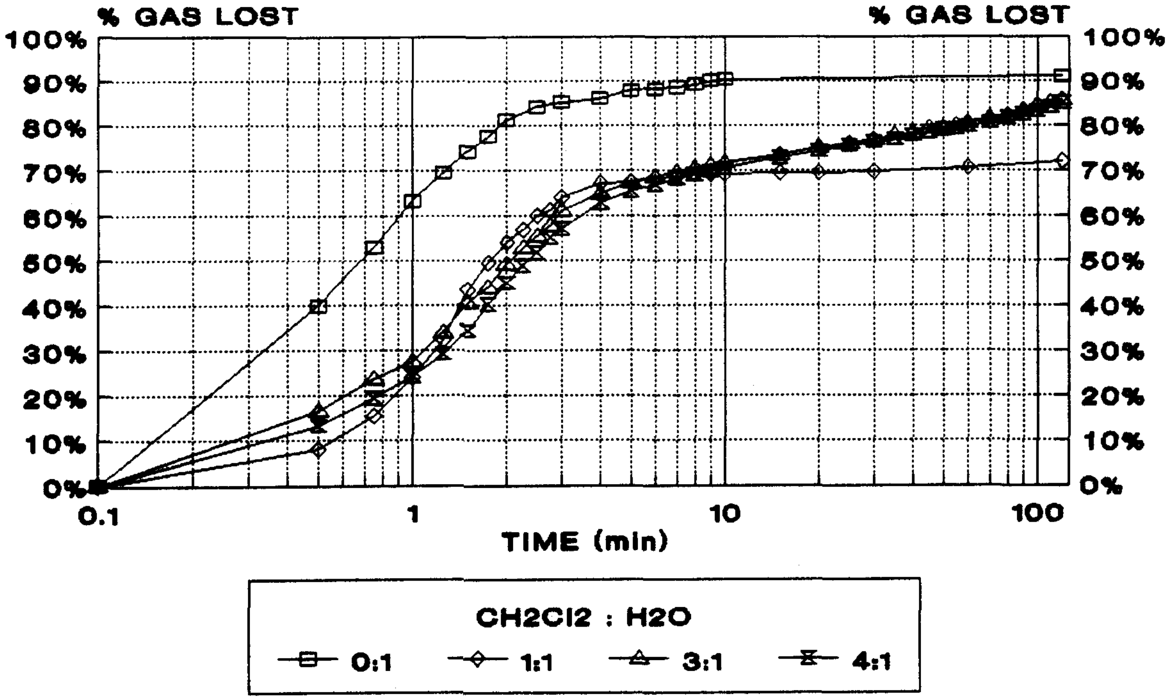

Figure 10 - Normalized Mass Loss Profiles - Laboratory Foams

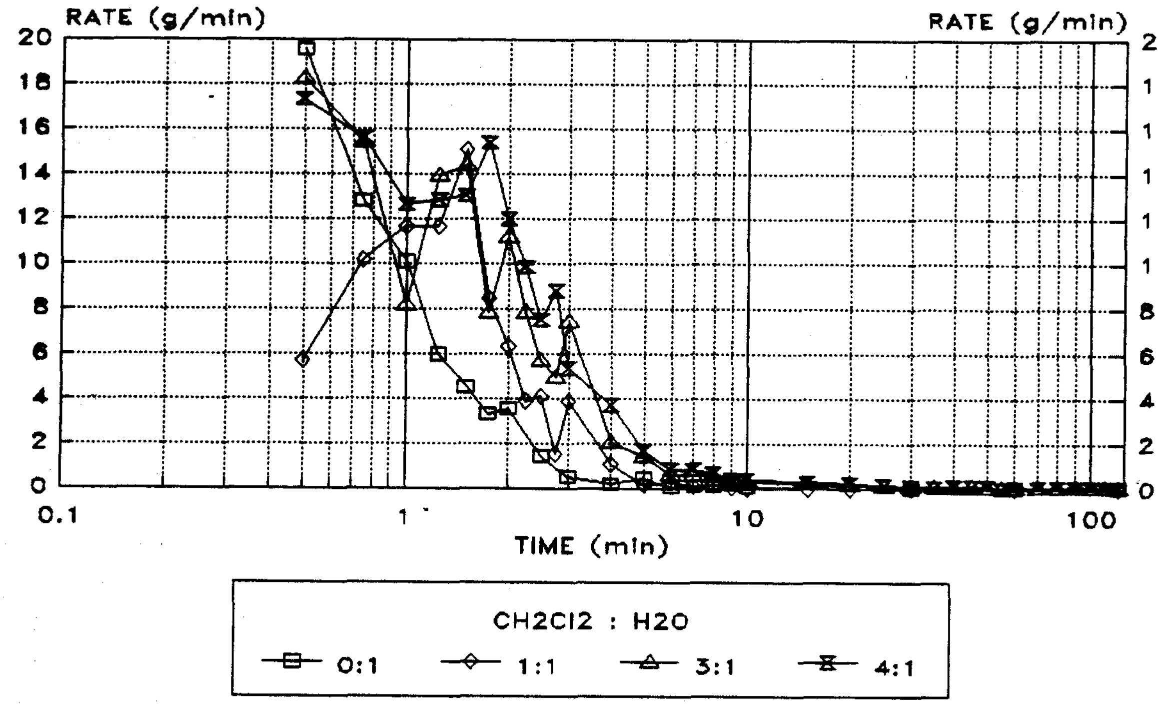

Figure 11 - Rates of Mass Loss - Laboratory Foams

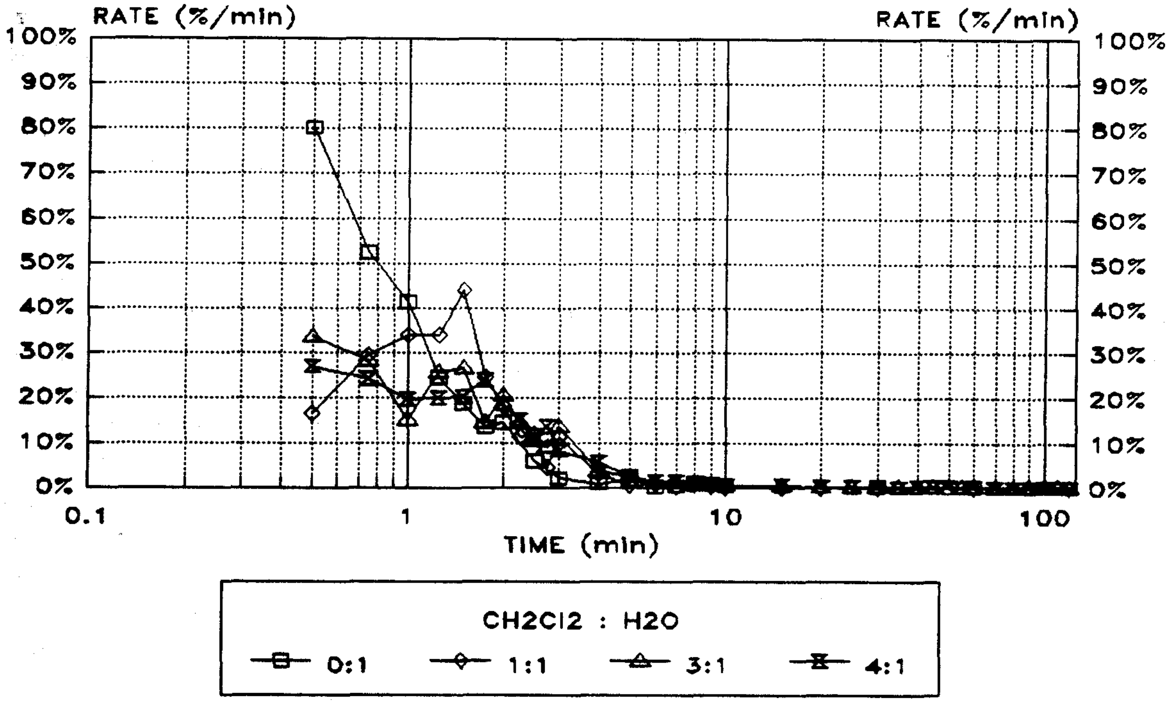

Figure 12 - Normalized Rates of Mass Loss - Laboratory Foams

COLLECTION OF VOLATILES IN A CLOSED SYSTEM

To further understand the loss of volatiles from soft polyurethane foam and develop potential strategies for recovery/reuse of the auxiliary blowing agent, a successive batch collection of both carbon dioxide and methylene chloride was developed.[18] Methylene chloride was gravimetrically determined by condensation in a tared alcohol/solid CO_2 cold trap. Carbon dioxide was adsorbed onto solid ascarite (primarily NaOH) forming sodium bicarbonate and water; CO_2 evolution equaled the increase in mass of the ascarite scrubber and an anhydrous $CaSO_4$ trap (for H_2O).

RELIABILITY TESTS FOR COLLECTION METHODS

The quantitative validity of each method was checked for each gas independently and for a mixture of the two volatiles (Table 12). In order to establish the collection efficiency of the dry ice/alcohol cold trap system, about 30g of CH_2Cl_2 was warmed with a heating mantle. The heating rate was controlled with a Variac and adjusted so that the liquid boiled over completely in 5 minutes (which was estimated to be the fastest rate of CH_2Cl_2 emission from earlier PUF mass loss experiments. A stream of dry air was used to transport the CH_2Cl_2 from the heated flask to the cold traps. Three traps in series were needed to collect 92% of the original material in the flask. Possible loss mechanisms for 92% efficiency include air stripping of the methylene chloride and adsorption of methylene chloride onto the connecting tubes of the apparatus. The method was considered adequate for quantification of collected CH_2Cl_2. The collection efficiency of adsorption onto ascarite and subsequent entrapment of generated water on drierite was determined in an analogous fashion. A stream of dry air transported the gaseous CO_2 given off from a weighed block of dry ice. Collected CO_2 was determined by weighing the absorber train before and after each test run; 98% of the available CO_2 was accounted for. Under certain conditions, solid NaOH and chlorinated hydrocarbons can react; therefore, an additional calibration test was conducted with both gases present. The dry air stream was passed first over solid CO_2 ice and then over the heated CH_2Cl_2. The collection system consisted of the series of cold traps followed by the ascarite and drierite adsorbers. For each individual constituent, 98% was collected which proved no chemical interference between the two species in the system. Using gas collection intervals representing tunnel and post tunnel (curing and storage) residence times, CH_2Cl_2 and CO_2 could therfore be serially trapped and quantified.

APPARATUS/METHOD

A polyethylene lined cakebox was fitted with two inlet and outlet tubes located about 50 mm from the bottom and positioned within a wire cage to support the air inlets, gas outlets, and an ingredients loading tube. This entire assembly was placed within a sealed (airtight) large plastic bag (Figure 13). Foam preparation was carried out in the usual manner; after stirring, the foaming liquid was poured through the filling tube which was quickly closed with a screw cap. A vacuum pump connected to the end of the first absorber train was started and gas collection was initiated for the first time period. At 10 minutes, the gas outlets were switched to a different absorber train for collection of volatiles for the second time frame. Each absorption train consisted of four cold traps in series (for collection of CH_2Cl_2) and one packed ascarite absorber with two drierite tubes (for collection of CO_2 as $NaHCO_3$ and H_2O); the gas collection system is schematically depicted in Figure 14. Particular care was exercised when the absorbers were disconnected for gravimetric determinations; tared drying tubes were connected to each sub-assembly to prevent entry of atmospheric water vapor.

VOLATILE	ORIGINAL WT	COLLECTED WT	% COLLECTED
CH_2Cl_2	28.0g	23.9g	85.4%
	30.2g	28.2g	93.4%
	33.0g	32.2g	97.6%
			92.1% AVG
CO_2	23.1g	21.8g	94.4%
	22.3g	22.1g	99.1%
	23.0g	22.9g	99.6%
	26.1g	26.0g	99.6%
			98.2% AVG
MIXED			
CH_2Cl_2	28.1g	27.3g	97.2%
CO_2	22.8g	22.3g	97.8%

Table 12 - Reliability Tests For The Collection Of Volatiles

RESULTS/DISCUSSION

Average volatile collection data for 1:1, 3:1, and 4:1 formulations are presented in Table 13 and graphically displayed in Figure 15. Independent of formulation, the ratio of methylene chloride collected to carbon dioxide collected increases as a function of time. When the data are normalized for percent of volatiles, the data are consistent with the normalized weight loss profiles. These observations support a rapid consumption of water (generation of CO_2) and a time delayed evolution of methylene chloride from polyurethane foams.

For the less dense foam formulations (3:1 and 4:1), the greatest amounts of the available methylene chloride were recovered in the first ten minutes; however, the relative concentrations of methylene chloride were found to be greater in the subsequent twenty minutes. Although the noted trends are consistent with theoretical considerations, the absolute magnitudes of individual components are probably low due to time lags in gas evacuation and pressure drop problems with overpacked ascarite traps.

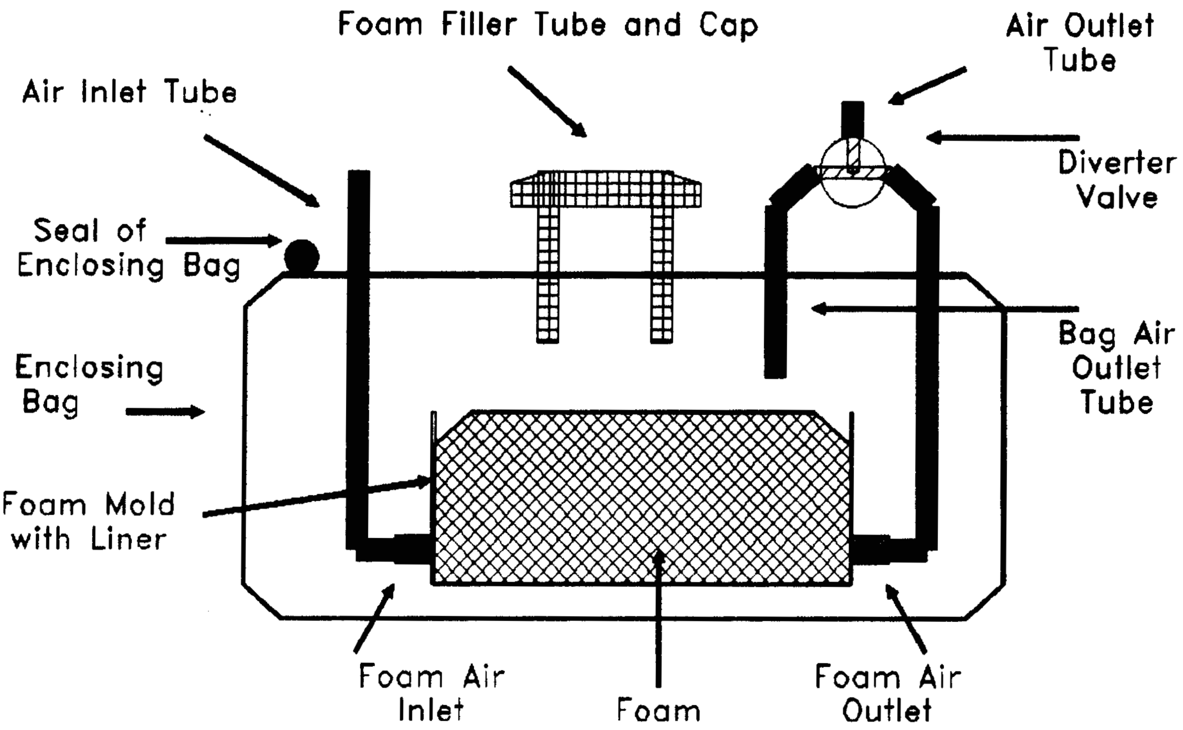

Figure 13 - Foam Mold Assembly - Closed System

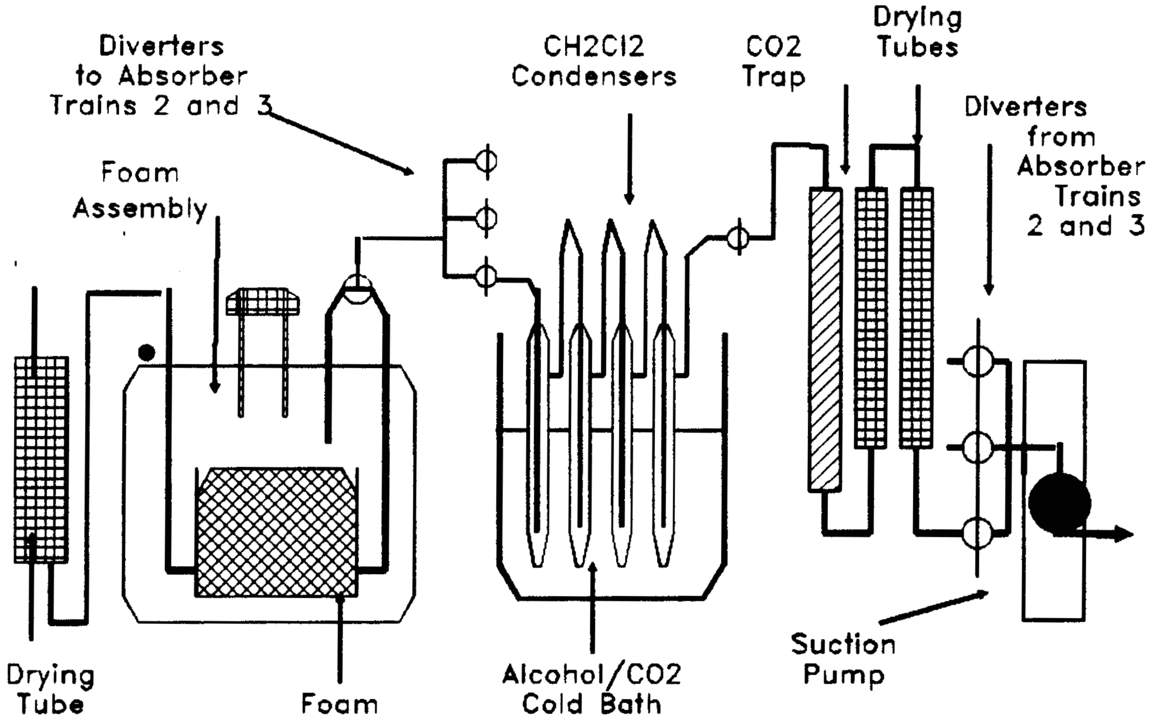

Figure 14 - Foam Mold Assembly - Collection of Volatiles

1:1	0 - 10 min	10 - 30 min	Batch
CH_2Cl_2	1.59g	3.18g	10.00g
CO_2	5.62g	7.37g	24.42g
Ratio	0.28	0.43	0.41

3:1	0 - 10 min	10 - 30 min	Batch
CH_2Cl_2	7.62g	7.35g	30.00g
CO_2	9.84g	6.79g	24.42g
Ratio	0.77	1.08	1.23

4:1	0 - 10 min	10 - 30 min	Batch
CH_2Cl_2	10.52g	8.40g	40.00g
CO_2	9.52g	4.62g	24.42g
Ratio	1.11	1.82	1.64

Table 13 - Collection Of CH_2Cl_2 And CO_2 In A Closed System

In an attempt to get a better understanding of the loss profile for auxiliary blowing agents from polyurethane foams, normalized mass loss data for water blown foams with only CO_2 evolution were graphically subtracted from normalized mass loss data for the lower density foams that evolved both CO_2 and CH_2Cl_2 (3:1 and 4:1 formulations). The higher methylene chloride content (lower density) foams have the greatest potential for recovery/ reuse strategies. These extrapolated data are compiled in Tables 14 and 15 and graphically presented in Figures 16-23. Calculated CH_2Cl_2 : CO_2 ratios increase as a function of time and thus exhibit the same patterns (but of greater magnitudes) observed for the closed system data described above. Since these data are calculated from averages of separate experiments, caution must be exercised in interpreting actual magnitudes. However, the observable trends are consistent with the reaction kinetics; i.e., a rapid loss of CO_2 and a time displaced loss of CH_2Cl_2. Calculated CH_2Cl_2 : CO_2 ratios from the data in Tables 14 and 15 yields values for the 0 - 10 minute interval of 0.77 (3:1) and 1.06 (4:1) which compare very favorably with the data displayed in Table 13. Figures 20-23 compare the calculated 3:1 and 4:1 data; not surprisingly, the data coalesces when normalized on a percent of CH_2Cl_2 lost.

Approximately 40% of the auxiliary blowing agent is left in the foam bun as it exits the tunnel. As the foam proceeds through the plant, the concentration of CH_2Cl_2 relative to CO_2 is enriched. These data emphasize the two phase nature of volatile loss and are critical information in understanding the time (plant location) dependent loss of the auxiliary blowing agent. Only by understanding the magnitude and rates of loss can appropriate recovery technologies be selected.

