Chemistry and chemical engineering process for making PET from bio based monomers.

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Polyesters are one of the most important and versatile polymers in use today. They are produced by the polycondensation reaction of a glycol or dialcohol with a difunctional carboxylic acid. Polyesters are continuously used for several purposes ranging from bottles for water, carbonated drinks, health care products to fibers or carpet.

Poly ethylene terephthalate (PET) is polyester formed by step-growth polymerization from ethylene glycol (EG) and terephthalic acid (PTA). EG is traditionally obtained from the oxidation of ethylene over metal catalyst. PTA is obtained from liquid phase oxidation of p-xylene. The synthesis of PET requires a two stage process: esterification and polycondensation. PET raw material EG and PTA are currently obtained through reforming process of oil and natural gas. There are alternative chemical routes identified on how to successfully transform the sugars obtained from biomass material into terephthalic acid and ethylene glycol. Yield of final product obtained is still in the range of low molecular weight material and effective separation represents a challenging step for researchers. In this project we produce PET using EG and PTA obtained from oil and also with both raw materials obtained from a bio based source. Polymer produced with each set of raw material is characterized and compared to identify similarities or differences between them. In our approach we separate PTA precursor (p-xylene) from a bio-based aromatic mixture. This mixture can come from any of the following chemical routes: 1) bio based oil (BTX) provided to us, 2) product from Diels Alder reaction of 2,5-dimethylfuran (DMF) and ethylene, 3) product effluent from pyrolysis reaction of 2-methylfuran (2MF) and propylene. It is anticipated that in any of the separations there might be impurities (other organic compounds) that may affect the purity of the final product obtained; therefore our main objectives of the project are to determine the effect of these low molecular weight compounds (impurities) on the polymerization and characteristics of PET and identify critical areas on the separation train of precursor.

Thermochemical transformation of biomass produces furanic compounds by dehydration of sugar molecules present in the cellulose and hemicellulose. These compounds can be reacted with olefins via Diels-Alder reaction to produce aromatics. Using CDS Analytical Pyroprobe 2-methylfuran and propylene react at 600 °C over zeolite catalyst. Product obtained contains p-xylene along with other high carbon aromatics. This experiment was done to prove the concept on the formation of desired chemicals. The next step is to do pyrolysis in a fixed bed reactor to collect the product effluent and do separation of p-xylene. As extension of the work with furanic compounds, 2-5 dimethylfuran is reacted with ethylene over zeolite Y catalyst in a 4590 Micro Bench Top Parr Reactor. This reaction follows a cyclo addition mechanism producing aromatics with mono, di and tri substituted groups.

Bio oil and liquid samples obtained from separation train of experiments in the research are characterized using Shimadzu GC2010 with flame ionization detector, Bruker GC450 with mass spectrometer and Shimadzu VP HPLC with UV detector. In all cases PTA precursor is separated from each of the mixture using fractional distillation and crystallization. For the first step, we use a packed bed and a plate column along with a

reflux distillation head to separate streams containing aromatics with different boiling point. The stream containing xylene isomers is cooled down to temperatures below -50 °C, this allows us to crystallize p-xylene and separate it via vacuum filtration. P-xylene, cobalt acetate, acetic acid and air are fed to Parr reactor to do oxidation. The product obtained is a low grade crude terephthalic acid that contains different impurities, i.e. 4-carboxylbenzaldehyde (4-CBA). The subsequent step is the purification, the crude acid is mixed with Pd over carbon and deionized water to create a slurry of 13% w acid. This mixture is placed in the same Parr reactor and hydrogen is used to pressurize the system. A hydrogenation reaction takes place, transforming the 4-CBA into toluic acid. The solid/liquid product is separated by vacuum filtration obtaining purified terephthalic acid in solid form. This bio based acid and bio based ethylene glycol (provided to us) are used to do polymerization on Parr reactor and produce PET. To make a comparison with traditional process, EG and PTA are obtained from industry and used to make polymer with the same procedure and reactor as the bio based.

Table 1 show the results obtained from analysis of bio oil. Benzene, toluene and xylenes account for 76% w of the total mixture, p-xylene in specific is present at 10% w. At the current stage of the research we are able to separate meta-, ortho- and para-xylene as a combined stream with 78% purity; we are working on crystallization to obtain p-xylene as a purified product.

Table 1 – Identified components in Bio oil.

A	Benzene	M	Benzene, 1,2,4,5-tetramethyl-
B	Toluene	N	1-propenal, 3-phenyl-
C	Ethylbenzene, m-p-xylene	O	Benzofuran, 2-methyl-
D	o-xylene	P	Benzene, 4-ethenyl-1,2-dimethyl-
E	Benzene-propyl	Q	2-methylindene
F	Benzene, 1-ethyl-3-methyl-	R	1H-Indene, 1-methyl-
G	Benzene, (1-methylethyl)-	S	Naphthalene
H	Benzene, 1,2,4-trimethyl-	T	Naphthalene, 1,2-dihydro-3-methyl
I	Benzene, 1,3,5-trimethyl-	U	Naphthalene, 1,2-dihydro-4-methyl
J	Indane	W	Naphthalene,2-methyl-
K	Indene	X	Naphthalene,2-ethyl-
L	Benzene, (2-methyl-1-1propenyl)-	Y	Naphthalene,1,2-dimethyl-

On the thermochemical approach, we followed a stage test to determine the effect of catalyst and propylene on the formation of aromatic material. 2MF is tested on pyroprobe unit; the effluent of the reaction is send to Bruker GCMS for characterization. Once the chromatogram is obtained, the area under the curve for the desired peaks is measured. Table 2 show the ratio of the area under the curve considering the pyrolysis of sole 2MF as the reference value. We can see an increase in the formation of aromatics by adding catalyst to the system. Then when we add propylene to the reaction media there is a dramatic increase in the formation of xylenes. This proves the idea that the formation of aromatics follows Diels Alder process and the feed of an olefin boost reaction rate. In each of the chemical routes we have promising results towards obtaining polymer precursor from bio derived source.

Table 2 – Area ratio for selected aromatics in 2MF pyrolysis.

	Catalyst Location			Area Ratio			
Material	Tube	Reactor	Gas	Benzene	Toluene	EB + m/p-xylene	o-xylene
2-MF	X		He	1.0	1.0	1.0	1.0
2-MF		X	He	8.1	7.5	13.4	12.9
2-MF		X	HePro	11.3	22.1	65.3	73.0