Pyrolysis of Polycarbonate in a Steam Environment

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Application Note
Polymer

Abstract
This application note investigates the thermal decomposition of Polycarbonate with the presence of steam.

Introduction
The effects of steam pyrolysis has been studied for both fuel and recycling applications. For example, steam pyrolysis of biomass as an approach for bio-oil production and upgrading has been examined, showing that steam affects the yields and chemical nature of gas, liquid, and char of biomass[1]. On the recycling side, pyrolysis of polycarbonate in the presence of water has been studied, where pyrolysis of polycarbonate can yield some valuable monomer material, but often with too many by-products. On the other hand, hydrolysis of polycarbonate has been shown to increase monomer material[2]. In this application, pyrolysis of Lexan (poly(bisophenol A carbonate)) was studied under different inert and reactive pyrolysis conditions, including temperature ramps, and the presence of steam as a reactant gas.

Experiment Setup
The sample was first added into a DISC (Drop-In-Sample Chamber) tube and then analyzed using Evolved Gas Analysis (EGA) as a screening step. Using the information from this step, single step pyrolysis was performed. After which, pyrolysis with a 70°C ramp rate was performed both with and without steam as a reactant gas on a Pyroprobe 6200 with Steam Option.

EGA

Pyroprobe 6200		GC-MS	
DISC:		Column:	Fused silica (1m x 0.10mm)
Initial:	100°C	Carrier:	Helium 1.25mL/min
Ramp Rate:	100°C per min		80:1 split
Final:	800°C	Injector:	360°C
		Oven:	300°C
Interface:	300°C	Ion Source:	230°C
Transfer Line:	300°C	Mass Range:	35-600amu
Valve Oven:	300°C		

Pyrolysis

Pyroprobe 6200 with Steam		GC-MS	
DISC:	800°C 30s	Column:	5% phenyl (30m x 0.25mm)
		Carrier:	Helium 1.25mL/min
Interface:	300°C		80:1 split
Transfer Line:	300°C	Injector:	360°C
Valve Oven:	300°C	Oven:	40°C for 2 minutes
			10°C/min to 320°C(15min)
		Ion Source:	230°C
		Mass Range:	35-600amu

Ramp Rate Pyrolysis with Steam

Pyroprobe 6200 with Steam		GC-MS	
DISC:		Column:	5% phenyl (30m)
Initial:	300°C 2min	Carrier:	Helium 1.00mL/min
Ramp:	70°C/minute		50:1 split
Final:	800°C 20s	Injector:	300°C
		Oven:	50°C for 2 min
Purge Gas:	He		15°C/min to 315°C
Flow Rate:	25mL/min	Source:	230°C
		Range:	35-600 amu
Reactant Gas:	Steam		
WaterFlow Rate:	0.02mL/min		
Trap Contents:	Tenax TA		
Trap Rest:	40°C		
Trap Final:	300°C		
Top Block:	200°C		
Interface:	300°C		
Transfer Line:	300°C		
Valve Oven:	325°C		

Results and Discussion

When subject to a heating rate of 100°C per minute from 100°C to 1000°C, thermal decomposition of polycarbonate begins at 500°C, and is finished by 800°C. So a single step pyrolysis at 800°C was used to initially study the polycarbonate.

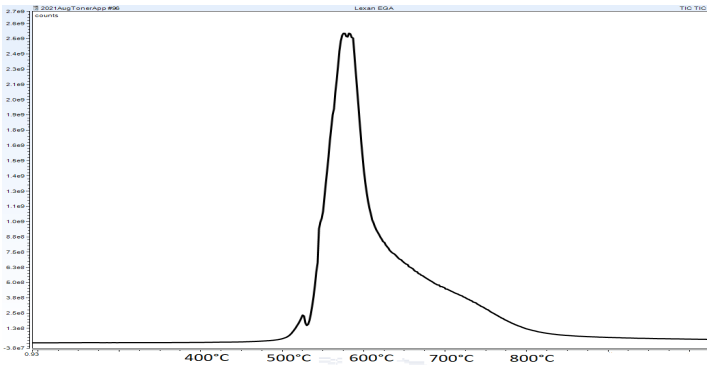
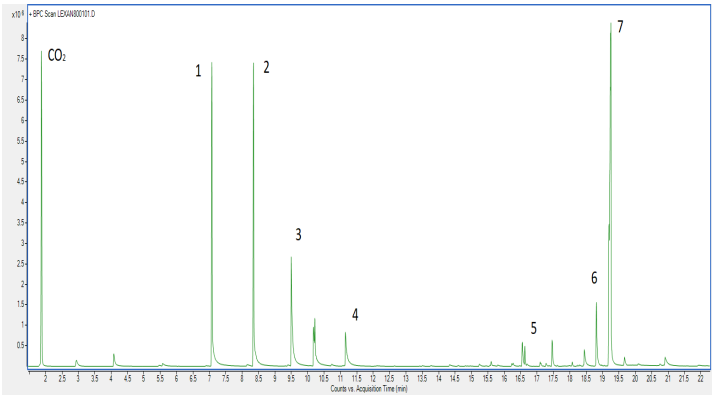