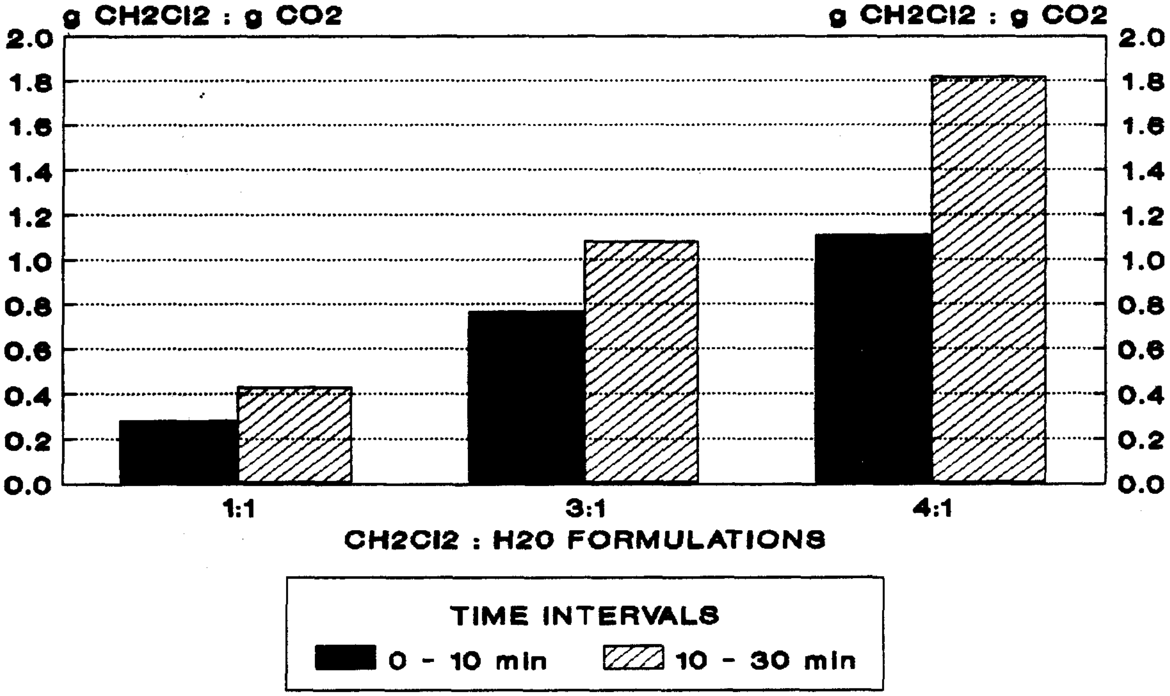

Figure 15 - Collection of Volatiles - Ratios of CH_2Cl_2: H_2O

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	0.00	0.00	0.00	0.00	0.00	0.00
0.75	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00
1.25	1.51	6.04	1.51	5.03	20.13	5.03
1.50	2.45	9.80	3.96	8.17	32.67	13.20
1.75	1.14	4.56	5.10	3.80	15.20	17.00
2.00	1.90	7.60	7.00	6.33	25.33	23.33
2.25	1.59	6.36	8.59	5.30	21.20	28.63
2.50	1.07	4.28	9.66	3.57	14.27	32.20
2.75	1.10	4.40	10.76	3.67	14.67	35.87
3.00	1.73	6.92	12.49	5.77	23.07	41.63
4.00	1.83	1.83	14.32	6.10	6.10	47.73
5.00	0.94	0.94	15.26	3.13	3.13	50.87
6.00	0.55	0.55	15.81	1.83	1.83	52.70
7.00	0.50	0.50	16.31	1.67	1.67	54.37
8.00	0.39	0.39	16.70	1.30	1.30	55.67
9.00	0.00	0.00	16.70	0.00	0.00	55.67
10.00	0.27	0.27	16.97	0.90	0.90	56.57
15.00	0.97	0.19	17.94	3.24	0.65	59.81
20.00	0.86	0.17	18.80	2.87	0.57	62.68
25.00	0.53	0.11	19.34	1.77	0.35	64.45
30.00	0.47	0.09	19.81	1.57	0.31	66.02
35.00	0.48	0.10	20.29	1.61	0.32	67.63
40.00	0.26	0.05	20.55	0.87	0.17	68.50
45.00	0.53	0.11	21.08	1.77	0.35	70.27
50.00	0.10	0.02	21.18	0.34	0.07	70.61
55.00	0.26	0.05	21.45	0.87	0.17	71.49
60.00	0.26	0.05	21.71	0.87	0.17	72.36
70.00	0.58	0.06	22.29	1.95	0.19	74.30
80.00	0.31	0.03	22.60	1.05	0.10	75.35
90.00	0.68	0.07	23.29	2.28	0.23	77.63
100.00	0.47	0.05	23.76	1.58	0.16	79.21
110.00	0.37	0.04	24.14	1.25	0.12	80.45
120.00	0.30	0.03	24.44	1.01	0.10	81.46

Table 14 - Calculated CH_2Cl_2 Loss Data - 3 : 1 CH_2Cl_2 : H_2O

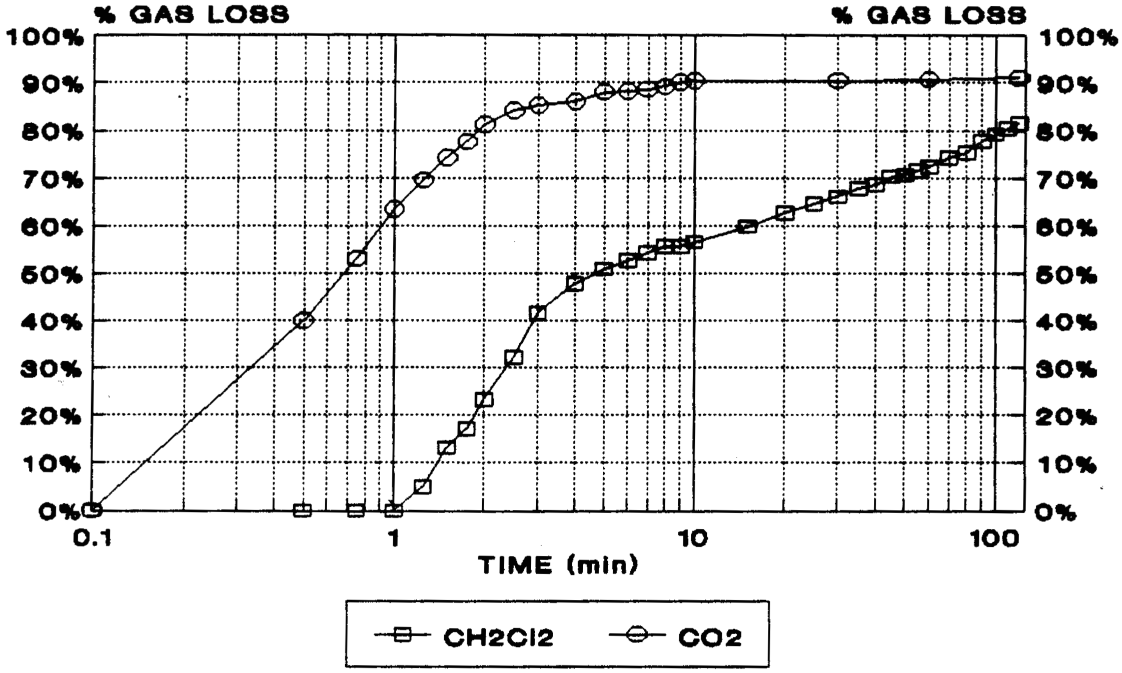

Figure 16 - Calculated CH_2Cl_2 and CO_2 Loss Profiles
3 : 1 CH_2Cl_2 : H_2O

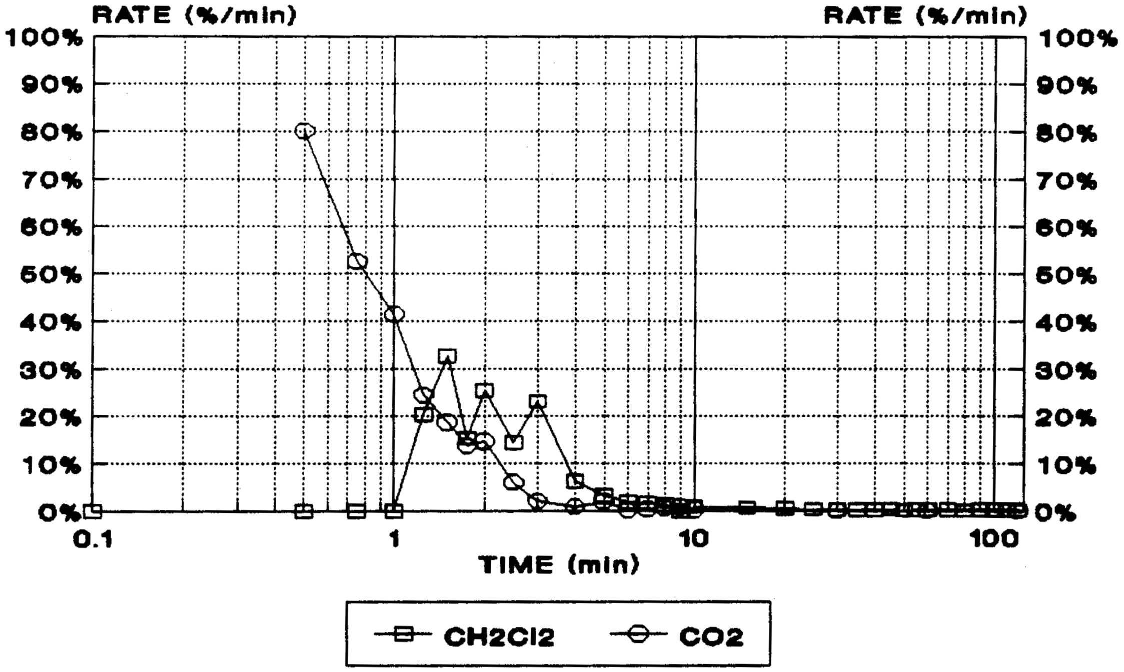

Figure 17 - Calculated CH_2Cl_2 and CO_2 Rates of Mass Loss
3 : 1 CH_2Cl_2 : H_2O

TIME min	GAS LOSS g	RATE g/min	CUM LOSS g	GAS LOSS %	RATE %/min	CUM LOSS %
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	0.00	0.00	0.00	0.00	0.00	0.00
0.75	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.21	0.84	0.21	0.53	2.10	0.53
1.25	1.72	6.88	1.93	4.30	17.20	4.83
1.50	2.12	8.48	4.05	5.30	21.20	10.13
1.75	3.03	12.12	7.08	7.58	30.30	17.70
2.00	2.10	8.40	9.18	5.25	21.00	22.95
2.25	2.10	8.40	11.28	5.25	21.00	28.20
2.50	1.51	6.04	12.79	3.78	15.10	31.98
2.75	2.06	8.24	14.85	5.15	20.60	37.12
3.00	1.21	4.84	16.06	3.03	12.10	40.15
4.00	3.48	3.48	19.54	8.70	8.70	48.85
5.00	1.18	1.18	20.72	2.95	2.95	51.80
6.00	0.81	0.81	21.53	2.02	2.02	53.83
7.00	0.75	0.75	22.28	1.87	1.87	55.70
8.00	0.54	0.54	22.82	1.35	1.35	57.05
9.00	0.21	0.21	23.03	0.53	0.53	57.57
10.00	0.32	0.32	23.35	0.80	0.80	58.37
15.00	1.54	0.31	24.89	3.85	0.77	62.23
20.00	1.01	0.20	25.90	2.53	0.51	64.76
25.00	0.68	0.14	26.59	1.70	0.34	66.46
30.00	0.57	0.11	27.16	1.43	0.29	67.89
35.00	0.31	0.06	27.47	0.78	0.16	68.67
40.00	0.58	0.12	28.05	1.45	0.29	70.13
45.00	0.42	0.08	28.47	1.05	0.21	71.18
50.00	0.42	0.08	28.89	1.05	0.21	72.24
55.00	0.04	0.01	28.94	0.10	0.02	72.34
60.00	0.37	0.07	29.31	0.93	0.19	73.27
70.00	0.51	0.05	29.82	1.28	0.13	74.55
80.00	0.62	0.06	30.44	1.56	0.16	76.11
90.00	0.57	0.06	31.02	1.43	0.14	77.55
100.00	0.46	0.05	31.48	1.16	0.12	78.71
110.00	0.46	0.05	31.95	1.16	0.12	79.86
120.00	0.67	0.07	32.62	1.68	0.17	81.55

Table 15 - Calculated CH_2Cl_2 Loss Data - 4 : 1 CH_2Cl_2 : H_2O

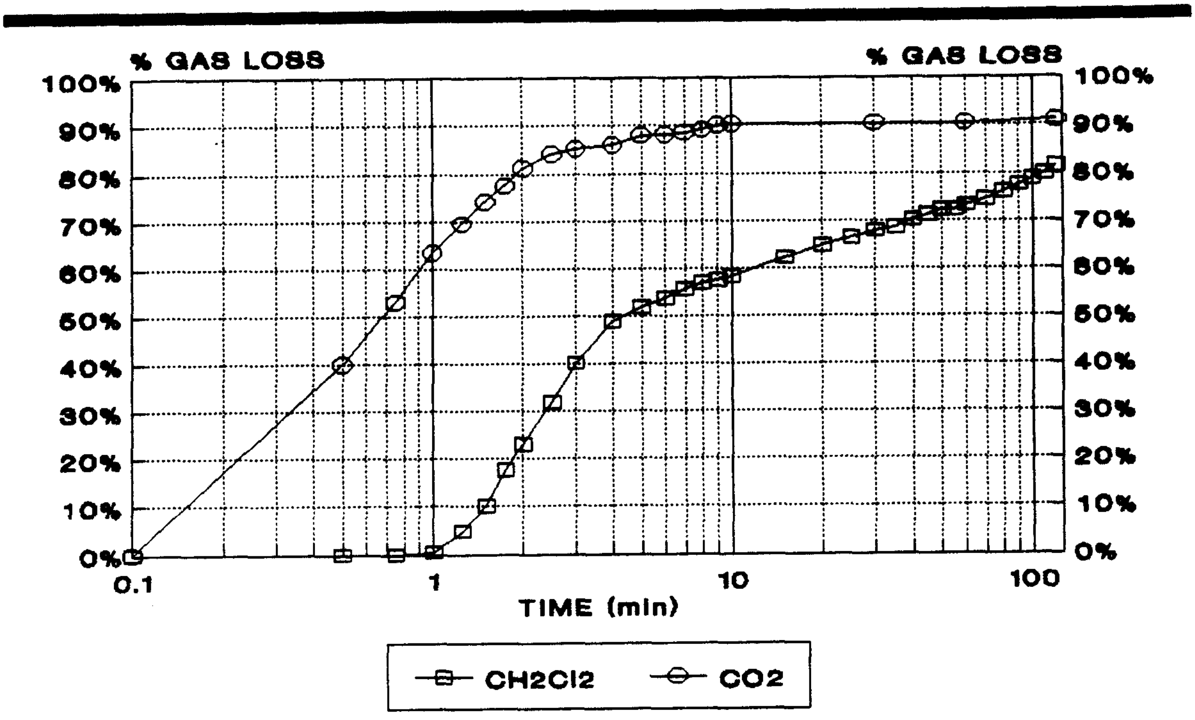

Figure 18 - Calculated CH_2Cl_2 and CO_2 Loss Profiles
4 : 1 CH_2Cl_2 : H_2O

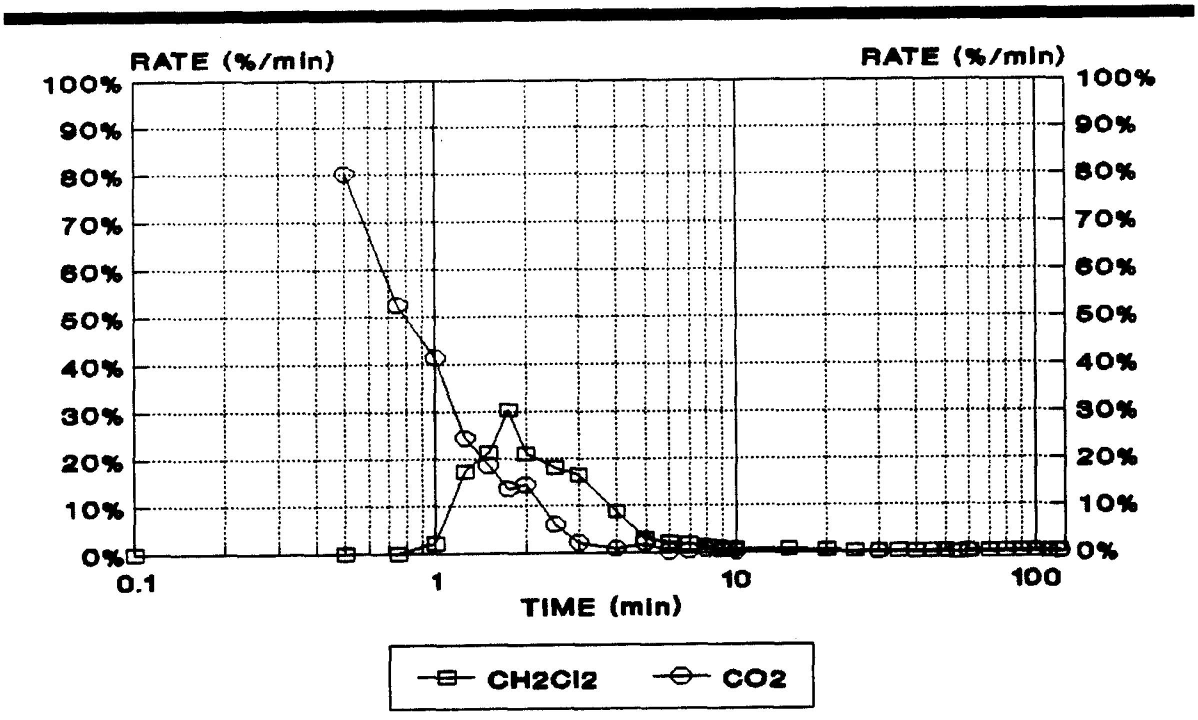

Figure 19 - Calculated CH_2Cl_2 and CO_2 Rates of Mass Loss
4 : 1 CH_2Cl_2 : H_2O

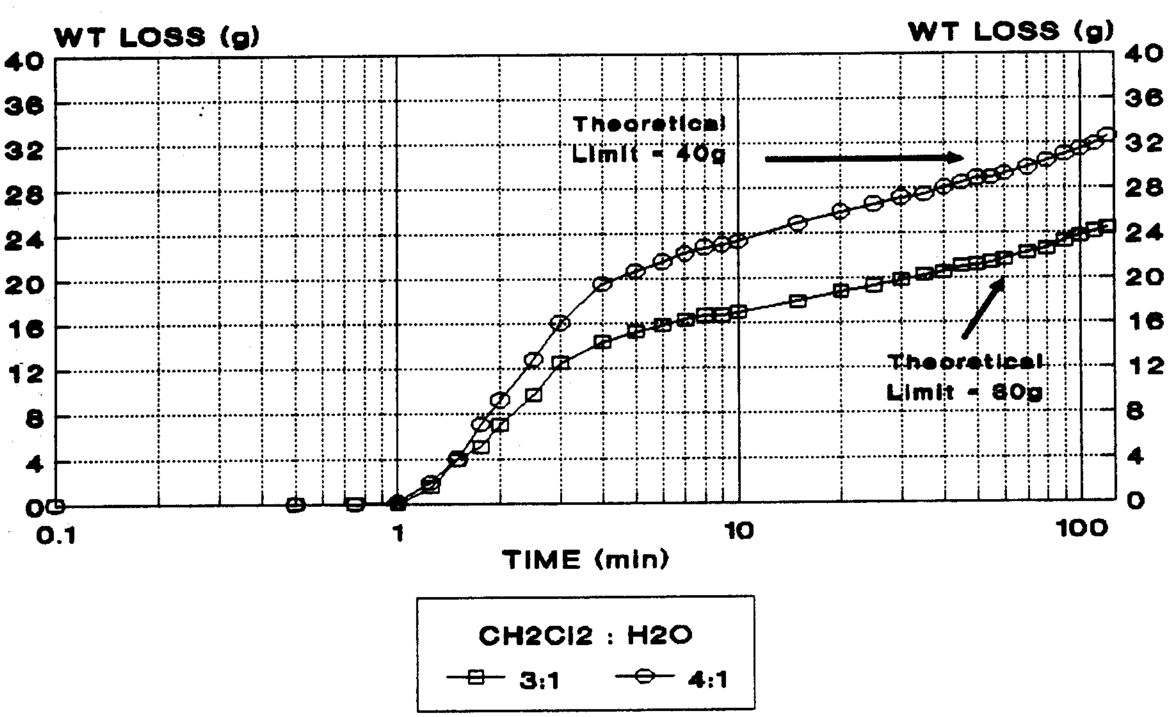

Figure 20 - Calculated CH_2Cl_2 Loss Profiles

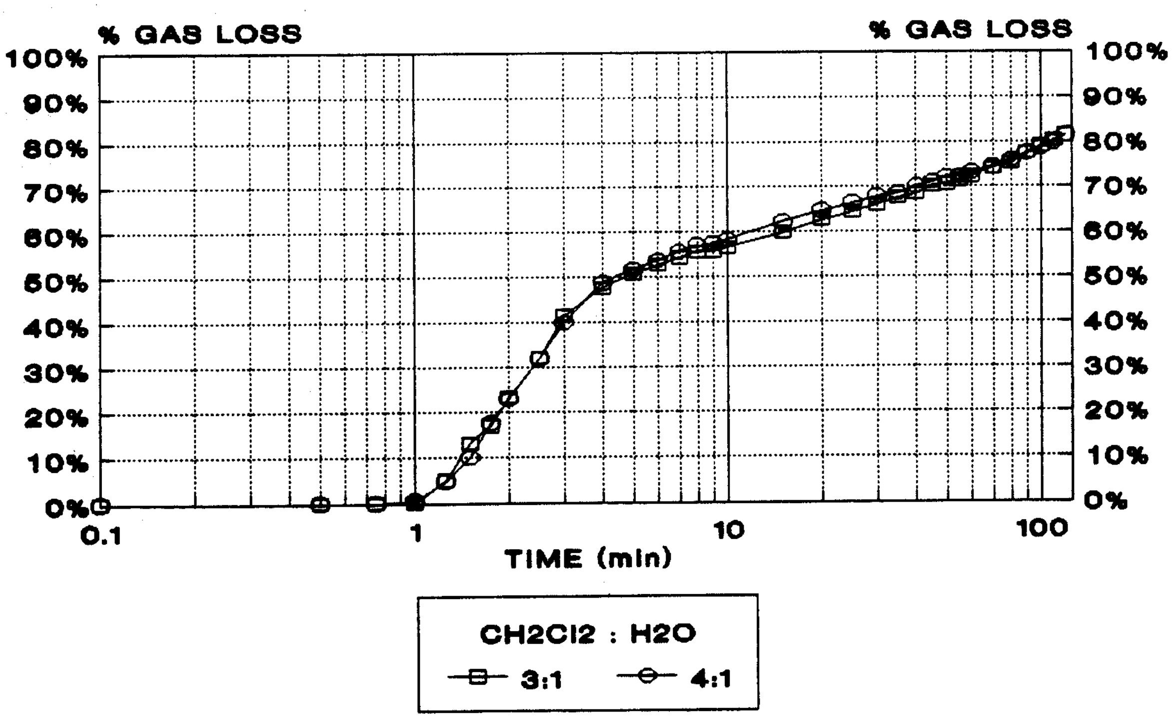

Figure 21 - Normalized CH_2Cl_2 Loss Profiles (Calculated)

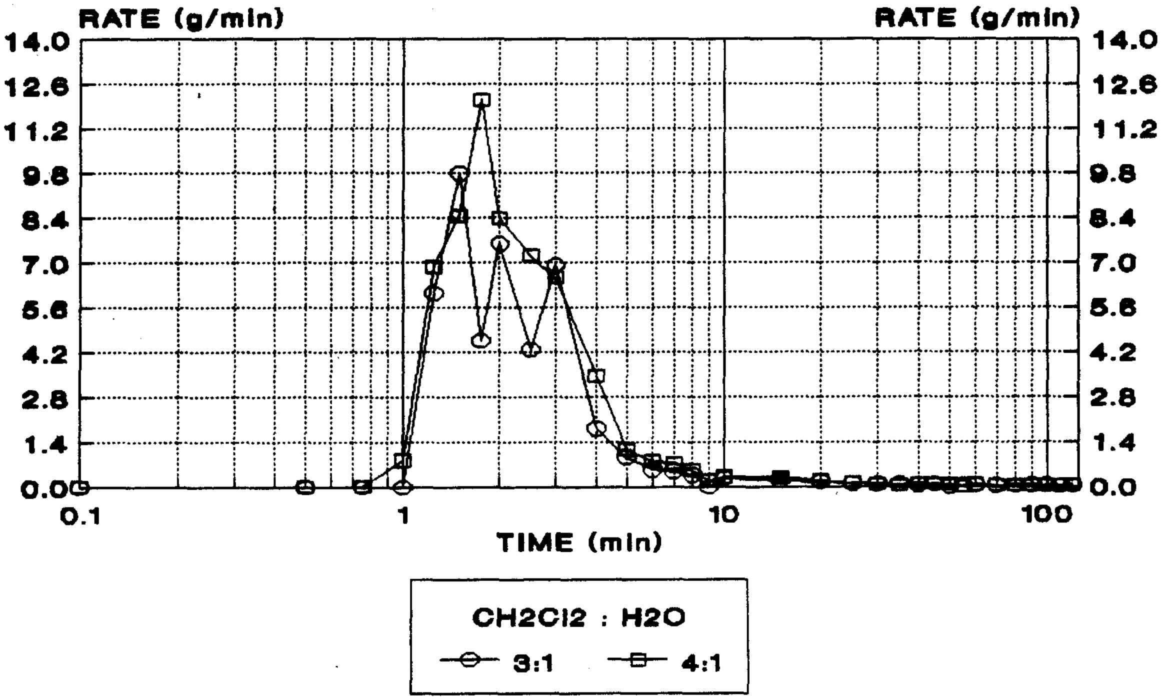

Figure 22 - Calculated CH_2Cl_2 Mass Loss Rates

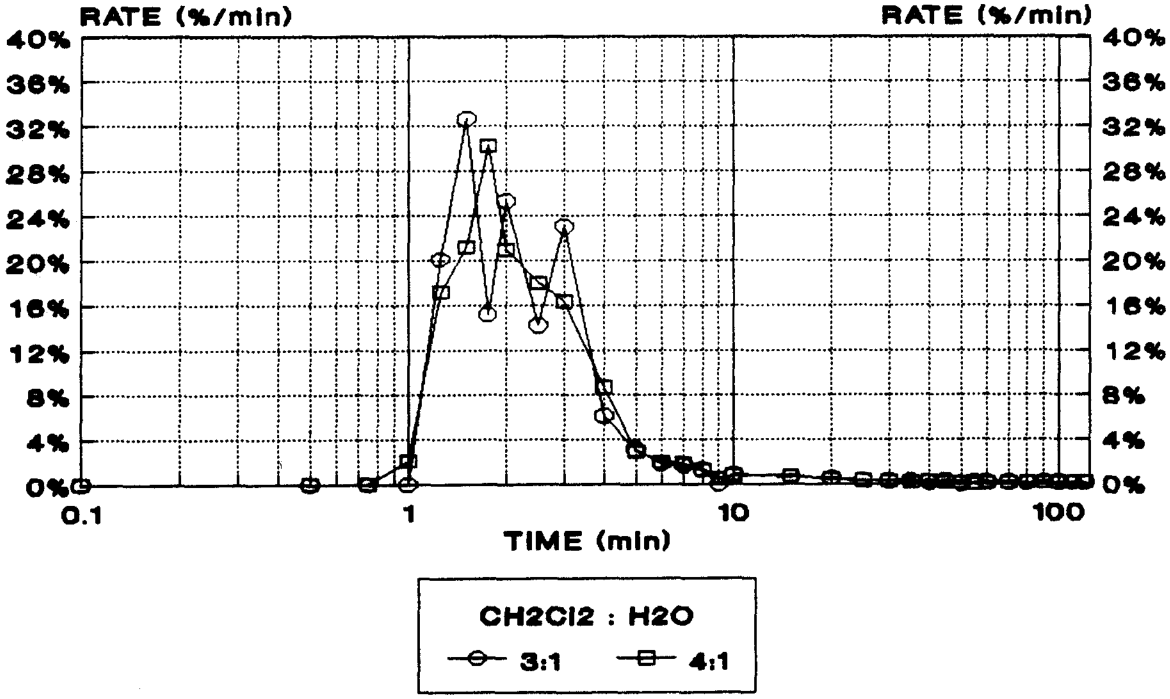

Figure 23 - Normalized CH_2Cl_2 Rates of Mass Loss (Calculated)

DuPont[4] investigators utilized an organic vapor analyzer, a portable gas chromatograph and an infrared analyzer (the preferred method) to determine the CFC (F-11) emissions profile from flexible polyurethane foam plants. They concluded that 50-60% of the chlorofluorocarbon employed can be captured in the first six minutes after pour and before the cut-off saw (Figure 24). Furthermore, they observed in the manufacture of super-soft (low density) foams that approximately 5% of the CFC is emitted immediately after pouring while in the fluid state. Thus, relatively little appears to be lost during foam rise until the time of cell rupture. Following rupture, which occurred 2-4 minutes after pour, emissions began at a rapid rate of approximately 14%/minute followed by a rapid decrease in emission rate. Cutting of the bun accelerates the loss rate by introducing fresh surfaces to the air (Figure 25). DuPont data on F-11 loss are compared to calculated CH_2Cl_2 loss in Figures 26 and 27; the shape and magnitude of the mass loss curves are comparable. However, the data surprisingly displays that CH_2Cl_2 comes off earlier and more rapidly than CCl_3F and may relate to the approximations used to generate the CH_2Cl_2 loss curve. A relatively small time shift (<30 seconds) would significantly shift the CH_2Cl_2 loss data and alter any conclusions. Realistically, in the manufacturing operation, the temperature rise of the foam mass is quite rapid. The time differential to reach the boiling point of CCl_3F (75°F) and the boiling point of CH_2Cl_2 (104°F) would be expected to be small and therefore insignificant. Using temperature data collected at NCSU (discussed in a later section), the time differential between the two temperatures is less than one minute. Therefore, the loss behavior of CH_2Cl_2 and CCl_3F from polyurethane foams are expected to be quite similar.

Unifoam AG (Switzerland)[21] also conducted investigations of gas emissions from F-11 blown flexible polyurethane slabstock which were in conjunction with the design and development of a completely enclosed batch foam manufacturing process. Although the formulations were not listed, foams ranged in density from 1 to 2.5 lbs per cubic foot. The author reports preparing foam in a small cup and then placing the cup on an electronic balance. The loss of 28-30% of the theoretical gas loss took place in the first 4-5 minutes of the foaming process. If the polyethylene film on the sides of the foam was not removed, it was possible to retain the rest of the gas production for more than an hour in the mold and after 75 minutes, the gas exchange started and would be finished after 28 hours. If the polyethylene film was removed 4 minutes after full rise, the residual gas would evolve in 70 minutes (Figure 28). Tests were conducted on larger samples (0.75m x 1.2m x 0.8m) with conclusions similar to the cup tests. Approximately 30% of the generated fumes left the system via the top surface and 3-4 minutes after full rise, the remaining 70% diffused after a small panel in the bottom of the mold was opened. The surface of this panel was 2% of the total area of the bottom surface. The author observed that 90% of the total gas generation was exchanged for air in less than 20 minutes and complete exchange was achieved in approximately one hour independent of the foam formulation (Figure 29). The final tests involved pulling the generated fumes away from the foam top surface and after 10 minutes, traps at the bottom of the foam were opened and heavier fumes (F-11 and CO_2) were extracted into a filtering system. Greater than 80% of the F-11 was captured on an active carbon filter. In analogous experiments using methylene chloride, greater than 65% of the CH_2Cl_2 was recovered.

Two Unifoam observations are consistent with NCSU data (Figure 30). First, approximately 30% of the total weight loss occurs in the first 3-4 minutes. Second, normalized weight loss rates are independent of formulation. However, there are several anomalies in the small-scale (cup size) Unifoam data. The data show a two phase loss profile but the loss rate levels off much quicker and at a significantly lower level than either the NCSU or the Dupont studies. Additionally, it is unclear why no gas loss was recorded prior to 2 minutes, and why there was an acceleration of weight loss rate at 150 minutes. For the tests where the polyethylene film was removed 4 minutes after full rise, the weight loss profile is nearly linear wehn plotted against the log of elapsed time. After exposure of fresh surfaces, it would be expected that there would be a surge in gas loss followed by a flattening in the weight loss profile as the diffusive stage was attained quicker. These inconsistencies remain unexplained.

Researchers at Union Carbide[2] utilized infrared analyses to identify the chemical species present in the reacting foam and to determine the order and relative loss rates of these species. In the work described, three water-blown urethane formulations were used to produce foams with a density of 2.0-2.6 lb/cubic foot. Foam preparation involved intensive mixing in a baffled one quart container for 60 seconds prior to pouring into an open one or two gallon container. The end of mixing was taken as time "zero" for kinetic measurements from which foam rise profile, foaming pressure, gel profile, and carbon dioxide evolution were monitored. For the formulations investigated, the maximum rate of foam rise occurred 20-40 seconds after the end of mixing and full foam rise (5-6 inches) was achieved in about 3 minutes. At the lowest water concentrations, foam rises more abruptly but reaches a maximum at about the same time. For these formulations, the maximum foam pressure (measured with a transducer at the side near the bottom of the container) of 0.02-0.03 psig was observed at about the same time as the maximum rate of foam rise. A foam viscosity (calculated from the foam pressure and rate of rise) of 104 cps was attained between 30 and 60 seconds after the end of mixing. The authors conclude that the very low foaming pressure in free-rise coupled with the rapid rise rate intuitively supports a low liquid phase viscosity (about the same as the virgin polyol).

Union Carbide researchers also used Karl Fischer titrations to determine the water content in a reacting foam mass. The reaction of water appeared to follow first order kinetics during the first minute of foaming. In a separate experiment, nitrogen (as a carrier gas) was passed over the foam mixture which had been poured into a closed container. The carrier gas was then sparged into lime water and a cloud point detector was used to detect a surge in carbon dioxide. A surge in carbon dioxide was observed coincident to an inflexion in the rate of foam rise curve. Infrared analyses of carbon dioxide were performed in an analogous arrangement. Nitrogen was passed over a reacting foam mass in a closed container and analyzed in a flow through cell at 2320 cm^{-1}. The infrared data showed a maximum in CO_2 absorbance at about 90 seconds (cell opening and blow-off) from the end of mixing which corresponded to the inflexion in the rate of rise curve after which the rate of CO_2 evolution sharply declines (Figures 31 and 32). NCSU data on the rate of mass (CO_2) loss from water-blown foams are compared to the Union Carbide data in Figure 33. Analogous loss profiles are observed; i.e., the NCSU data exhibits an approximate first order loss of CO_2 through the first 2-3 minutes followed by a very rapid decline in loss rate. The discrepancy in observed times between the NCSU and Union Carbide data can be explained in terms of a difference in mixing times (10-15 seconds at NCSU versus 60 seconds at Union Carbide).

In general, the NCSU calculated data on auxiliary blowing agent loss are consistent with experimentation by other investigators. The similarities in the loss profiles for CO_2 from water-blown foams (NCSU and Carbide) and for the auxiliary blowing agents (NCSU CH_2Cl_2 and Dupont CCl_3F) lends credence to the proposed two phase loss of volatiles. The general trends observed from the Unifoam data are consistent with the other investigations; however, the discrepancies in specific behavior are at present unexplained.

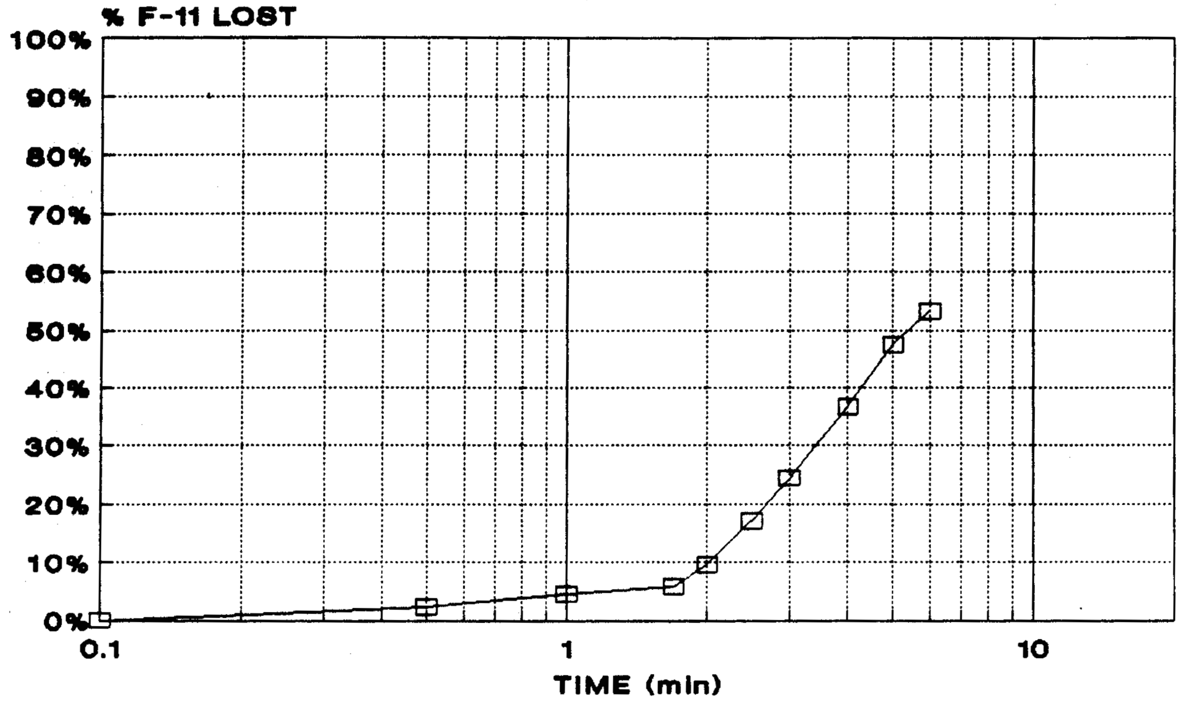

Figure 24 - Mass Loss Profile - DuPont Data

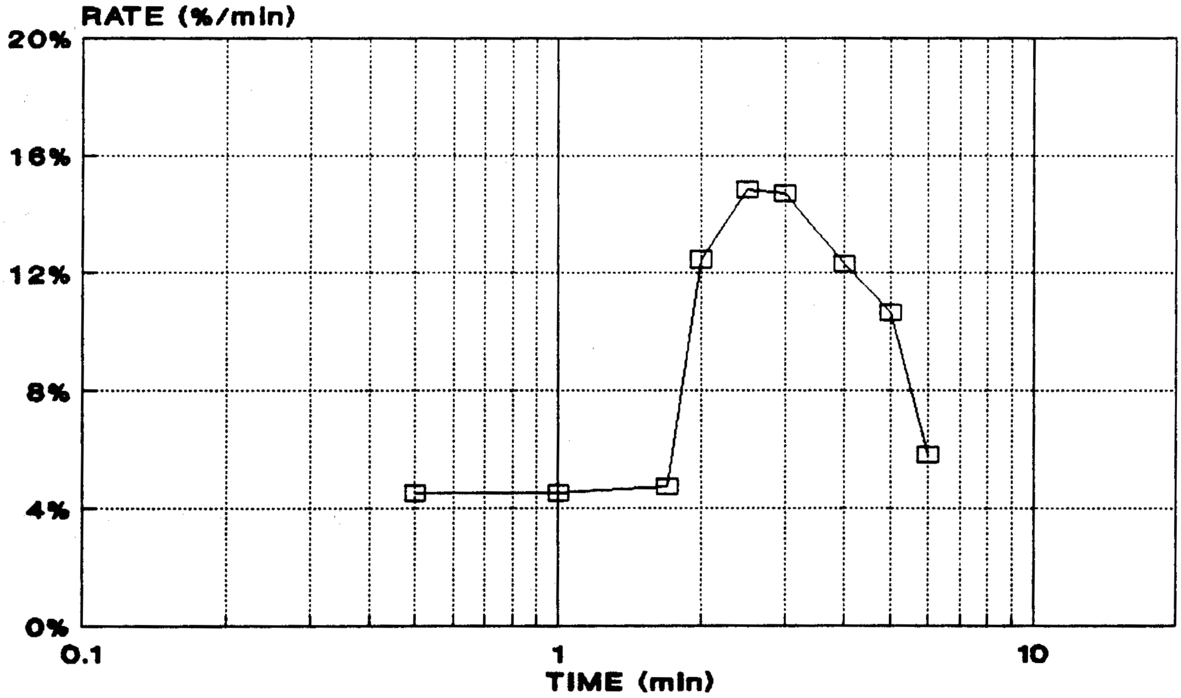

Figure 25 - Rate of Mass Loss - Dupont Data

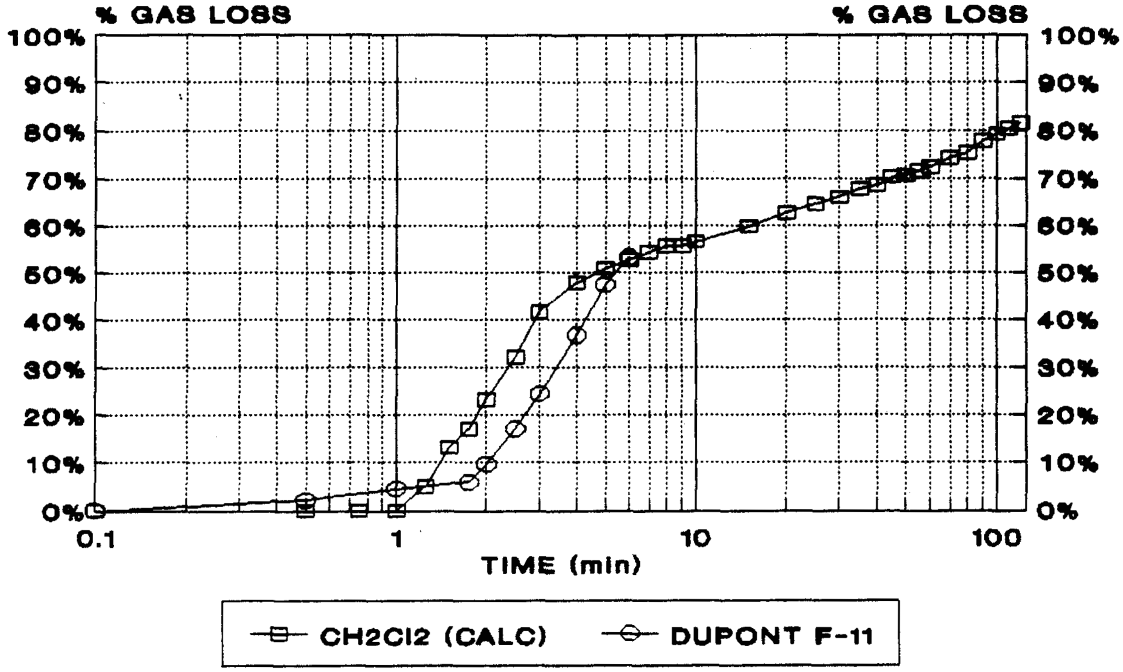

Figure 26 - Comparison of Mass Loss Profiles
Auxiliary Blowing Agents

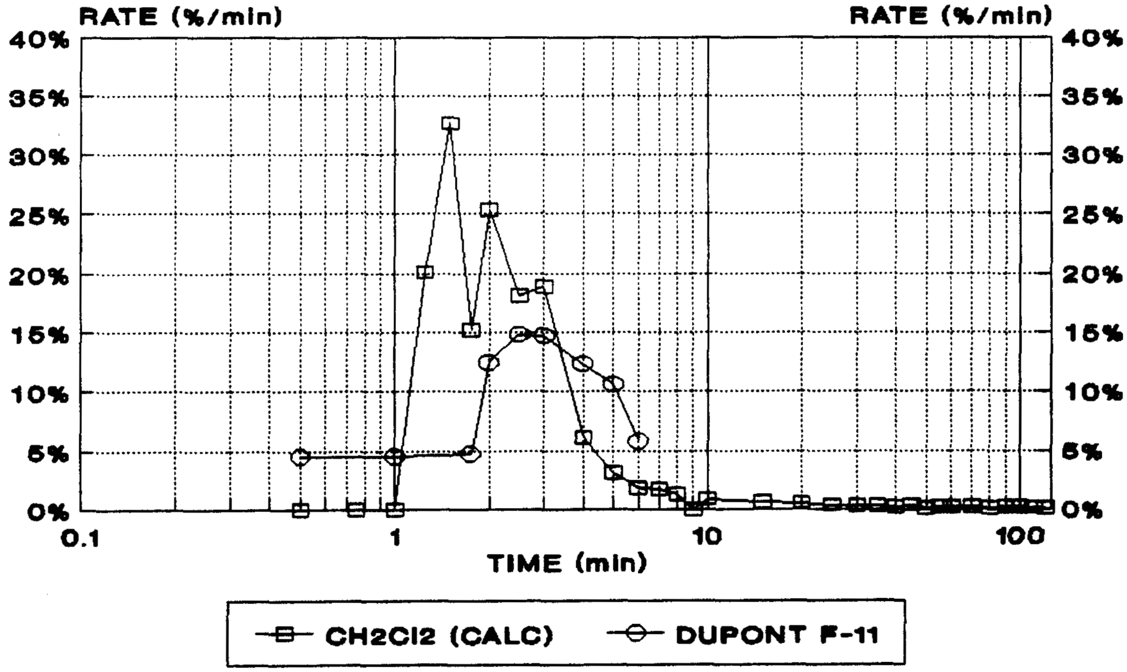

Figure 27 - Comparison of Rates of Mass Loss
Auxiliary Blowing Agents

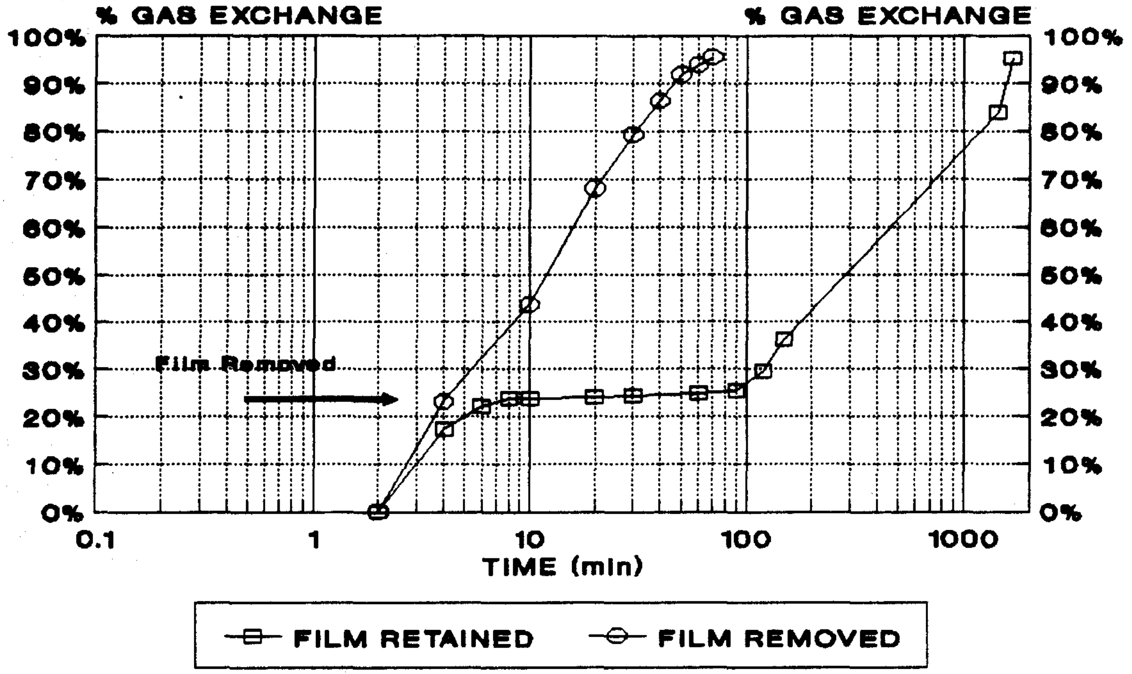

Figure 28 - Mass Loss Profile - Adapted from Unifoam Data (Small Scale)

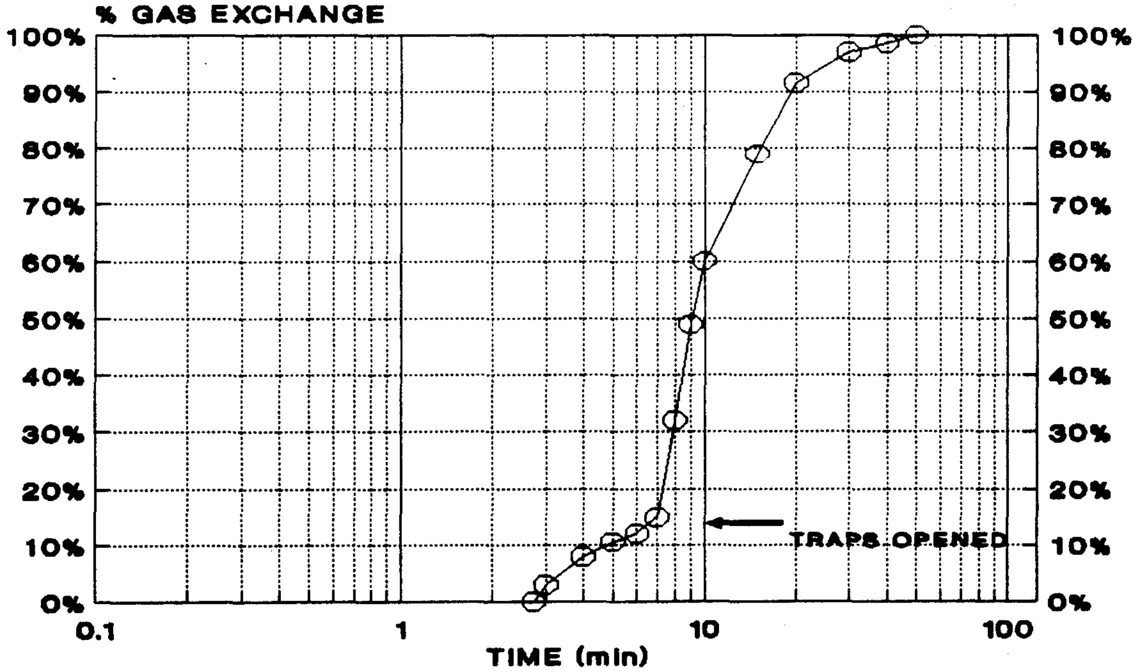

Figure 29 - Mass Loss Profile - Adapted from Unifoam Data (Large Scale)