Figure 1. Evolved Gas Analysis of Lexan poly(bisphenol A carbonate) from 100°C to 1000°C at 100°C per minute.

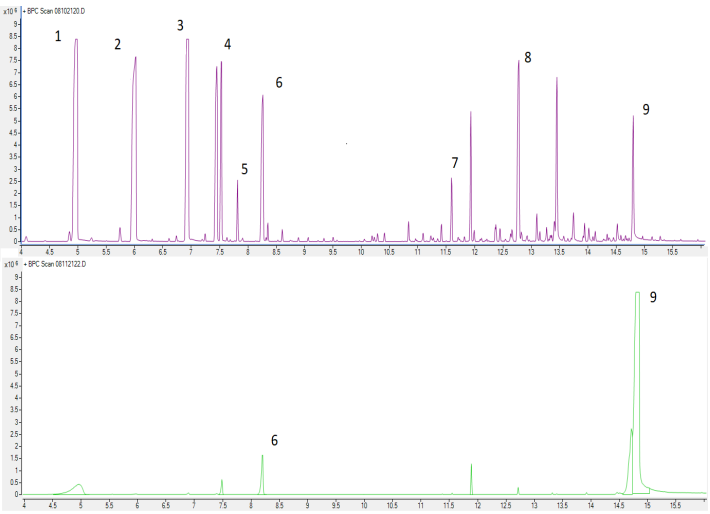
At 800°C, Bisphenol A, Lexan's monomer, is a prominent pyrolysis product, along with phenol, cresol, and p-Isopropyl phenol.

Lexan was then pyrolyzed at a 70°C pyrolysis ramp from 300°C to 800°C to a sorbent trap, both with and without steam as a reactant gas. A slow ramp was chosen to allow time for steam to interact with the polymer.



Peak	Identification	Peak	Identification
1	Phenol	5	Phenol, 4-(1-methyl-1-phenylethyl)-
2	p-Cresol	6	4,4'-Ethylidenediphenol
3	Phenol, 4-ethyl-	7	Bisphenol A
4	p-Isopropenylphenol		

Figure 2. Pyrolysis of Lexan at 800°C.



Peak	Identification	Peak	Identification
1	Phenol	6	p-Isopropenylphenol
2	p-Cresol	7	Diphenyl carbonate
3	Phenol, 4-ethyl-	8	Phenol, 4-(1-methyl-1-phenylethyl)-
4	p-Cumenol	9	Bisphenol A
5	Phenol, 4-propyl-		

Figure 3. Pyrolysis of Lexan at 70°C per minute to 800°C in Helium (top), and steam (bottom).

When Lexan (poly(bisphenol A carbonate)) is pyrolyzed with a 70°C ramp rate, most of the the same breakdown products are seen but with different relative intensities (Figure 3). When steam is added as a reactant, preliminary results show that bisphenol A is the main product, and much fewer of the other products remain. It is proposed that the main mechanism for production of bisphenol A is the presence of steam allowing for hydrolysis of the carbonate bonds within the polycarbonate polymer.

Conclusion

A new Steam Option expands the analysis capacity of the Pyroprobe 6200 from CDS Analytical. The reactions with, and the effects of steam on pyrolysis of different materials can be studied.

References

1. E. Kantarelis, W. Yang, W. Blasiak, Production of Liquid Feedstock from Biomass via Steam Pyrolysis in a Fluidized Bed Reactor., Energy and Fuels, 2013, 27, 4748-4759.

2. G. Bozzano, M. Dente, R. Del Roso, “Poly(bisophenol A carbonate) Recycling: High Pressure Hydrolysis Can be a Convenient Way”,Intertech Open, March 2012.