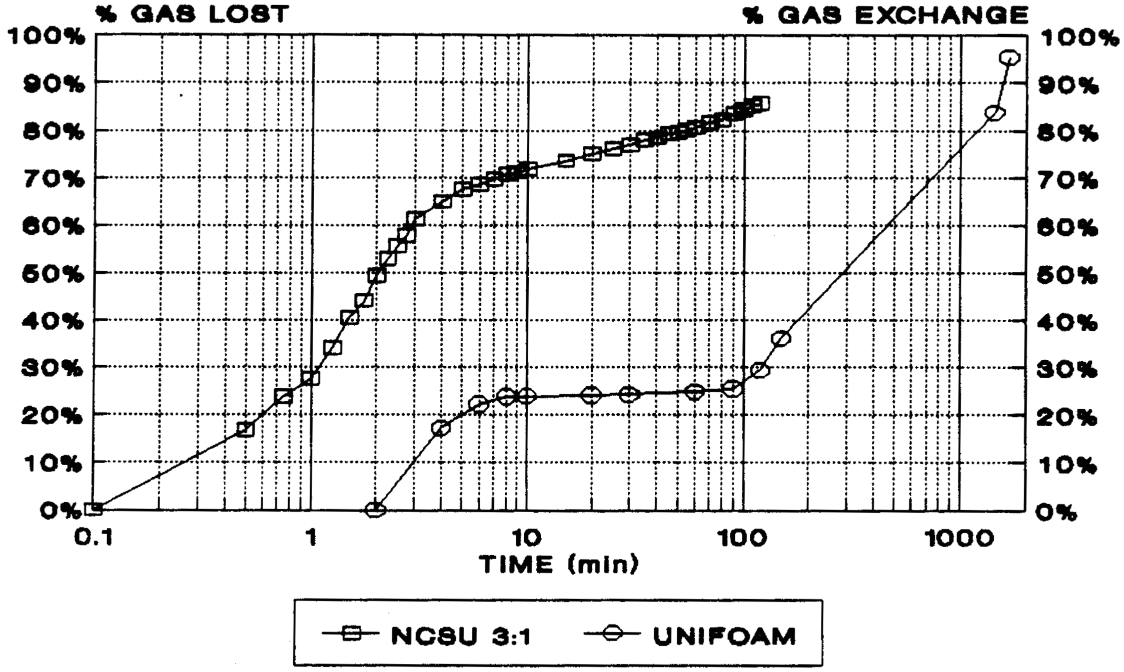

Figure 30 - Comparison of Mass Loss Profiles
NCSU vs. Unifoam Lab Data

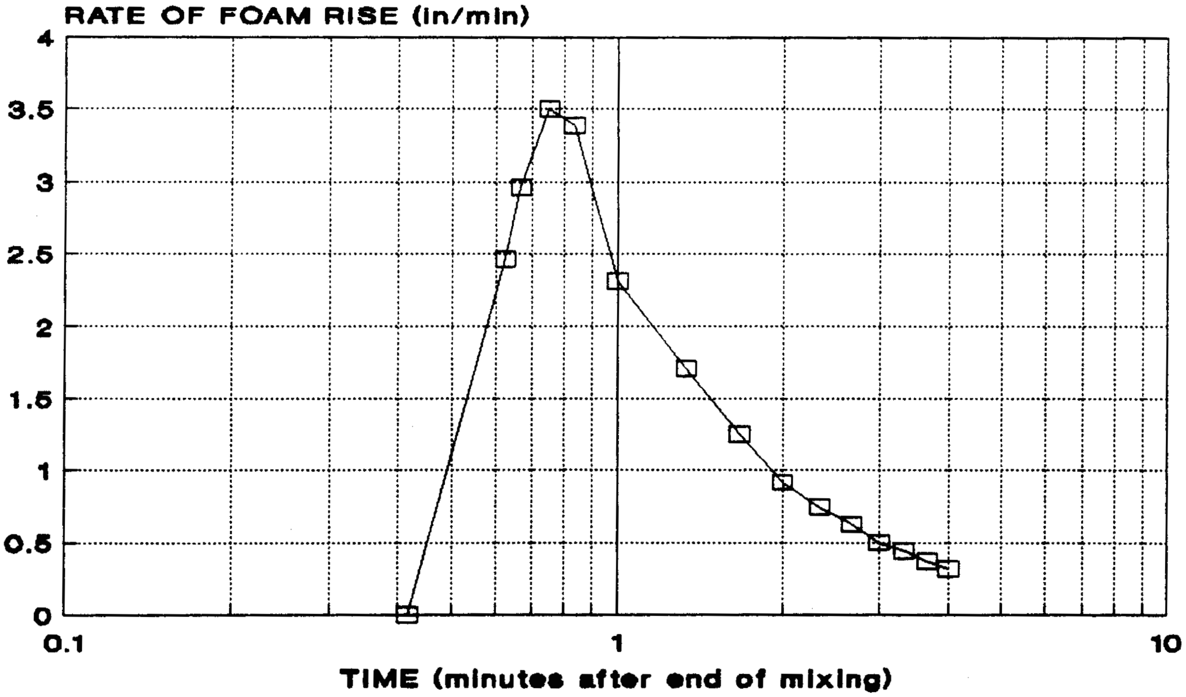

Figure 31 - Rate of Foam Rise - Union Carbide Data

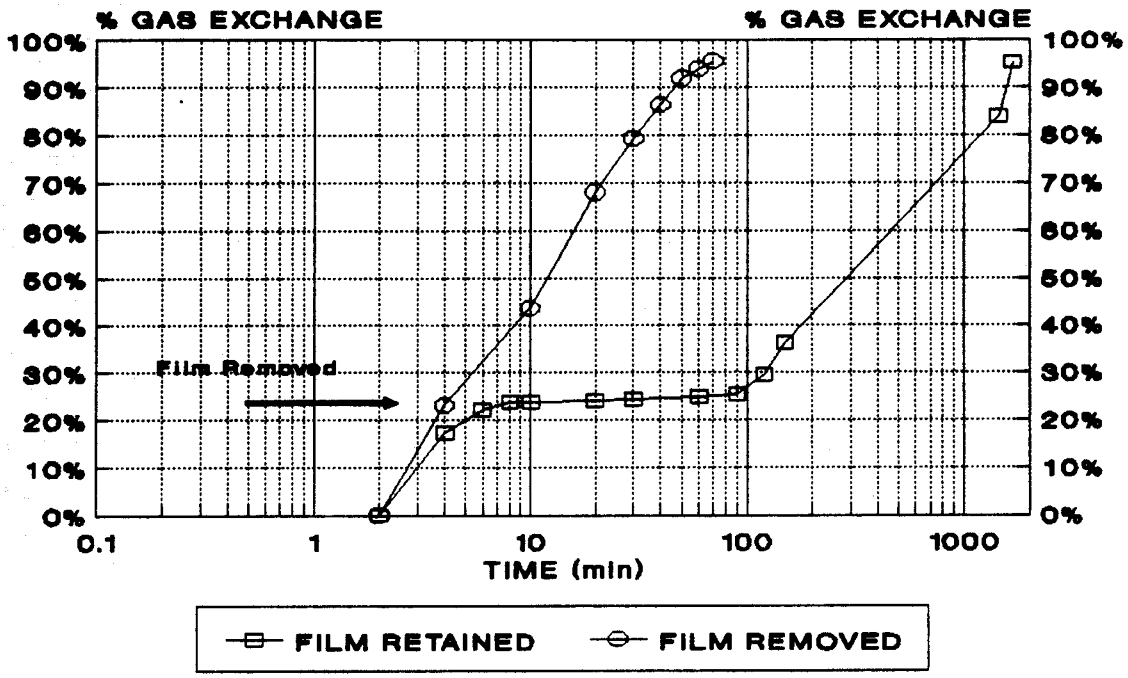

Figure 28 - Mass Loss Profile - Adapted from Unifoam Data (Small Scale)

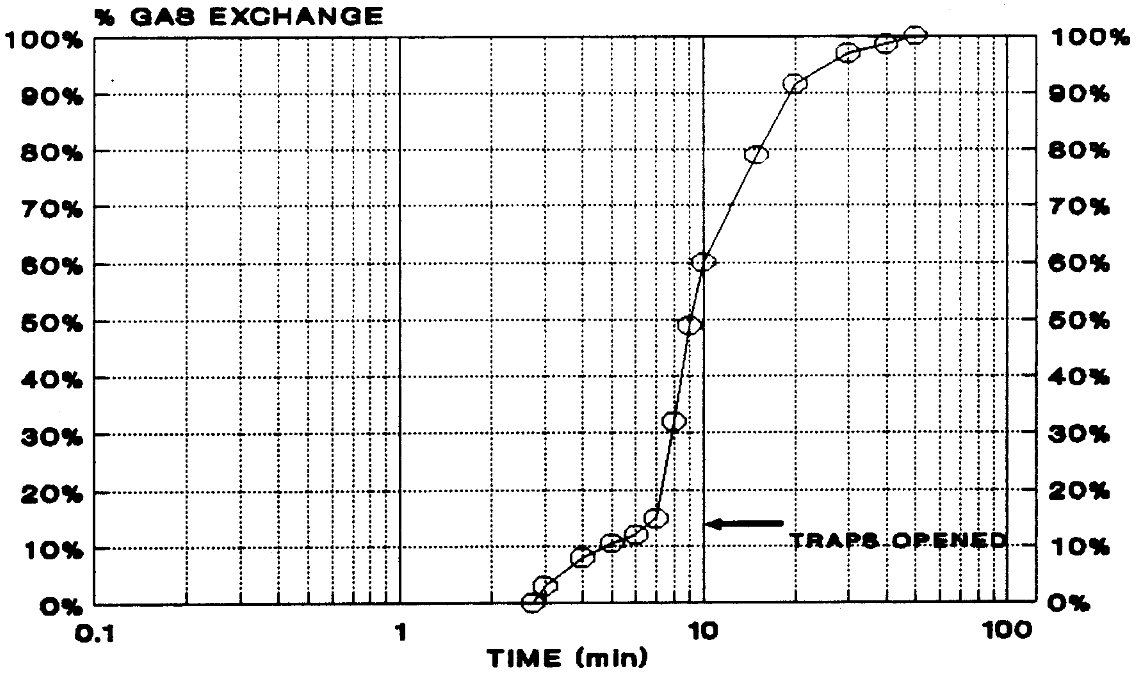

Figure 29 - Mass Loss Profile - Adapted from Unifoam Data (Large Scale)

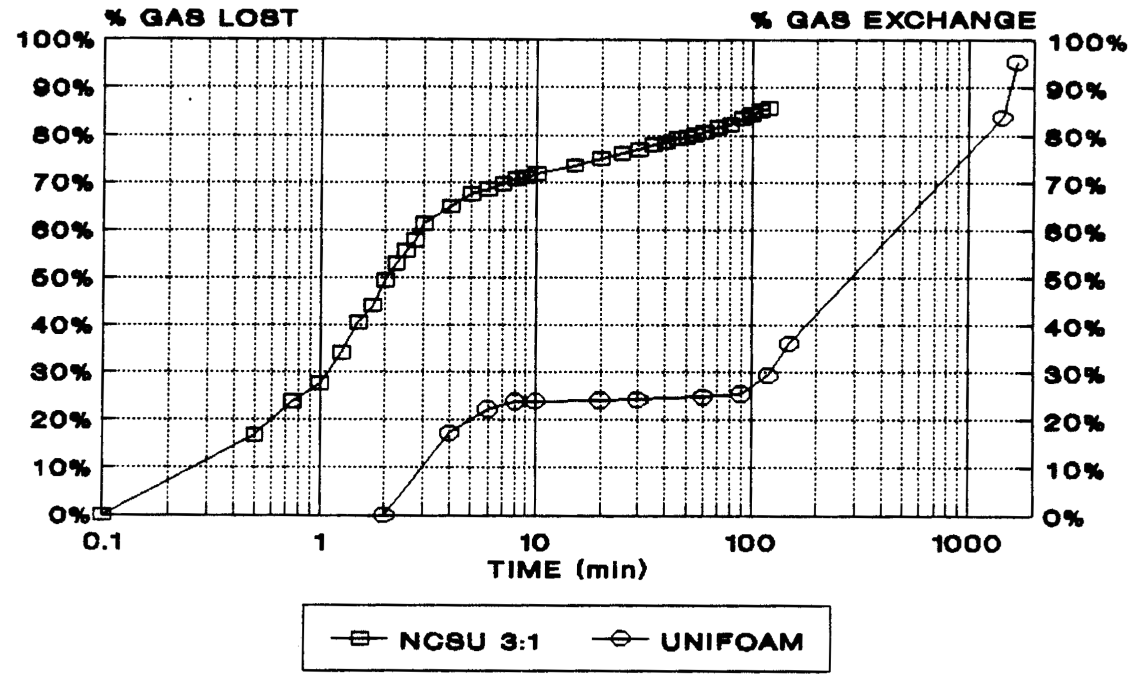

Figure 30 - Comparison of Mass Loss Profiles
NCSU vs. Unifoam Lab Data

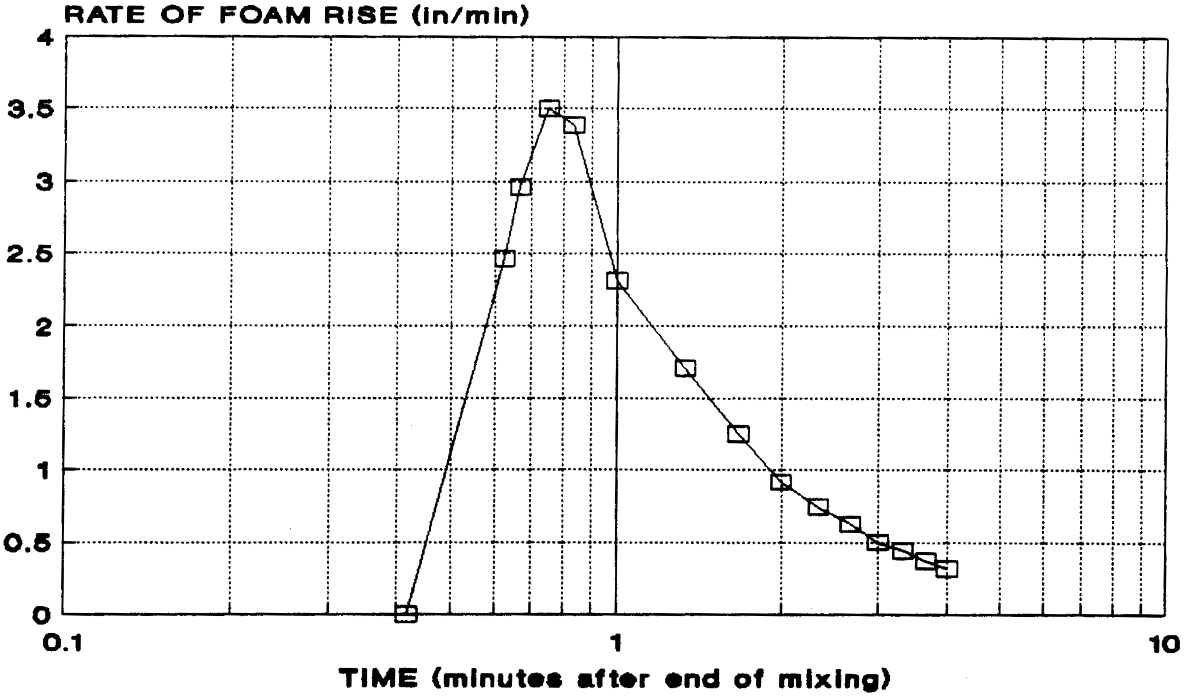

Figure 31 - Rate of Foam Rise - Union Carbide Data

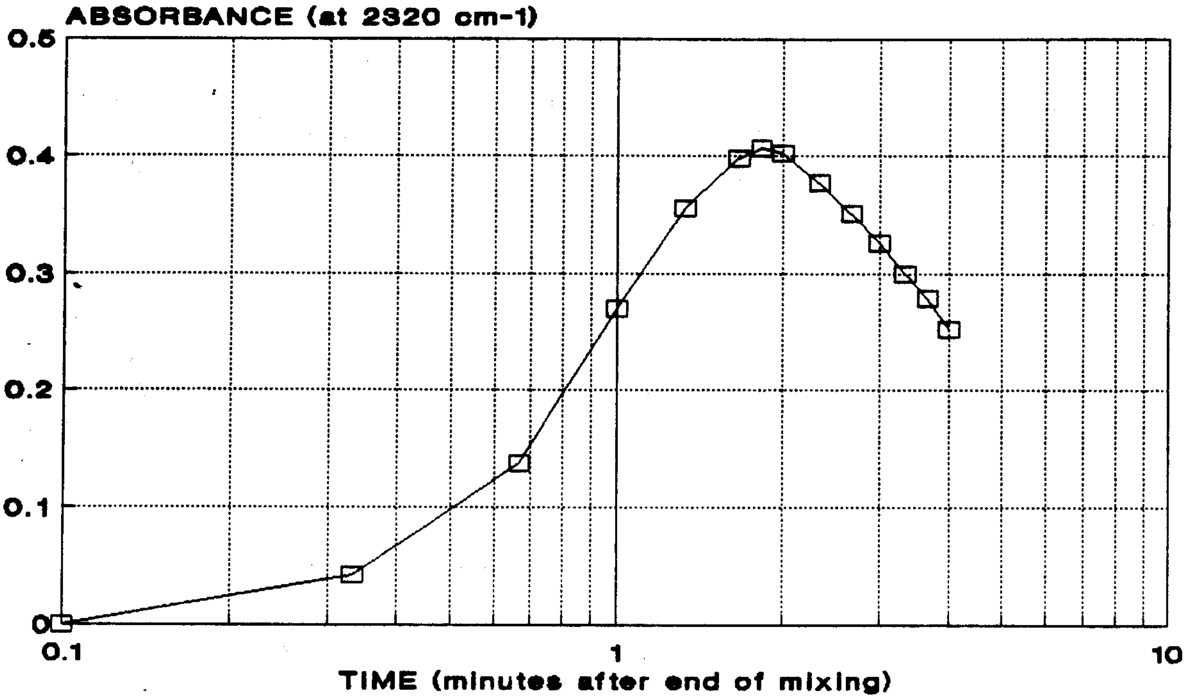

Figure 32 - Evolution of CO_2 - Union Carbide Data

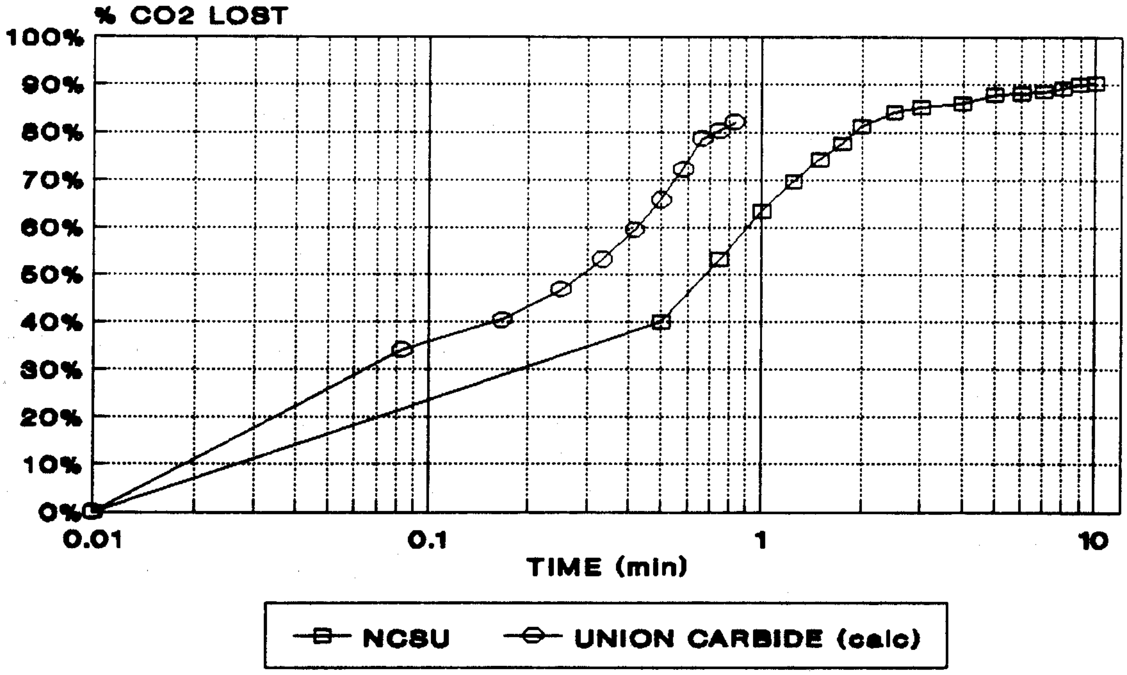

Figure 33 - Loss of CO_2 from Water Blown Foams
Union Carbide and NCSU Data

EFFECT OF VACUUM ON MASS LOSS

Recognizing the two regimes of mass loss from polyurethane foams, exploratory tests were conducted to determine whether the application of vacuum to a freshly set foam would accelerate the rate of volatile loss. These experiments address the slow diffusion of volatiles (primarily the auxiliary blowing agent) within the manufacturing curing and storage areas.

EXPERIMENTAL

Foam was prepared using the standard formulation listed in Table 6 at one-third of the normal batch weights (for a cakebox to fit in the available vacuum oven). Mass loss data were collected for foams in an open system (0 - 30 minutes). Analogous data were recorded for foams that were started in an open system (0 - 10 minutes) and then placed in a vacuum oven at ambient temperature (10 - 30 minutes). These collection times correspond to an average tunnel residence time of 10 minutes and an arbitrary post-tunnel interval of twenty minutes.

	OPEN SYSTEM	VACUUM APPLICATION
0 - 10 min wt loss	77.4%	
10 - 30 min wt loss	5.9%	21.2%
10 - 30 min loss rate	0.3%/min	1.1 %/min

Table 16 - Effect Of Vaccum On Mass Loss - 3 : 1 $CH_2Cl_2 : H_2O$

RESULTS/DISCUSSION

Mass loss data for the vacuum system are displayed in Table 16 and Figure 34. Given the dimensional change in the foam mold and the relative exposed surface area, the lack of significant differences between the mass loss profiles of the full and one-third size batch is noteworthy. The data demonstrate a significant effect of vacuum application on the rate of diffusive losses from polyurethane foams. The application of vacuum increases the rate of volatile loss from set laboratory foams by at least three-fold. Additional experimentation needs to be conducted to quantify the degree of vacuum, optimum temperature, and actual time required to collect the residual volatiles from a foam block. The feasibility of vacuum utilization coupled with entrapment by condensation within the manufacturing environment is unknown.

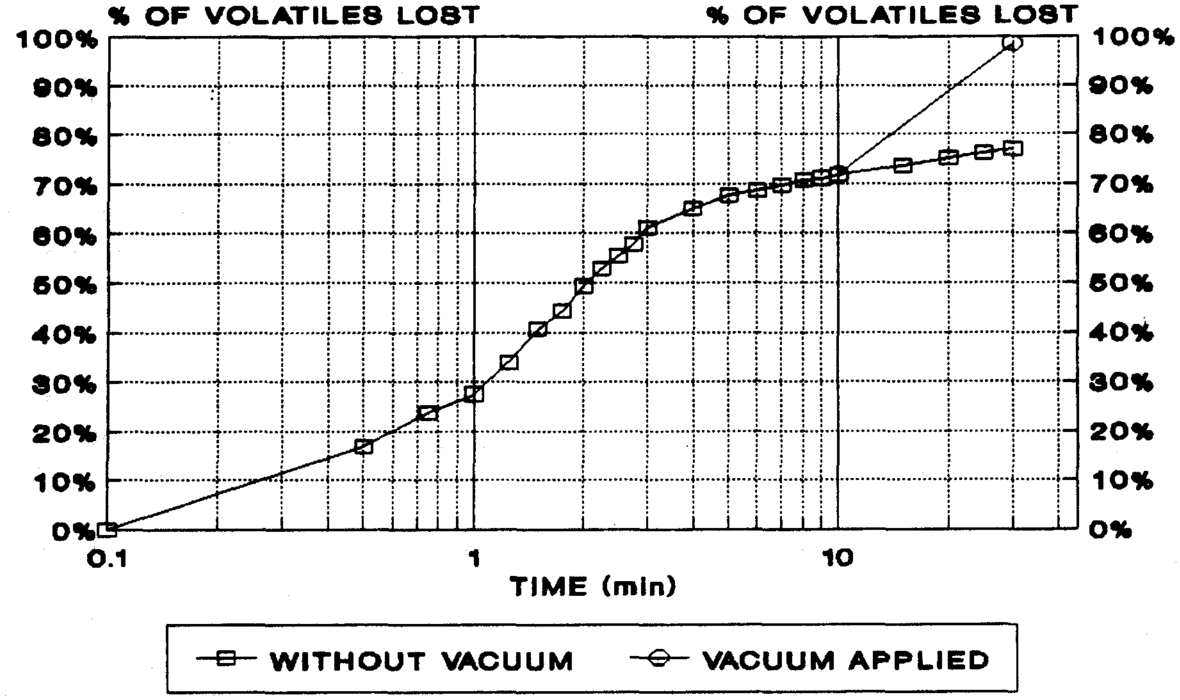

Figure 34 - Effect of Vacuum Application on Mass Loss
3 : 1 CH_2Cl_2: H_2O (1/3 Batch)

INTERNAL FOAM TEMPERATURE MEASUREMENTS

Reactions of the isocyanate with water, polyol, and urethanes are all highly exothermic. Internal foam temperature measurements were recorded to establish the rate of heat generation in this system. Cross-linking reactions during the curing period are also be affected by the way generated heat is conserved in the system or lost to the environment. Measurements of the time dependent temperature profiles at various spatial locations within insulated and uninsulated foams were used to determine the effects of convective and conductive heat losses.[16]

EXPERIMENTAL

Six calibrated copper-constantan thermocouples were supported on a laboratory stand and located in an empty mold box to correspond to the desired points of measurement. The foam mold was placed inside a larger box. Polyurethane foam was tightly packed in the 2-3 inch spaces (sides and bottom) between the foam mold and the larger box for insulation. Three different levels and three different locations were measured in insulated and uninsulated molds (not all levels and all locations were determined for each insulation condition). The three levels were chosen at 0.5", 2.5", and 4.5" from the bottom of the foam mold (foam height at full rise was approximately 6"); the three locations were 0.5" from a side, a corner, and the center of the mold. To improve reliability, readings were carried out in duplicate runs. The six thermocouples were connected to a Leeds and Northrup Speedomax H Multipoint recorder which was equipped with an internal temperature compensator and a 200 °F - 2200 °F range card. Foam was produced in the standard fashion and poured into the mold box with thermocouples appropriately positioned. Special care was taken not to pour the foam onto the thermocouples or disturb the thermocouple positions. After completion of each test, the thermocouples were carefully cleaned to prevent set foam (insulating) from interfering in subsequent runs.

RESULTS/DISCUSSION

Foam temperature data are presented in Table 17 and graphically displayed in Figures 35-38. Interior laboratory foam temperature rises at approximately a linear rate (versus log time) and reaches a maximum of 150 °F after about 15 minutes and then gradually decreases. Therefore, temperature continues to rise well after the blow off point (opening of cell structures and maximum loss of volatiles). This observation implies that the cooling effect associated with gas evolution may not significantly contribute to the heat loss of the total system. To more fully understand this effect, a series of controlled thermodynamic experiments would have to be conducted. For uninsulated laboratory foams, the initial temperature rise appears independent of the vertical position within the mold. However, as the reactions progress, the temperature at the mold bottom reaches the highest maxima. This observation indicates that heat conduction through the foam bottom surface is not a major factor; therefore, mass transfer through the foam top surface is a major mechanism of heat loss from the system. Internal foam temperatures are plotted along with the mass loss profile (Figure 39) and the calculated rate of CH_2Cl_2 loss (Figure 40). The initial loss of auxiliary blowing agent appears to nearly coincide with an internal foam temperature equal to the boiling point of methylene chloride (104 °F). There does appear to be a loss of CH_2Cl_2 at temperatures lower than its boiling point; this phenomenon was unexpected and and may relate to the fact that the CH_2Cl_2 loss data were calculated and not directly measured. If the loss of CH_2Cl_2 at temperatures below the boiling point is real, it conceivably might be explained by the thermal gradients present within the foam and that as there is a net flow of gas (CO_2) out of the system which could sweep CH_2Cl_2 in the vapor phase out of the foam.

INSULATION	N	N	N	N	N	N	I	I	I
POSITION	E	V	C	C	C	E	C	C	C
LEVEL	B	B	B	M	T	T	B	M	T
TIME(min)	TEMPERATURE READINGS (°F)								
0.5	72	75	77	75	74	77	80	77	76
1.0	93	90	89	85	78	80	94	84	80
1.5	103	99	93	97	95	83	101	97	91
2.6	108	105	101	107	105	100	109	109	106
4.6	123	116	113	120	116	118	118	125	120
6.7	136	128	122	133	115	123	128	136	125
8.8	143	135	131	141	113	125	139	144	127
10.9	148	139	139	144	110	123	148	148	126
12.9	150	140	146	146	107	122	154	150	125
15.0	150	139	149	146	105	122	157	150	124
17.1	149	136	152	144	103	117	159	148	121
19.2	147	134	153	142	100	114	160	146	118
21.2	144	131	153	139	98	111	160	144	116
26.4	135	123	150	131	93	106	159	137	110
31.6	127	116	145	123	90	101	154	130	106
36.8	117	110	139	116	87	98	149	123	101
42.0	114	104	134	111	85	95	143	118	98
47.1	109	100	125	106	84	91	138	113	95
52.3	105	97	119	102	83	90	132	108	93
57.5	102	93	114	98	81	88	127	105	91
62.7	96	91	111	95	81	86	122	101	89
73.0	91	87	101	90	79	84	117	96	86
83.4	89	87	91	89	79	84	109	92	84
93.8	87	85	88	87	78	82	103	90	83
104.1	85	83	86	85	77	81	98	87	82
114.5	83	82	85	83	77	80	95	85	81
124.9	81	80	82	81	76	79	93	84	80

INSULATION: N = NON-INSULATED I = INSULATED
POSITION: E = EDGE V = CORNER C = CENTER
LEVEL: B = BOTTOM M = MIDDLE T = TOP

Table 17 - Interior Foam Temperatures - 3 : 1 $CH_2Cl_2 : H_2O$

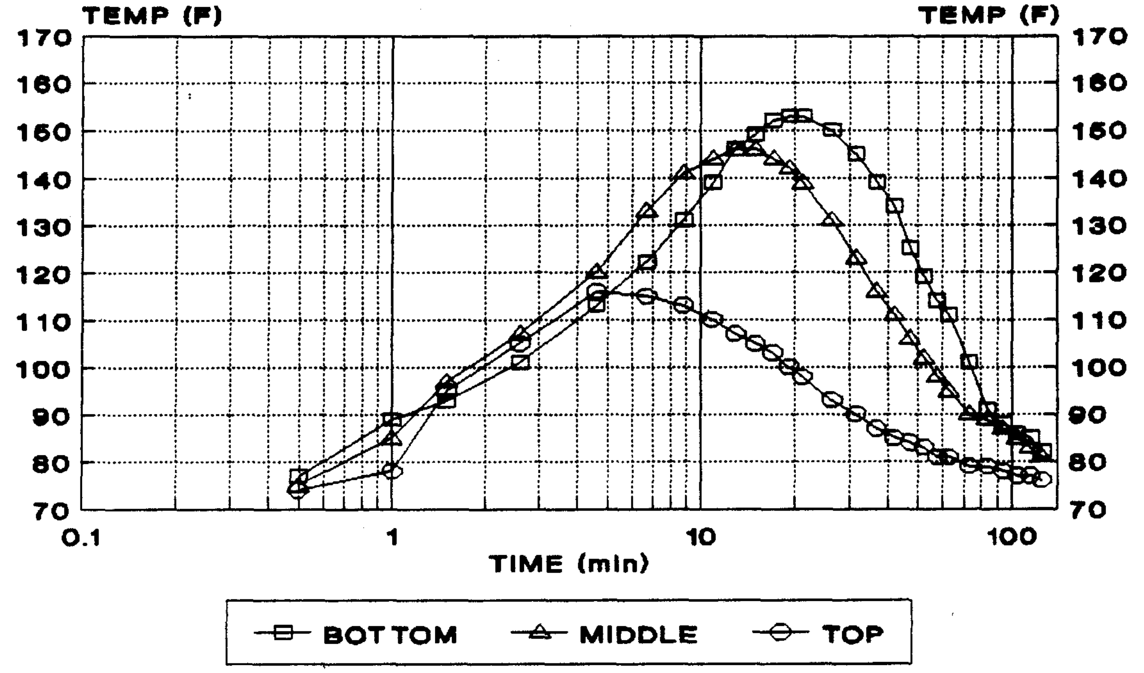

Figure 35 - Interior Foam Temperatures - 3 : 1 CH_2Cl_2: H_2O
Non-insulated Foams (Center of Mold)

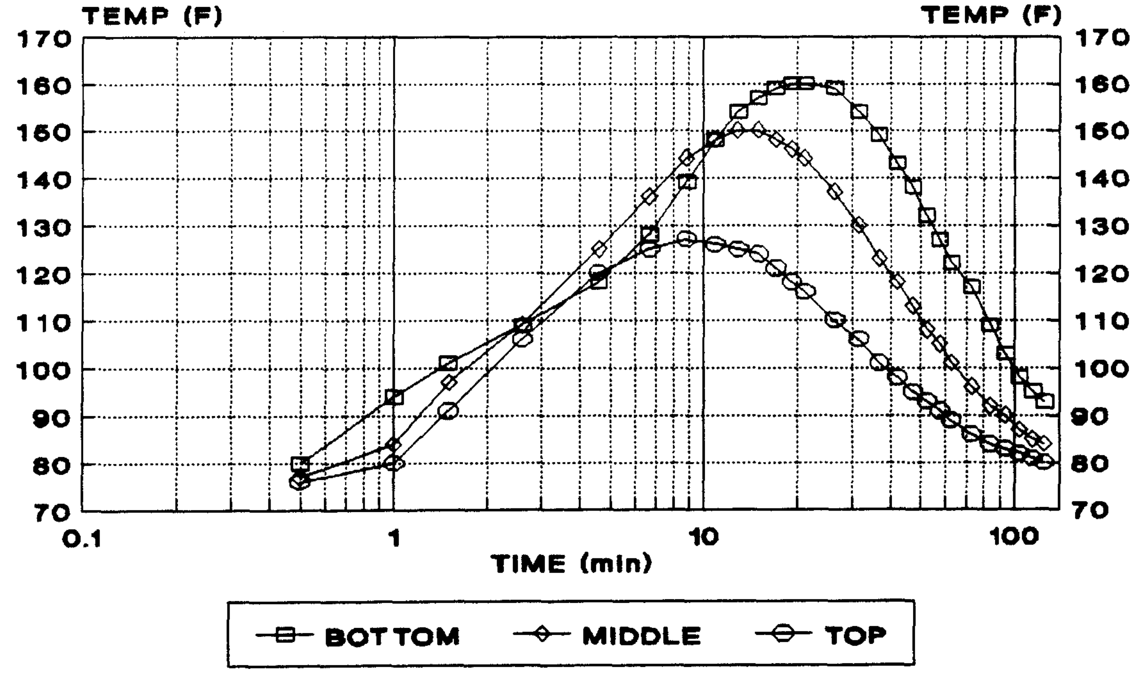

Figure 36 - Interior Foam Temperatures - 3 : 1 CH_2Cl_2: H_2O
Insulated Foams (Center of Mold)

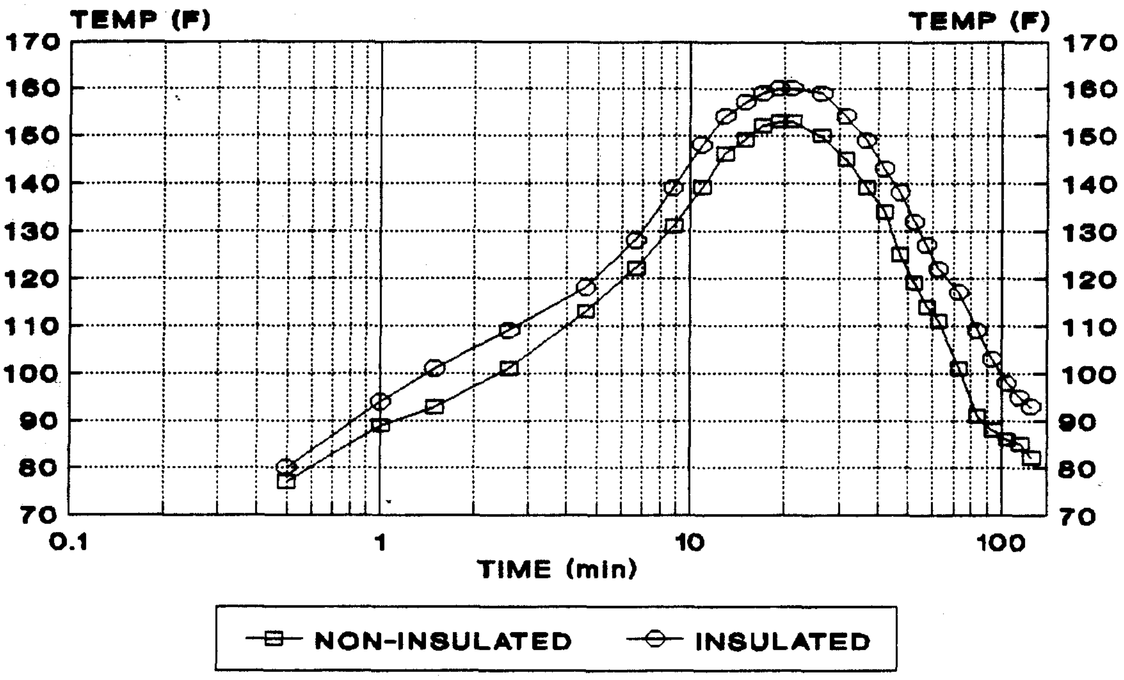

Figure 37 - Interior Foam Temperatures - 3 : 1 $CH_2Cl_2 : H_2O$ Insulated vs. Non-insulated Foams (Bottom of Mold)

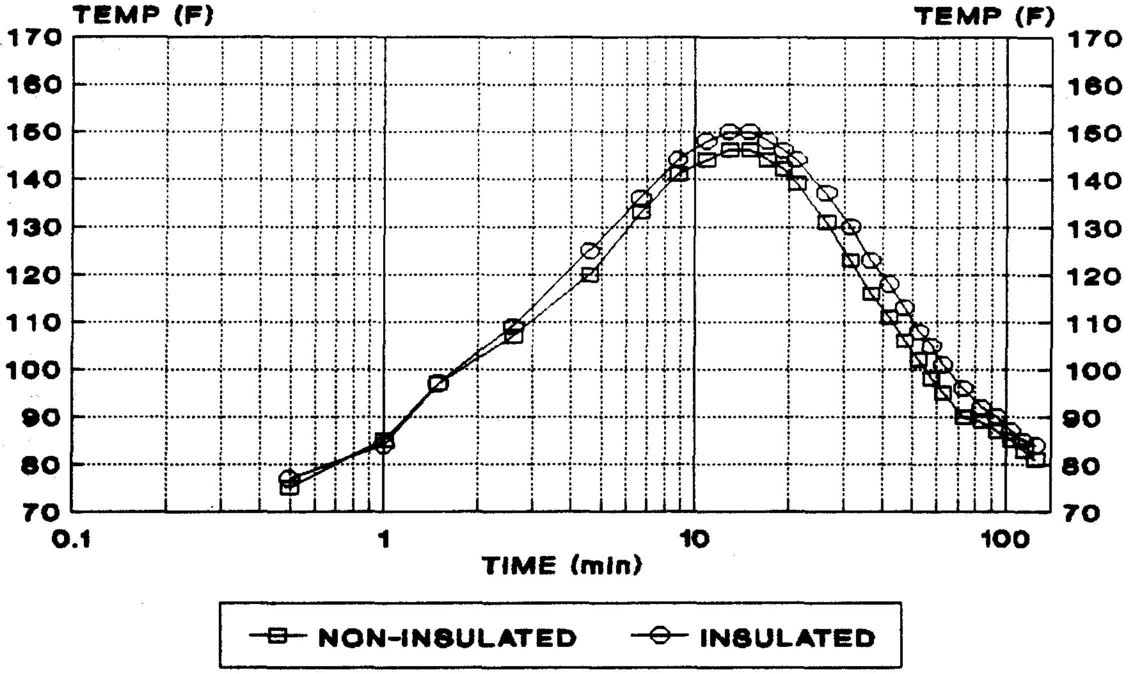

Figure 38 - Interior Foam Temperatures - 3 : 1 $CH_2Cl_2 : H_2O$ Insulated vs. Non-insulated Foams (Center of Mold)

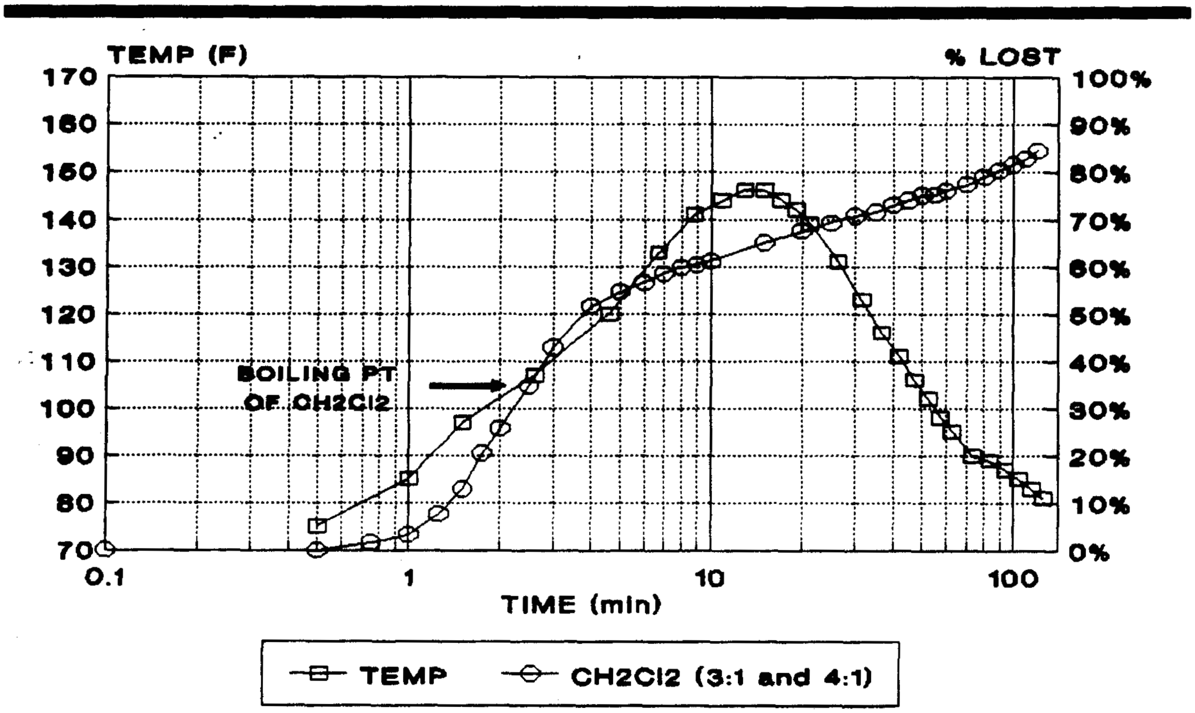

Figure 39 - CH_2Cl_2 Mass Loss and Interior Foam Temperatures
3 : 1 CH_2Cl_2 : H_2O

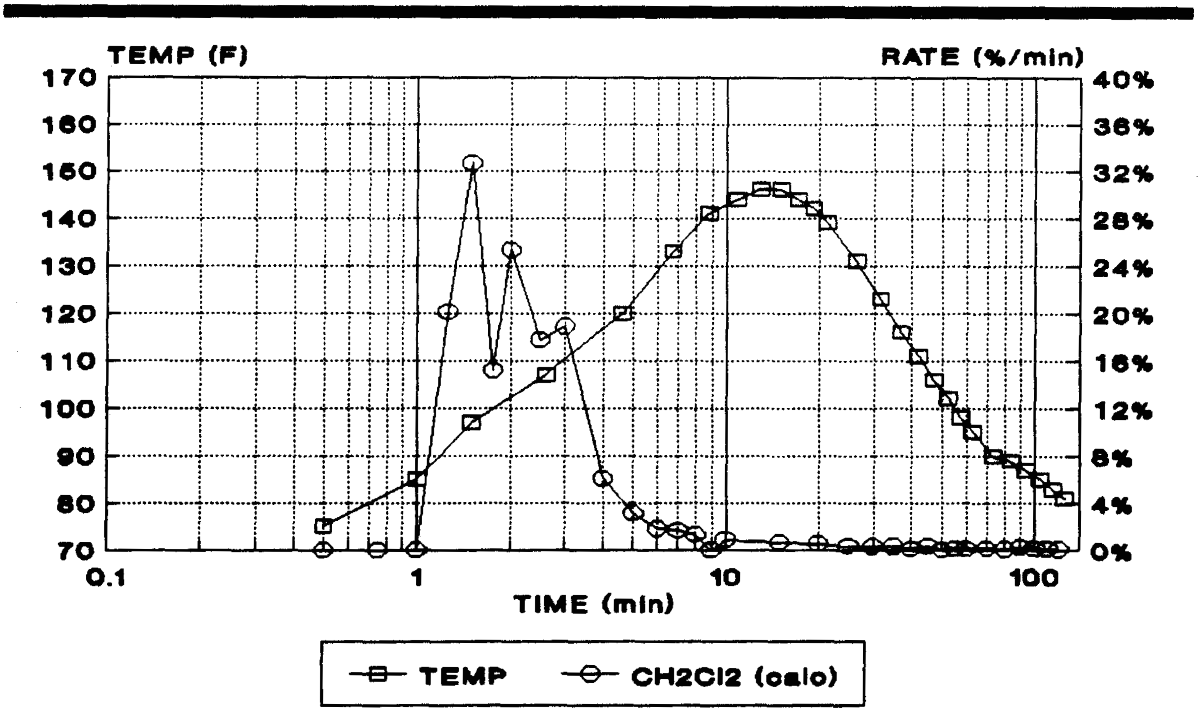

Figure 40 - Rate of CH_2Cl_2 Loss and Interior Foam Temperatures
3 : 1 CH_2Cl_2 : H_2O

COLLECTION OF MANUFACTURING MASS LOSS DATA

Data were collected at three polyurethane manufacturing plants for comparison to and validation of laboratory experiments. Two of the plants (Hickory Springs and Leggett and Platt) utilize methylene chloride while the third plant (Olympic Products) utilizes trichlorofluoromethane (CFC-11) as the auxiliary blowing agent.

EXPERIMENTAL

Formulations for each foam and input material flow rates are displayed in Table 18. Samples of production foam were cut and suspended; periodic mass loss data on each bun were obtained using a load cell. Initial bun weight (i.e., sum of input material weights) and initial bun volatiles were calculated and are also presented in Table 18.

RESULTS/DISCUSSION

Mass loss data for the six manufactured foam samples are listed in Tables 19-24 and graphically displayed in Figures 41-52. The plant data percent weight loss profiles and rate curves have the same general shape independent of the type or level of auxiliary blowing agent (analogous to observations on laboratory foams). Figures 53 and 54 display all of the plant foams for comparison. The percent weight loss curves exhibit the same general shape; however, there is a spread to the data. There doesn't appear to be any pattern to the variations related to a specific plant, sample size, a specific auxiliary blowing agent, or a specific level of auxiliary blowing agent. These data are believed to reflect random variations within the various manufacturing operations. The relative flatness of the mass loss profiles and mass loss rates of the plant foams are comparable to what is observed with laboratory foam at analogous measurement times (Figures 3-8).

Based on the 30 °F difference in boiling points, the chlorofluorocarbon would be expected to be volatilized earlier than methylene chloride. Figures 55 and 56 compare mass loss profiles for foams of comparable formulation but with different auxiliary blowing agents. These data are conflicting with CCl_3F coming off earlier in one comparison and CH_2Cl_2 coming off earlier in the other. This same irregularity was also observed in the comparison of NCSU CH_2Cl_2 data with Dupont CCl_3F data. As previously mentioned, the time differential between the two boiling point temperatures in the manufacturing operation is small. Therefore, the loss behaviors of methylene chloride and trichlorofluoromethane from flexible polyurethane foams are expected to be similar. The diffusion constants are close (0.098 for CH_2Cl_2; 0.082 for CCl_3F; calculated at 25°C). Consequently, the diffusion phase of the loss profiles should also be comparable. In general, there is good correlation between the data on plant and laboratory foams with analogous formulations (Figure 57). The data suggest that the loss of volatiles from laboratory foams is more rapid than from plant foams. Lab foams have a higher percentage of exposed surface area per unit weight than large plant foams. Additionally, gases have a shorter distance (and probably a less tortuous path) to exit from lab foams and volatiles should escape more rapidly. Based on the mass loss profiles of the plant foams, there are significant amounts of volatiles (30 - 45%) remaining in the bun after the first ten minutes. Considering the reaction kinetics, this residual volatile material is theorized to be essentially only the auxiliary blowing agent which is lost by slow diffusion from the cooling foam mass. These experiments validate the laboratory data and confirm the bi-modal behavior of volatile loss from polyurethane foams. Consequently, any strategy for the recovery and recycle of auxiliary blowing agents must take into account the two distinct regions of loss rates.

Formulation (pph polyol)	Bun A	Bun B	Bun C	Bun D	Bun E	Bun F
Polyol	100.0	100.0	100.0	100.0	100.0	100.0
Water	4.1	3.5	4.5	5.6	3.8	3.5
Amine	0.5	0.4	0.4	0.1	0.3	0.2
CH_2Cl_2	11.3	16.3	2.0	0.0	0.0	16.0
CCl_3F	0.0	0.0	0.0	7.0	20.0	0.0
Surfactant	1.5	1.5	1.1	1.2	1.7	1.9
Sn Catalyst	1.1	1.4	0.5	0.6	0.6	0.4
TDI	52.6	45.9	59.9	66.8	47.8	45.5
Aux Blowing Agt : H2O	2.8	4.7	0.4	1.2	5.3	4.6
Raw Material Feeds (lbs/hr)						
Polyol	370.0	355.0	375.0	286.0	297.0	308.0
Water	14.8	12.1	16.8	16.0	11.1	10.8
Amine	1.7	1.5	1.5	0.3	0.7	0.5
CH_2Cl_2	41.8	57.9	7.5	0.0	0.0	49.3
CCl_3F	0.0	0.0	0.0	20.4	59.4	0.0
Surfactant	5.4	5.3	4.1	3.4	5.0	5.8
Sn Catalyst	4.1	4.9	1.8	1.6	1.8	1.4
TDI	194.5	163.3	224.6	191.0	141.9	140.8
Total	632.3	600.1	631.5	518.3	516.9	516.0
Calculated Parameter						
Batch Run Time (min)	52.0	99.2	29.0	24.5	3.4	14.1
Conveyor Speed (ft/min)	18.5	16.9	16.7	23.0	18.0	16.7
Foam Produced (lbs)	32879.6	59529.9	18313.5	12698.4	1757.5	7275.6
Foam Produced (ft)	962.0	1676.5	484.3	563.5	61.2	235.5
Batch CH_2Cl_2 or CCl_3F (lbs)	2173.6	5743.7	217.5	499.8	202.0	695.1
CO_2 Produced in Batch (lbs)	1879.6	2931.5	1189.9	957.4	92.2	371.9
Total Gas In Batch (lbs)	4053.2	8675.2	1407.4	1457.2	294.1	1067.0
Sample Length (ft)	2.67	2.38	3.08	2.67	2.67	44.50
Initial Sample Weight (lbs)	91.14	84.33	116.58	60.09	76.58	1374.97
Total Gas In Sample (lbs)	11.24	12.29	8.96	6.90	12.82	201.65

Buns A, B, and C - Hickory Springs
Buns D and E - Olympic Products
Bun F - Leggett & Platt

Table 18 - Plant Foams

TIME min	FOAM WT lbs	GAS LOSS %	RATE %/min	CUM LOSS %
0	91.1	0.00	0.00	0.00
9	84.8	56.41	6.27	56.41
14	84.2	5.34	1.07	61.74
19	83.7	4.45	0.89	66.19
24	83.3	3.56	0.71	69.75
29	83.1	1.78	0.36	71.53
34	83.0	0.89	0.18	72.42
39	82.9	0.89	0.18	73.31
44	82.8	0.89	0.18	74.20
49	82.8	0.00	0.00	74.20
54	82.7	0.89	0.18	75.09
59	82.6	0.89	0.18	75.98
64	82.6	0.00	0.00	75.98
69	82.6	0.00	0.00	75.98
129	82.0	5.34	0.09	81.32
189	81.8	1.78	0.03	83.10
249	81.8	0.00	0.00	83.10
309	81.8	0.00	0.00	83.10

Table 19 - Mass Loss Data - Bun A (2.8 : 1 CH_2Cl_2 : H_2O)

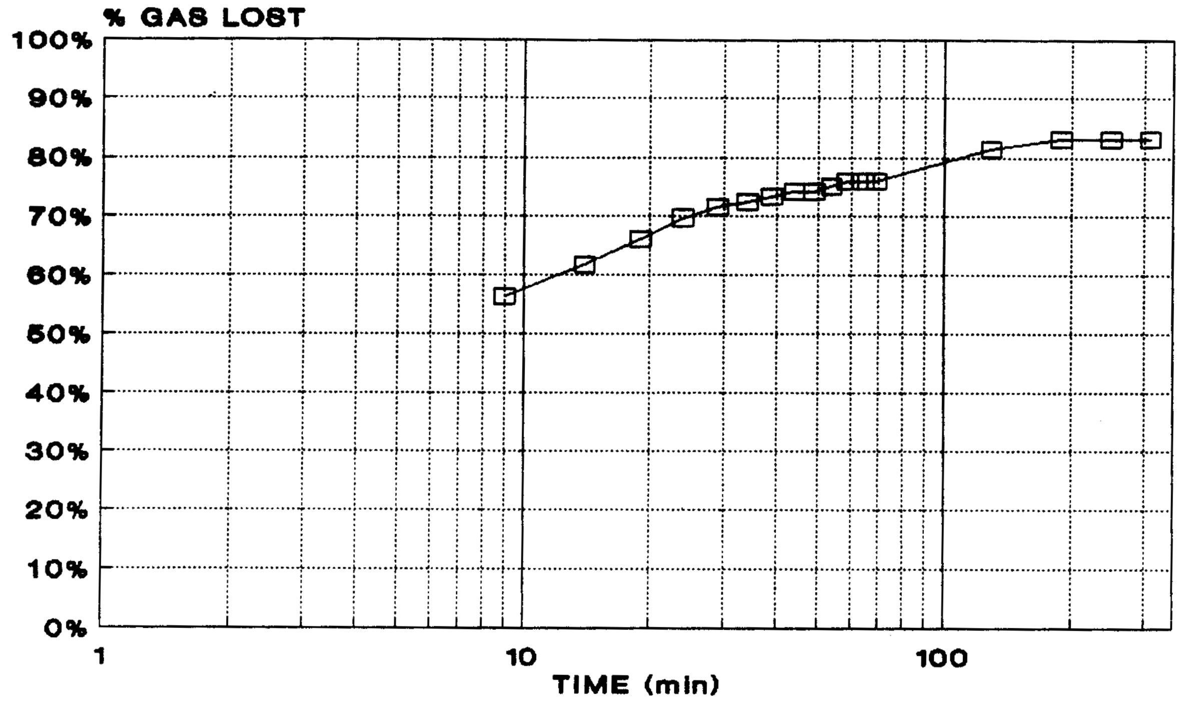

Figure 41 - Mass Loss Profile - Bun A - 2.8 : 1 CH_2Cl_2: H_2O

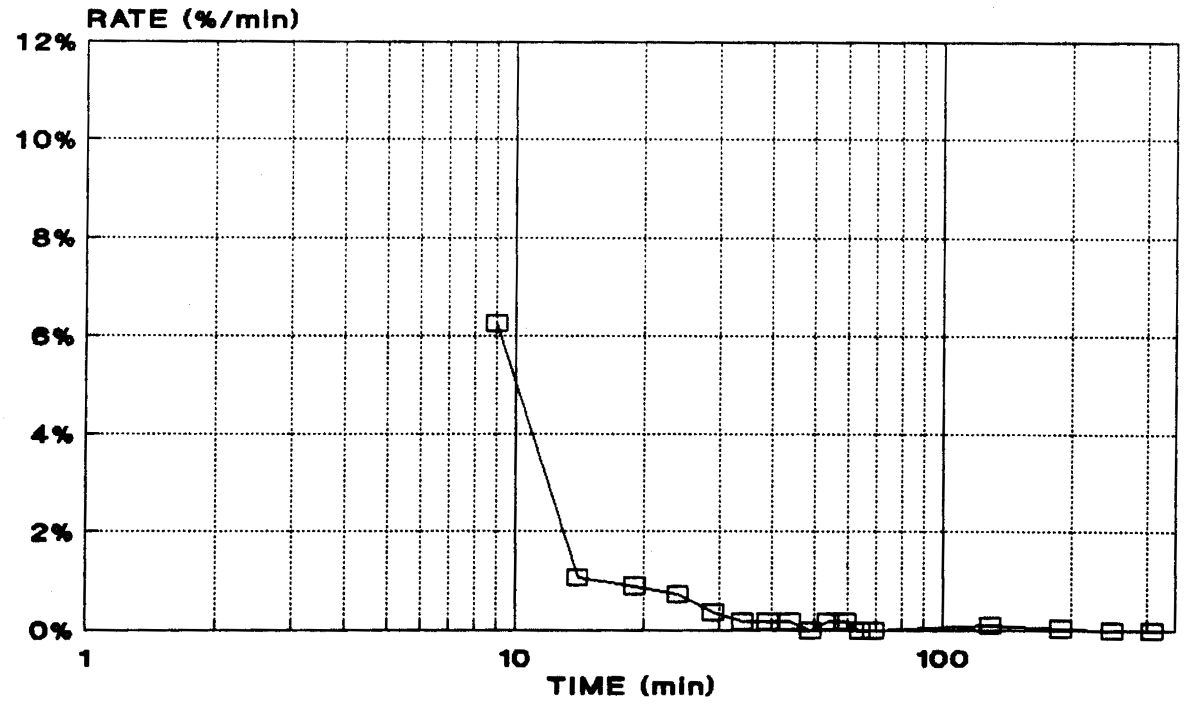

Figure 42 - Rate of Mass Loss - Bun A - 2.8 : 1 CH_2Cl_2: H_2O

TIME min	FOAM WT lbs	GAS LOST %	RATE %/min	CUM LOSS %
0	84.3	0.00	0.00	0.00
10	75.4	72.66	7.27	72.66
15	74.4	8.14	1.63	80.80
20	73.8	4.88	0.98	85.68
25	73.5	2.44	0.49	88.12
30	73.3	1.63	0.32	89.75
35	73.2	0.81	0.16	90.56
40	73.1	0.81	0.16	91.38
45	73.0	0.81	0.16	92.19
50	73.0	0.00	0.00	92.19
55	72.9	0.81	0.16	93.00
60	72.9	0.00	0.00	93.00
65	72.9	0.00	0.00	93.00
70	72.8	0.81	0.16	93.82
130	72.3	4.07	0.07	97.88
190	72.3	0.00	0.00	97.88
250	72.2	0.81	0.01	98.70
310	72.2	0.00	0.00	98.70

Table 20 - Mass Loss Data - Bun B (4.7 : 1 CH_2Cl_2 : H_2O)

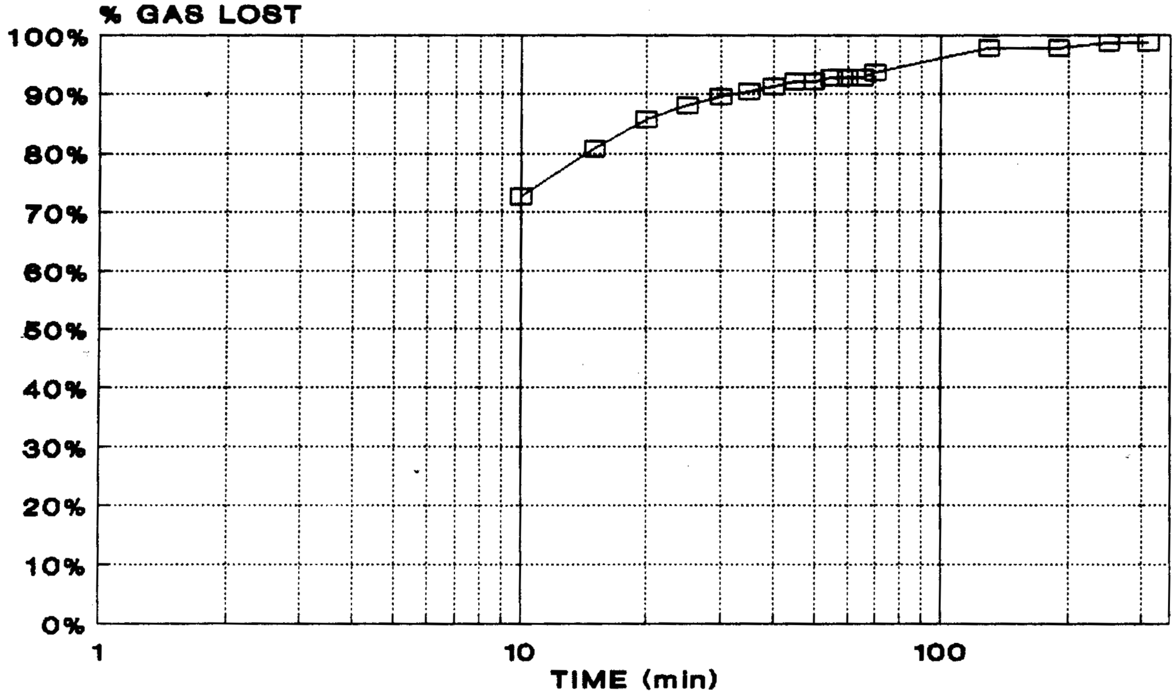

Figure 43 - Mass Loss Profile - Bun B - 4.7 : 1 CH_2Cl_2: H_2O

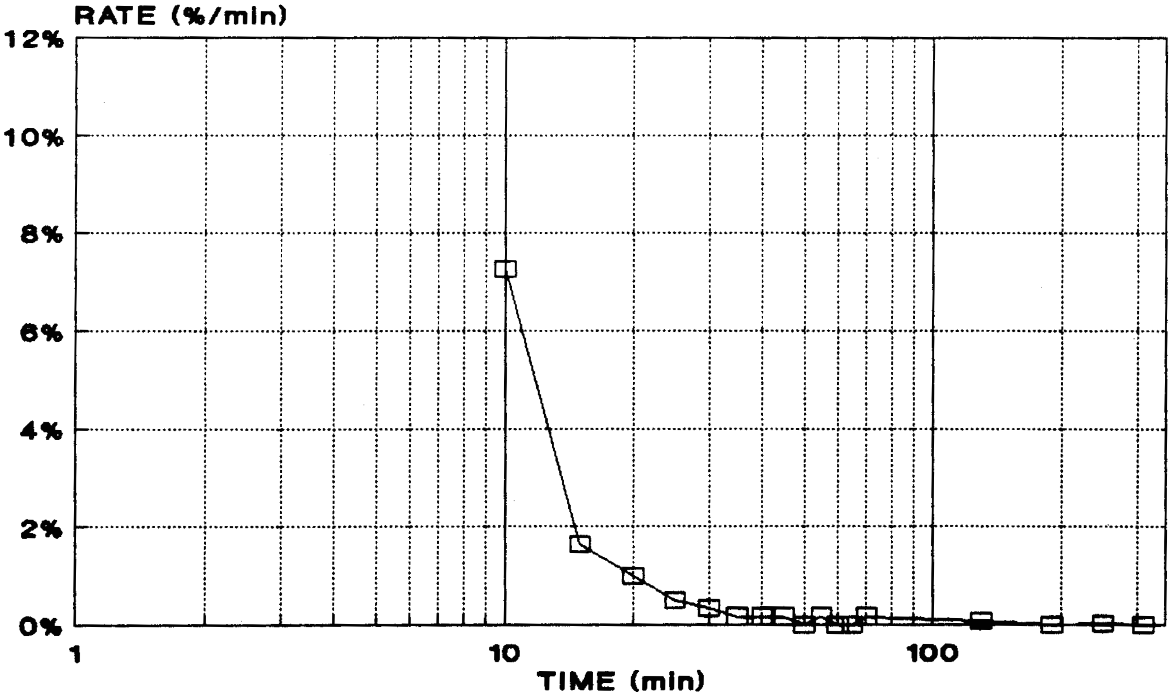

Figure 44 - Rate of Mass Loss - Bun B - 4.7 : 1 CH_2Cl_2: H_2O

TIME min	FOAM WT lbs	GAS LOST %	RATE %/min	CUM LOSS %
0	116.6	0.00	0.00	0.00
9	109.6	77.90	8.66	77.90
14	109.0	6.70	1.34	84.60
19	108.7	3.35	0.67	87.95
24	108.6	1.12	0.22	89.06
29	108.6	0.00	0.00	89.06
34	108.4	2.23	0.45	91.29
39	108.3	1.12	0.22	92.41
44	108.2	1.12	0.22	93.53
49	108.1	1.12	0.22	94.64
54	108.1	0.00	0.00	94.64
59	108.0	1.12	0.22	95.76
64	107.9	1.12	0.22	96.88
69	107.8	1.12	0.22	97.99
129	107.3	5.58	0.09	103.57
189	107.3	0.00	0.00	103.57
249	107.3	0.00	0.00	103.57
309	107.3	0.00	0.00	103.57

Table 21 - Mass Loss Data - Bun C (0.4 : 1 CH_2Cl_2 : H_2O)

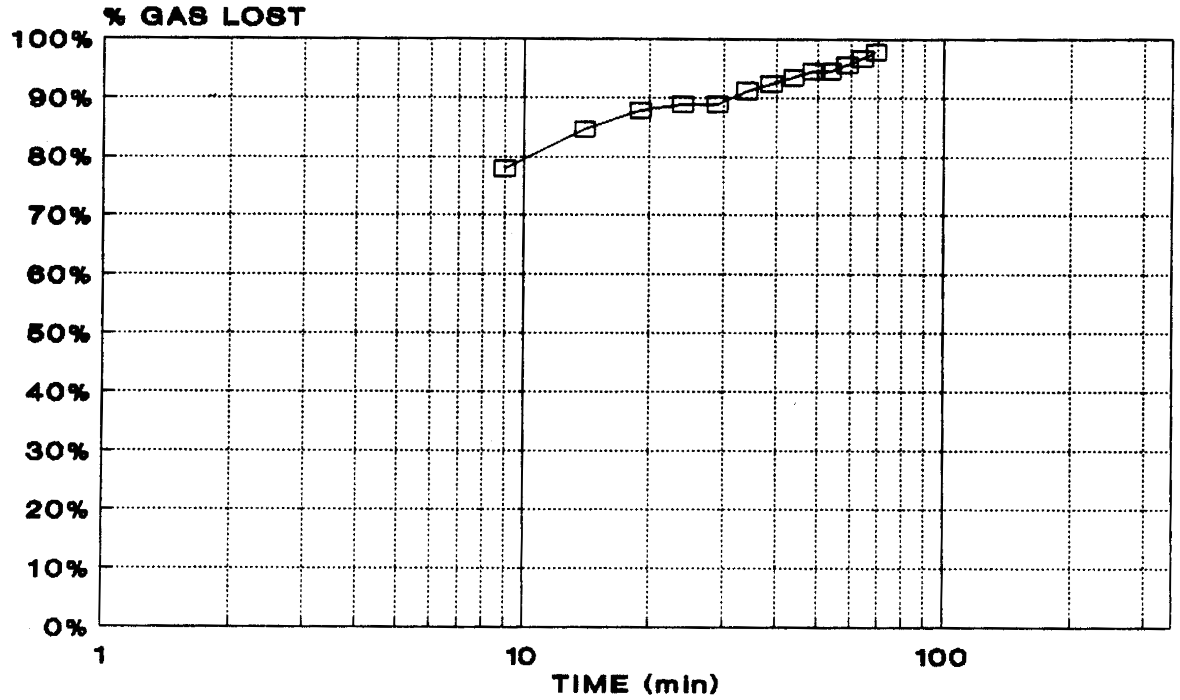

Figure 45 - Mass Loss Profile - Bun C - 0.4 : 1 CH_2Cl_2: H_2O

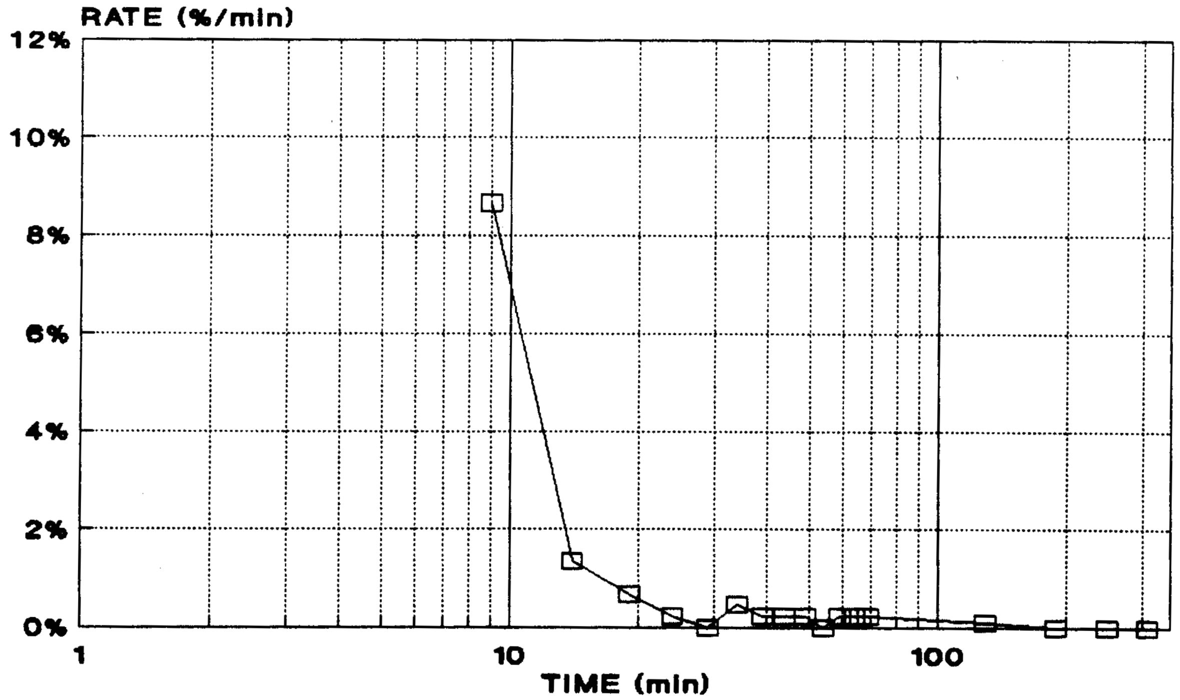

Figure 46 - Rate of Mass Loss - Bun C - 0.4 : 1 CH_2Cl_2: H_2O

TIME min	FOAM WT lbs	GAS LOST %	RATE %/min	CUM LOSS %
0	60.0	0.00	0.00	0.00
9	55.2	70.87	7.87	70.87
14	55.1	1.45	0.29	72.32
19	55.0	1.45	0.29	73.77
24	54.8	2.90	0.58	76.67
29	54.7	1.45	0.29	78.12
34	54.5	2.90	0.58	81.01
39	54.4	1.45	0.29	82.46
44	54.3	1.45	0.29	83.91
49	54.2	1.45	0.29	85.36
54	54.2	0.00	0.00	85.36
59	54.1	1.45	0.29	86.81
64	54.1	0.00	0.00	86.81
69	54.1	0.00	0.00	86.81
129	53.7	5.80	0.10	92.61
189	53.6	1.45	0.02	94.06
249	53.6	0.00	0.00	94.06
309	53.6	0.00	0.00	94.06

Table 22 - Mass Loss Data - Bun D (1.2 : 1 CCl_3F : H_2O)

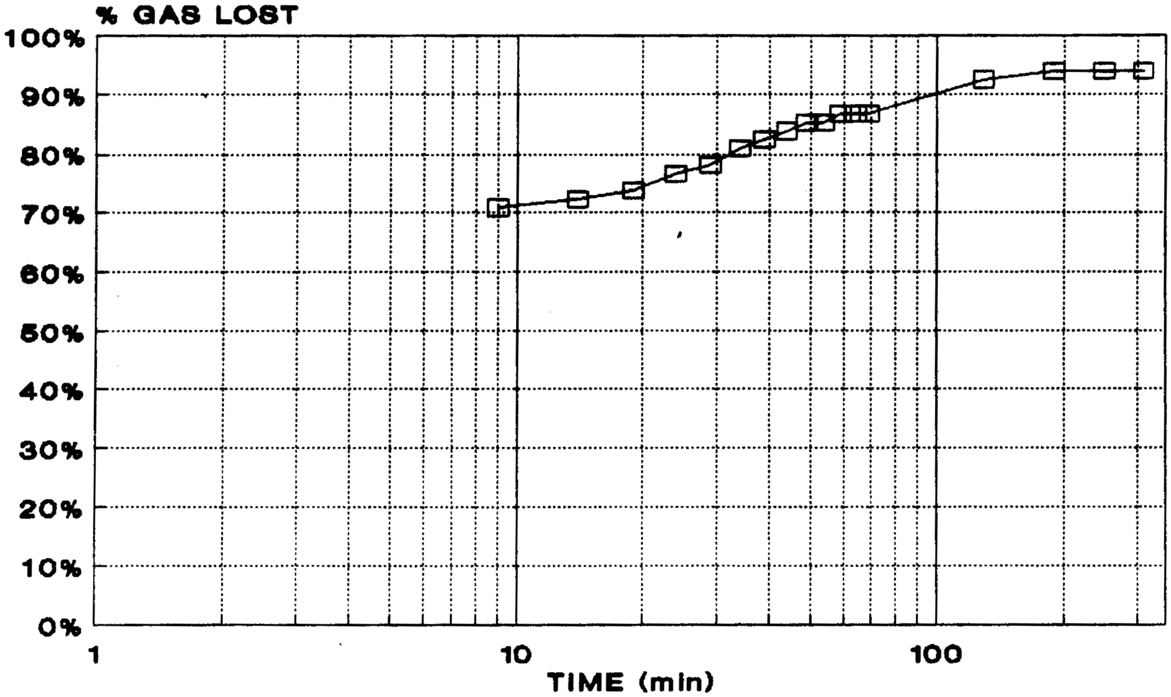

Figure 47 - Mass Loss Profile - Bun D - 1.2 : 1 $CCl_3F : H_2O$

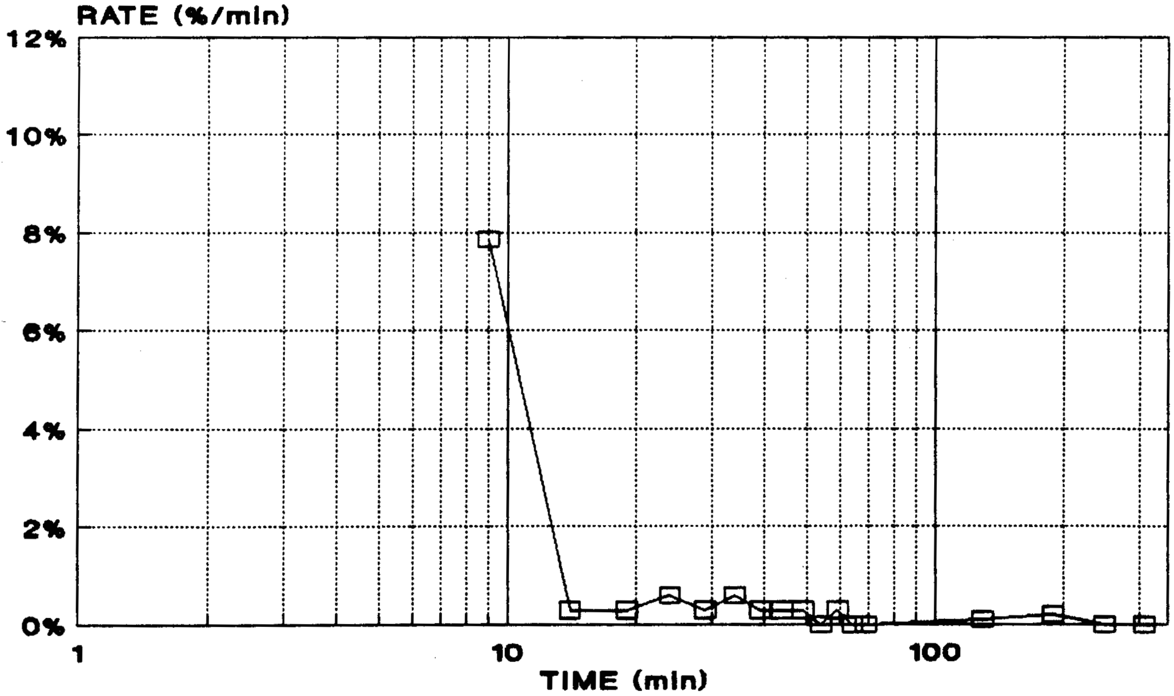

Figure 48 - Rate of Mass Loss - Bun D - 1.2 : 1 $CCl_3F : H_2O$

TIME min	FOAM WT lbs	GAS LOST %	RATE %/min	CUM LOST %
0	76.6	0.00	0.00	0.00
6	67.4	71.61	11.93	71.61
11	65.3	16.38	3.28	87.99
16	64.9	3.12	0.62	91.11
21	64.7	1.56	0.31	92.67
26	64.6	0.78	0.16	94.45
31	64.5	0.78	0.16	94.23
36	64.5	0.00	0.00	94.23
41	64.5	0.00	0.00	94.23
46	64.4	0.78	0.16	95.01
51	64.4	0.00	0.00	95.01
56	64.4	0.00	0.00	95.01
61	64.3	0.78	0.16	95.79
66	64.3	0.00	0.00	95.79
126	64.0	2.34	0.04	98.13
186	64.0	0.00	0.00	98.13
246	64.0	0.00	0.00	98.13
306	64.0	0.00	0.00	98.13

Table 23 - Mass Loss Data - Bun E (5.3 : 1 CCl_3F : H_2O)

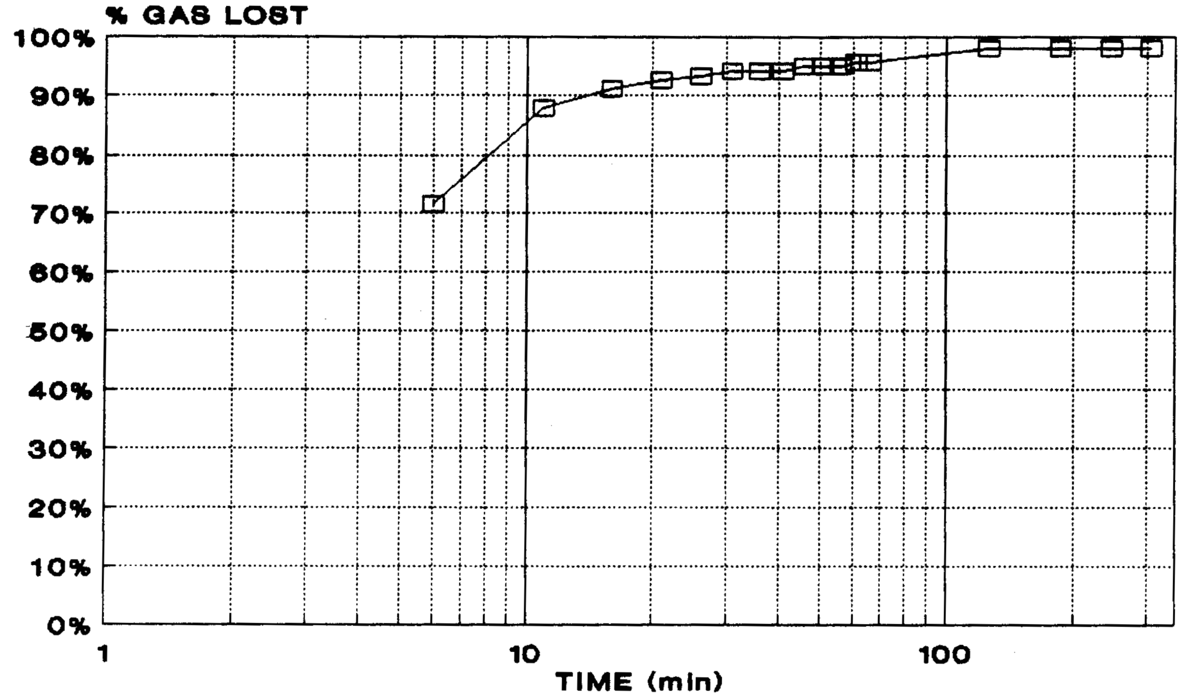

Figure 49 - Mass Loss Profile - Bun E - 5.3 : 1 $CCl_3F : H_2O$

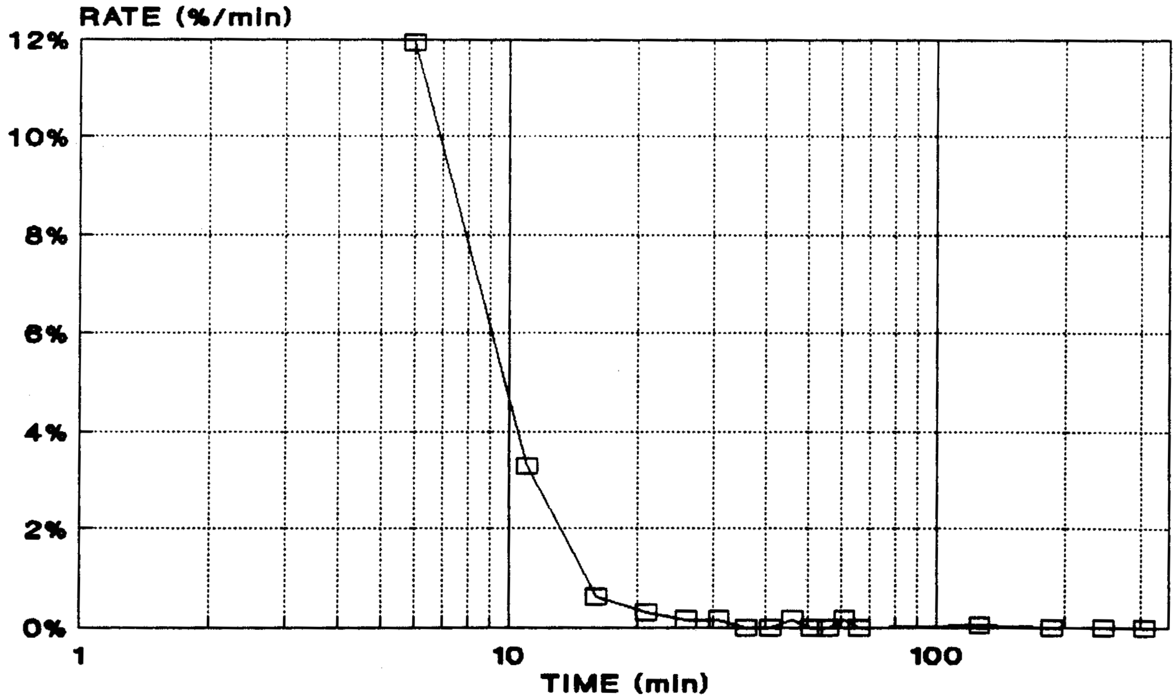

Figure 50 - Rate of Mass Loss - Bun E - 5.3 : 1 $CCl_3F : H_2O$

TIME min	FOAM WT lbs	GAS LOST %	RATE %/min	CUM LOSS %
0	1375.0	0.00	0.00	0.00
10	1271.0	51.56	5.16	51.56
15	1261.0	4.96	0.99	56.52
20	1255.0	2.98	0.60	59.49
25	1251.0	1.98	0.40	61.48
30	1248.0	1.49	0.30	62.97
35	1246.0	0.99	0.20	63.96
40	1244.0	0.99	0.20	64.95
45	1243.0	0.50	0.10	65.45
50	1242.0	0.50	0.10	65.94
55	1240.0	0.99	0.20	66.93
60	1240.0	0.00	0.00	66.93
65	1239.0	0.50	0.10	67.43
70	1238.0	0.50	0.10	67.92
130	1234.0	1.98	0.03	69.91
190	1230.0	1.98	0.03	71.89
250	1227.0	1.49	0.02	73.38
310	1226.0	0.50	0.01	73.88

Table 24 - Mass Loss Data - Bun F (4.6 : 1 CH_2Cl_2 : H_2O)

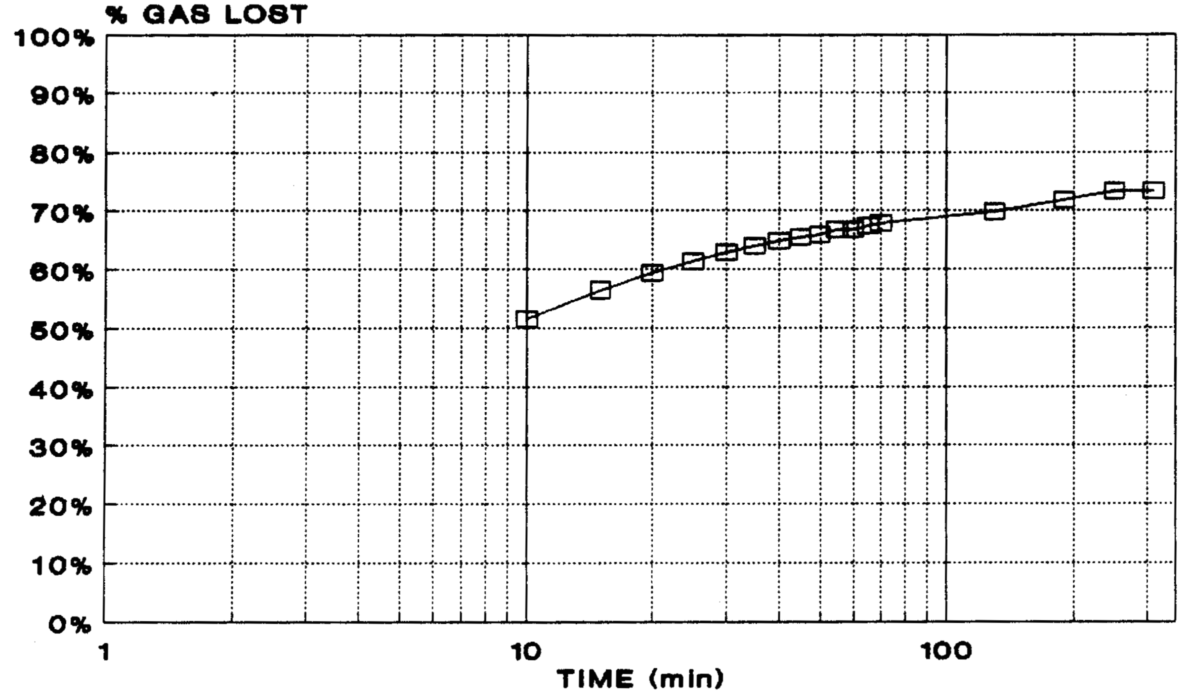

Figure 51 - Mass Loss Profile - Bun F - 4.6 : 1 CH_2Cl_2: H_2O

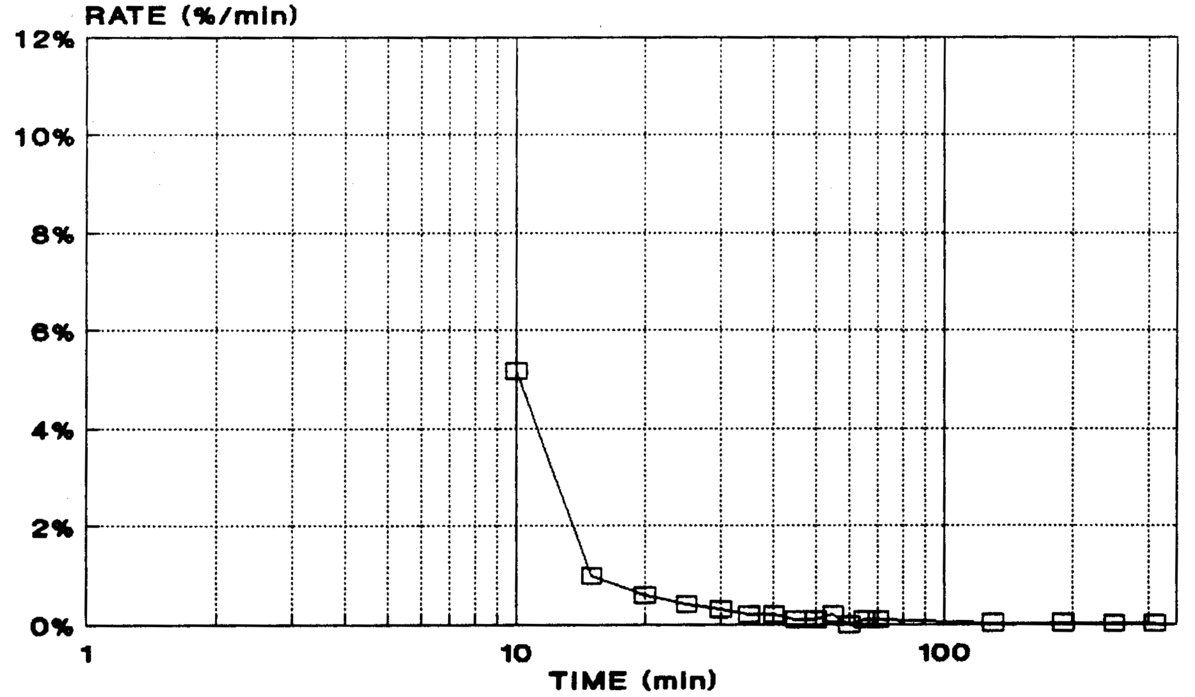

Figure 52 - Rate of Mass Loss - Bun F - 4.6 : 1 CH_2Cl_2: H_2O

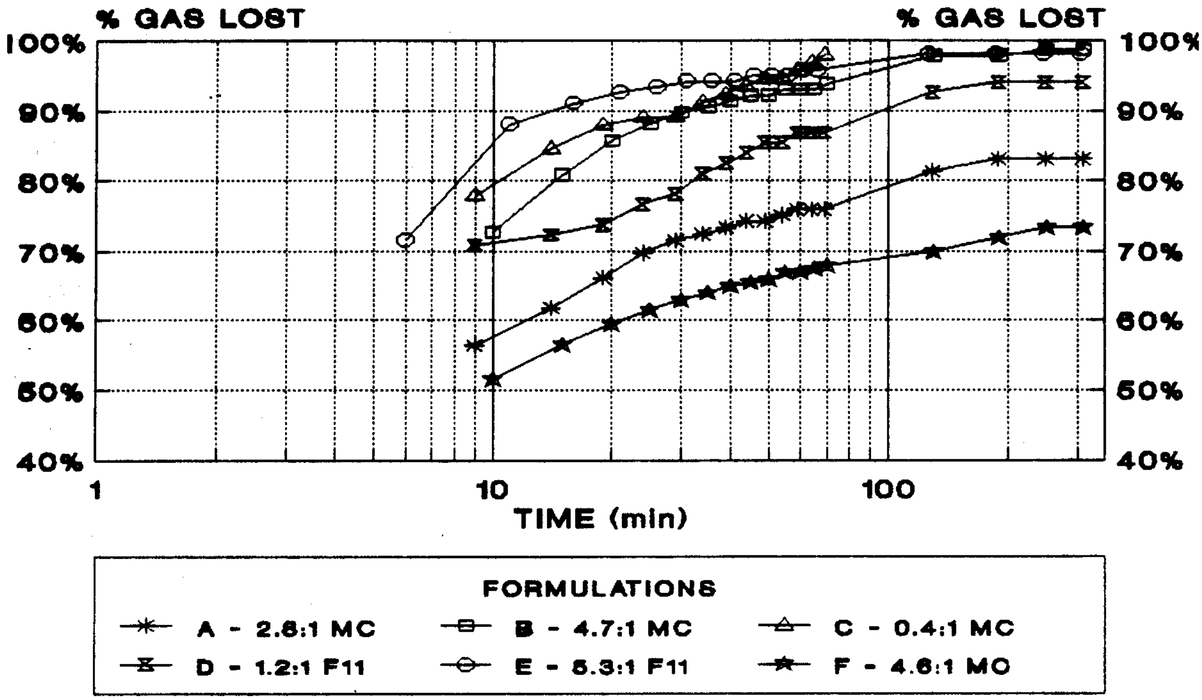

Figure 53 - Mass Loss Profiles - Comparison of Plant Foams

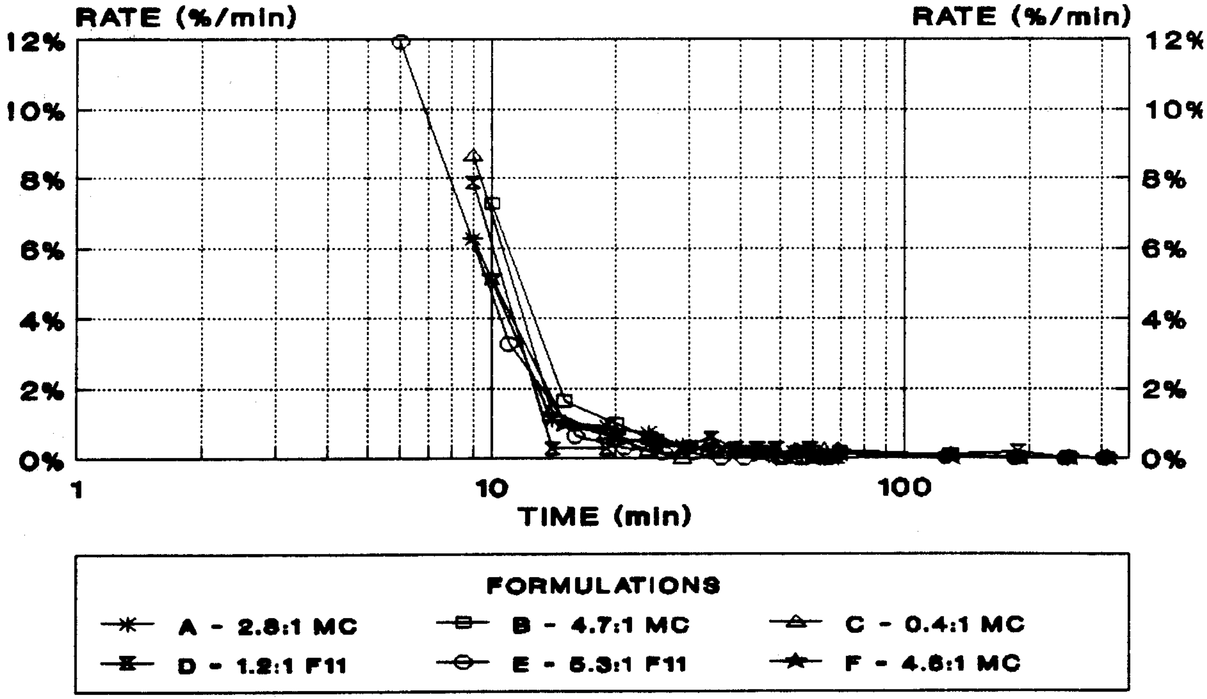

Figure 54 - Mass Loss Rates - Comparison of Plant Foams

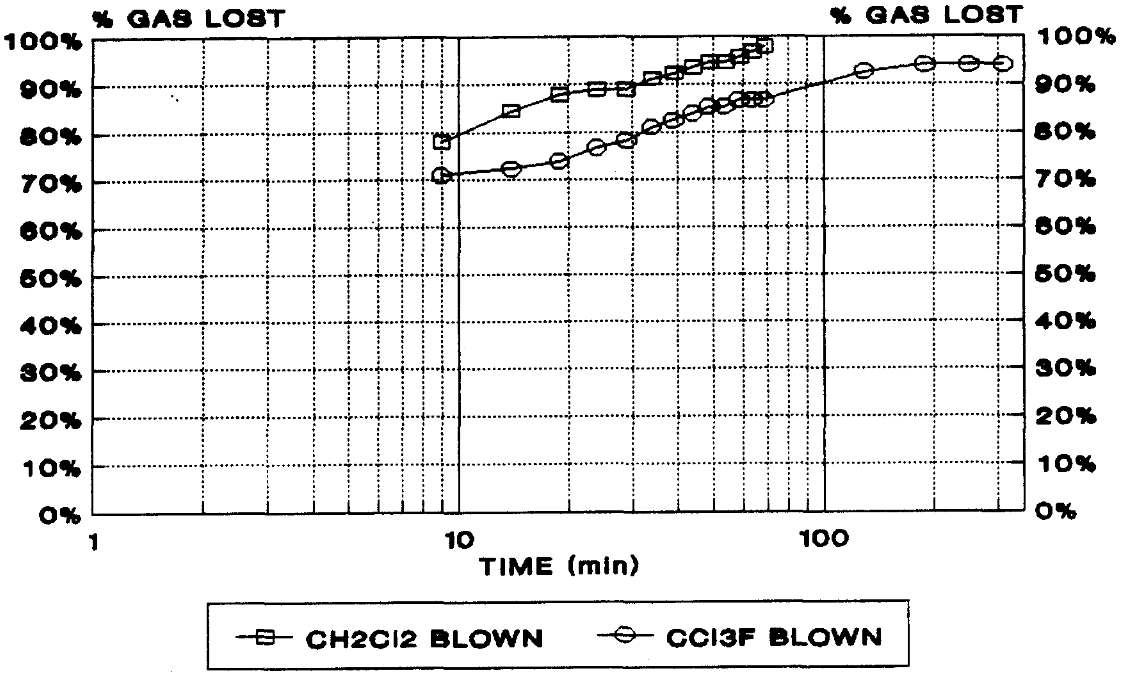

Figure 55 - Mass Loss Profiles - Auxiliary Blowing Agents
0.4 : 1 CH_2Cl_2 : H_2O vs. 1.2 : 1 CCl_3F : H_2O Blown Foams

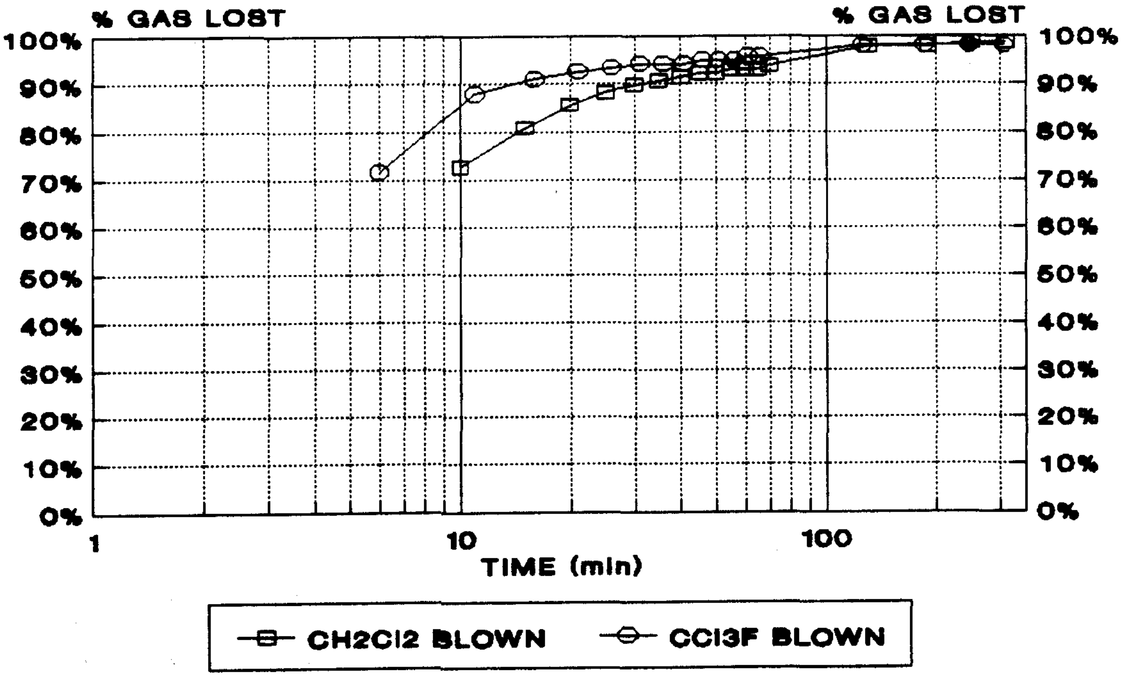

Figure 56 - Mass Loss Profiles - Auxiliary Blowing Agents
4.7 : 1 CH_2Cl_2 : H_2O vs. 5.3 : 1 CCl_3 : H_2O Blown Foams

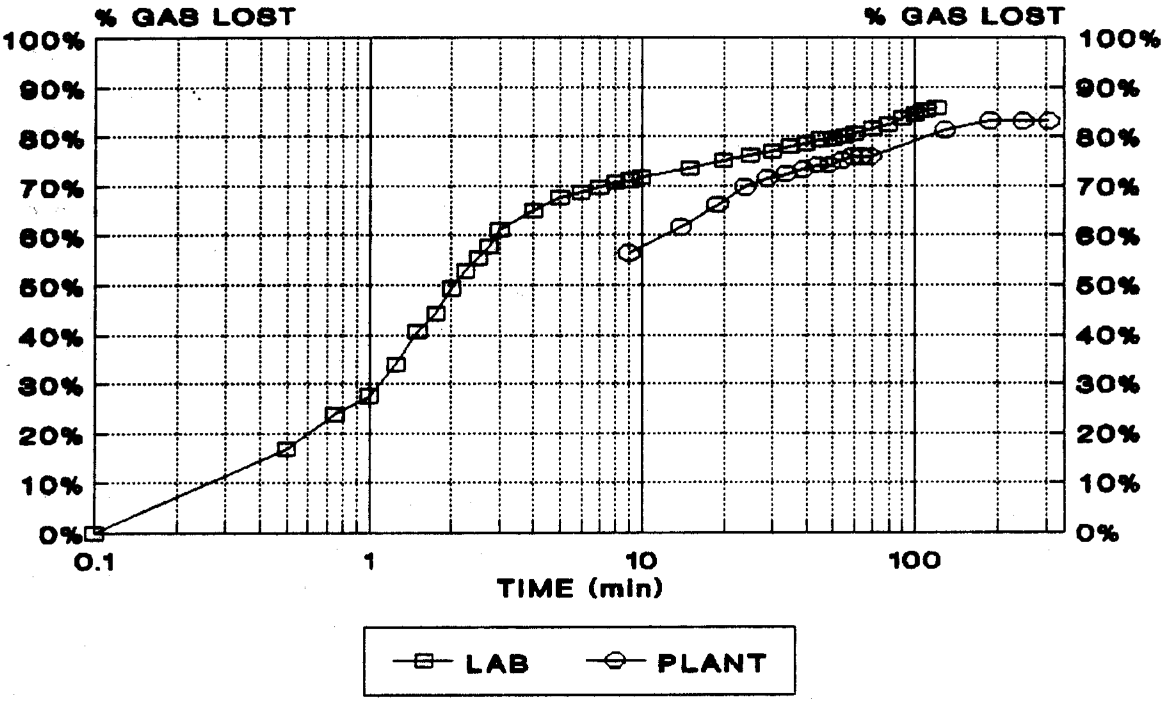

Figure 57 - Mass Loss Profiles - Comparison of Lab and Plant Foams - Approximately 3 : 1 CH_2Cl_2: H_2O Formulations

SUMMARY

The Research Center For Waste Minimization And Management at NCSU has completed an experimental investigation to quantify the volatilization dynamics of blowing agent loss and to examine innovative means to maintain safe worker conditions while simultaneously recovering the auxiliary blowing agent.

Polyurethane foams with representative formulations (varying ratios of primary to auxiliary blowing agents) were prepared in NCSU laboratories to determine overall weight loss, auxiliary blowing agent weight loss, and foam temperature profiles versus time. Representative foam physical properties were measured to ensure formulation quality. These data allow a basic understanding of the timing and sequence of events in the foam reactions. Additionally, data were collected from three flexible polyurethane foam manufacturing plants for comparison and validation of laboratory data. Representative conclusions from these investigations include:

> The laboratory data are characterized by an initial rapid loss of approximately 60-70% of the available volatiles in 10 minutes; the residual volatiles are then slowly lost over 24 hours. These two regimes of mass loss are logarithmically proportional to the elapsed time and represent a complex mechanism of volatilization. Simplistically, the first regime of mass loss is hypothesized to relate to the kinetically fast reaction between the diisocyanate and water generating CO_2 and heat. The heat generated by the competing reactions increases the temperature of the foaming mass and the liberation of CH_2Cl_2 is initiated. The rapid loss of volatiles occurs from the surface of the rapidly expanding multiphase foam and from the block interior as the foam becomes an open cell structure (blow-off point). The second regime of mass loss appears to be a slow diffusion of volatiles through a open cell foam mass as crosslinking reactions continue.
>
> As the amount of methylene chloride is increased in the formulation (at constant water content), the mass loss rates increase. When the data are normalized on a percent of total volatiles lost, the time dependent mass loss rates and total mass loss over the first 10 minutes for 1:1, 3:1, and 4:1 formulations appear independent of the amount of auxiliary blowing agent present in the formulation. After 10 minutes, the normalized 3:1 and 4:1 data continue to coincide. Conversely, the mass loss rate for the 1:1 formulation noticeably slows after 10 minutes and looks similar in shape to the analogous water-blown (0:1) foam data. The reason for this behavior is unknown but may relate to a density effect.
>
> Mass loss rates for water-only blown foams are consistent with other investigations; the generation of CO_2 appears first order.
>
> Independent of formulation, the ratio of CH_2Cl_2 to CO_2 collected increases as a function of time. This observation suggests a rapid consumption of H_2O (generation of CO_2) and a time delayed evolution of CH_2Cl_2 from polyurethane foams. For the less dense foam formulations, the greatest amount of the available methylene chloride were recovered in the first 10 minutes. This information is extremely valuable in determining possible modes of recovery.

Application of vacuum significantly increases the rate of diffusive losses from polyurethane foams. Additional experimentation is needed to determine plant feasibility of vacuum application coupled with entrapment of methylene chloride (or CFC) by condensation.

Interior temperature of laboratory foam rises at approximately a linear rate (vs log time) and reaches a maximum after about 15 minutes and then gradually decreases. Temperature continues to rise well after the blow-off point (opening of cell structures and maximum loss of volatiles). This observation implies that the cooling effect associated with gas evolution may not significantly contribute to the heat loss of the system; controlled thermodynamic experiments would have to be comducted to actually determine this effect. Heat conduction through the foam's bottom surface is not a major factor; therefore, mass transfer through the foam's top surface is a major mechanism of heat loss from the system.

In general, there is good correlation between data on plant and laboratory foams with analogous formulations. The plant data weight percent loss profiles and rate curves have the same general shape independent of the type or level of auxiliary blowing agent (analogous to observations on laboratory foams). The relative flatness (at times greater than 10 minutes) of the mass loss profiles and mass loss rates of the plant foams is comparable to what is observed with laboratory foam at analogous measurement times. Lab foams tend to lose mass slightly faster than plant foams and is probably due to the shorter distance for diffusive losses to exit the foam and a higher relative percentage of exposed area.

From analyses of plant mass loss data, the mass loss behavior of CH_2Cl_2-blown and $CClF_3$-blown foams are comparable. Theoretically, the CFC should be lost earlier in the process due to its lower boiling point (75°F for CCl_3F vs. 104°F for CH_2Cl_2). However in the manufacturing operation, temperature rise is so rapid that the time differential between the two boiling point temperatures would be expected to be small. Therefore, the emission profiles from F-11 blown foams and form methylene chloride blown foams would be anticipated to be similar.

Based on the mass loss profiles of the plant foams, there are significant amounts of volatiles (in the range of 30-45%) remaining in the bun after the first ten minutes. Considering the reaction kinetics, this residual volatile material is theorized to be essentially only the auxiliary blowing agent which is lost by slow diffusion from the cooling foam mass. These experiments validate the laboratory data and confirm the bi-modal behavior of volatile loss from polyurethane foams. Consequently, any strategy for the recovery and recycle of auxiliary blowing agents must take into account the two distinct regions of loss rates.

TUNNEL RETROFIT WITH RECOVERY/RECYCLE

Based on the firm belief that foamers will eventually be restricted in emitting any blowing agent amd the data gathered at NCSU, retrofit of a foam line to isolate the tunnel and drastically reduce exhaust flows will eliminate worker exposure to isocyanates and significantly increase tunnel concentrations of the auxiliary blowing agent. This increase in ambient blowing agent concentration should allow for recovery by conventional means.

TUNNEL CONCENTRATIONS OF AUXILIARY BLOWING AGENTS

A model has been developed which uses total air flow, methylene chloride input rates, CH2Cl2 loss rates (from NCSU experimental data), and conveyor speed (tunnel residence time) as inputs and predicts steady-state tunnel concentrations (molar ppm) of methylene chloride. Results can be scaled for changes in methylene chloride input (directly proportional) and ventilation rate (inversely proportional).

$$\text{ppm } CH_2Cl_2 = (\text{ratio}/\text{tcfm}) * [A + B(\text{fpm}) + C(\text{temp}) + D(\text{fpm})(\text{temp})]$$

where:ratio = phr CH_2Cl_2/phr H_2O
tcfm = thousand cubic feet of air
fpm = conveyor speed in feet per minute
temp = air temperature in °C
A = 7503.01; B = 1684.84; C = 27.47; D = 6.17

	Example 1		Example 2	
Formulation	pph Polyol	Feed Rate lbs/min	pph Polyol	Feed Rate lbs/min
Polyol	100.0	355.0	100.0	375.0
Water	3.5	12.1	4.5	16.8
Amine Catalyst	0.4	1.5	0.4	1.5
CH_2Cl_2	16.3	57.9	2.0	7.5
Surfactant	1.5	5.3	1.1	4.1
Sn Catalyst	1.4	4.9	0.5	1.8
TDI	45.9	163.3	59.9	224.6
Tunnel Length	100 ft		100 ft	
Conveyor Speed	17 fpm		14 fpm	
Total Air Flow (25°C)	60,000 cfm		40,000 cfm	
Calculated Tunnel CH_2Cl_2 Concentration	3150 ppm		380 ppm	

Dupont[4] measured the exhaust concentration of F-11 at three plants (different formulations, tunnel length, conveyor speed, and ventilation rates). Their values ranged from 150 - 3200 ppm which are at least comparable in magnitude to the values calculated at NCSU. The NCSU model needs to be compared with current measurements at various plant sites.

RECOVERY OF AUXILIARY BLOWING AGENTS

Japanese investigators[19,20] studied the feasibility of the adsorption-desorption process using granular activated carbon for removal and recovery of F-11 in waste gas from a polyurethane foam factory. The adsorption capacity of the activated carbon was found to be large enough in spite of the coexistence of triethylenediamine (catalyst) and water vapor at high relative humidity. The recovery efficiency of F-11 obtained by a general steam regeneration method was greater than 80%. The coexisting amine was desorbed slightly and accumulated on the activated carbon during the adsorption-desorption cycles. However, the adsorption ability of the washed activated carbon after the steam regeneration was completely recovered. In a separate series of experiments, the researchers addressed the potential poisoning of activated carbon by toluene diisocyanate (reaction of TDI with water and subsequent polymerization within the carbon pores). Trace TDI could be efficiently removed by granular activated carbon at a high space velocity. Since F-11, triethylenediamine, and water vapors coexist at higher concentrations than TDI in the actual waste gas, competitive adsorption occurred. F-11 which had a high concentration and large adsorption rate was adsorbed the most but leaked in a short time at a very high space velocity (due to its high concentration). Subsequently, the amine and TDI were adsorbed and replaced F-11 on the carbon. It was estimated that TDI could be adsorbed from the PUF waste gas by using granular activated carbon with large adsorption capacity in spite of low concentration at a very high space velocity. This sacrificial bed would be followed by another carbon bed at a general space velocity. The authors concluded that the adsorption-desorption process using granular activated carbon might be economically feasible for removal and recovery of F-11 from PUF factory exhaust gas.

Recovery of highly corrosive chlorinated organics on granular activated carbon has met with mixed success. During carbon regeneration, the presence of steam and catalytic amounts of transition metals (iron,copper, etc.) in the carbon may hydrolyze a portion of the solvent heel to form hydrochloric acid, chloroalcohols, and other organics. The acid in the presence of the condensed steam may cause stress corrosion cracking when alloy or carbon steels are uses for system construction. Use of exotic alloys (Hastelloy, Monel, titanium, etc. increase the capital costs and decrease (or eliminate) the economic viability of recovery. Kenson[7] investigated the use of activated carbon fiber systems for the recovery of solvents such as 1,1,1 trichloroethane and methylene chloride. Carbon fiber systems contain 50-90% less metals content than granular carbons so that the hydrolysis is inhibited. As a result, system corrosion potential is reduced and stainless steel (rather than an expensive alloy) can be used for vessels, valves, and piping. Desorption cycles with the carbon fiber are 5-10 minutes compared to 30-60 minutes for granular activated carbon. This reduction in desorption cycle was shown to improve the quality of recovered trichloroethane quality from an electronic industry application. The author concludes that the use of activated carbon fibers offer a cost effective approach to recycle/reuse of corrosive solvents.

Collection and recovery of halogenated hydrocarbons such as trichlorofluoromethane (F-11) and methylene chloride by adsorption onto activated carbon (or carbon fibers) followed by steam-out and condensation has been documented in the literature and commercial systems are available from many vendors. Two of the key parameters which drive the size and hence capital cost of a carbon-based recovery system are the concentration of the material to be collected and the flow velocity.[22] The Center's approach to isolating the foam tunnel and decreasing air flows would positively impact the economics of any recovery system. The higher the concentration of auxiliary blowing agent and the lower the total flow, the smaller the carbon bed required (lower cost). The recovery of auxiliary blowing agents from polyurethane foam exhaust gas appears to be technically feasible. Design parameters and economic feasibility of various recovery options including emerging technologies (membrane separations, etc.) need to be quantified in order to implement a waste minimization strategy to reduce environmentally damaging air emissions from PUF plants.

CONCLUSIONS/RECOMMENDATIONS

DuPont researchers concluded that current tunnel designs were inefficient in capturing the emitted auxiliary blowing agent (F-11) and that improvements in tunnel design to increase the effectiveness of capture while simultaneously minimizing ventilation rates would be needed prior to determining the economic viability of auxiliary blowing agent recovery by carbon adsorption. Based on analogous conclusions, Unifoam designed a completely enclosed batch system for manufacture of flexible polyurethane foams; the auxiliary blowing agent is captured on a carbon bed and recycled. Neither study dealt with emissive losses during bun cure and pre-converting storage.

Based on the data gathered at NCSU, retrofit of an existing continuous foam line to isolate the tunnel and drastically reduce exhaust flows will eliminate worker exposure to isocyanates and significantly increase tunnel concentrations of the auxiliary blowing agent. This increase in ambient blowing agent concentration should allow for recovery by conventional means. Vacuum technology has been demonstrated to enhance the rate (and concentration) of post-tunnel (or post-saw) diffusive losses. The Research Center For Waste Minimization And Management is in the process of forming a consortium of cooperative foam manufacturers, chemical suppliers, and relevant machinery manufacturers to develop the necessary design modifications for tunnel retrofit/isolation and collection of tunnel and post-tunnel emissions on one foam line. This represents the scale of development necessary to determine the feasibility of the concentration, recovery, and recycle strategy. The Center's approach offers a chance to address the environmental problems while maintaining worker safety and the existing continuous process and formulations. If the outcome of this demonstration indicates that even this approach is impractical, then this is critical information to the foam industry in discussions with regulatory agencies. The demonstration project at one plant would be delineated into the following three major areas of implementation with go/no-go decisions after each phase:

1. Design and install tunnel retrofit; modify tunnel exhaust system; and determine optimum tunnel exhaust concentrations for recovery of methylene chloride.

2. Design methylene chloride recovery system; quantify specifications of recovered methylene chloride; produce a range of foam products with recycled methylene chloride and compare product qualities to analogous foams prepared with virgin methylene chloride.

3. Design and quantify vacuum recovery system for collection and recycle of post-tunnel losses of methylene chloride.

Each implementation phase would be subjected to cost and product quality analyses, quantification of actual reductions in air emissions, and measurements of worker exposure to ambient TDI and CH_2Cl_2.

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