

Direct Production of Propene from the Thermolysis of Poly(β -hydroxybutyrate)

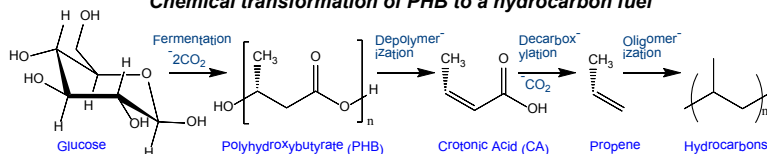
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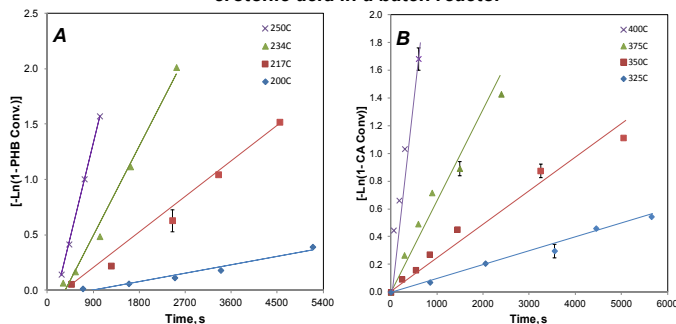
Abstract

To transform biomass components into hydrocarbon fuels it is clear that there are two main transformations that need to occur, i.e., deoxygenation and carbon chain extension. The potential routes for decreasing the oxygen content of biomass intermediates include dehydration, hydrodeoxygenation and decarboxylation. One route that is examined here is the conversion of polyhydroxyalkanoates (PHA) to alkenes that would be intermediates to hydrocarbon fuels. Thermal breakdown of PHA proceeds via an intermediate carboxylic acid, which can then be decarboxylated to an alkene. Oligomerization of alkenes by well-known commercial technologies would permit production of a range of hydrocarbon fuels from a carbohydrate derived intermediate. Moreover, polyhydroxybutyrate (PHB) can be produced in *Cupriavidus necator* (formerly known as *Ralstonia eutropha*) and *Alcaligenes eutrophus* on a variety of carbon sources including glucose, fructose and glycerol with PHB accumulation reaching 75% of dry cell mass. We conducted thermal conversion of PHB and pure crotonic acid (CA), the intermediate carboxylic acid produced by thermal depolymerization of PHB, in a flow-through reactor. The results of initial experiments on the thermal conversion of CA showed that up to 75 mole% yields of propene could be achieved by optimizing the residence time and temperature of the reactor. Further experiments are being investigated to optimize the reactor parameters and enhance propene yields via thermal conversion of PHB.

Chemical transformation of PHB to a hydrocarbon fuel



Kinetics for the depolymerization of PHB and decarboxylation of crotonic acid in a batch reactor



First-order reaction kinetics for (A) thermal depolymerization of PHB(B) decarboxylation of CA. The straight lines represent linear fits to the experimental data

Arrhenius parameters and Propene and CO₂ yields from batch experiments

	A (s ⁻¹)	E _a (kJ mol ⁻¹)	R ²
PHB depolymerization	1.6 × 10 ¹⁰	128.6	0.987
CA decarboxylation	1.65 × 10 ⁸	140.2	0.964

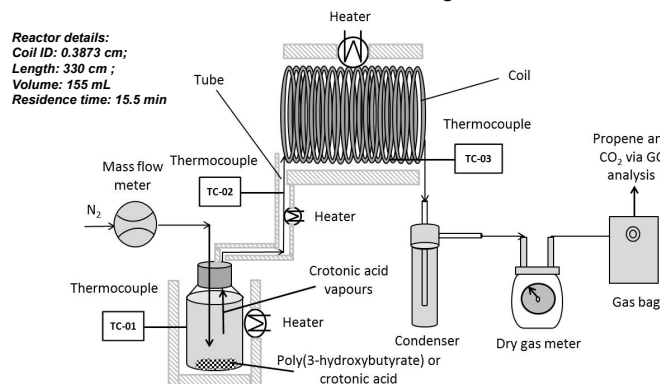
Arrhenius parameters for the conversion of PHB and crotonic acid through depolymerization and decarboxylation, respectively.

Temperature, °C	Time, min	Propene Yield (%)	CO ₂ Yield (%)
325	65	22 ± 3	32 ± 5
	100	28	42
350	60	43 ± 4	58 ± 5
	90	51 ± 1	67 ± 0.4
375	30	49 ± 2	59 ± 5
	60	64 ± 2	76 ± 4
400	10	50 ± 3	66 ± 3
	15	64 ± 2	81 ± 8

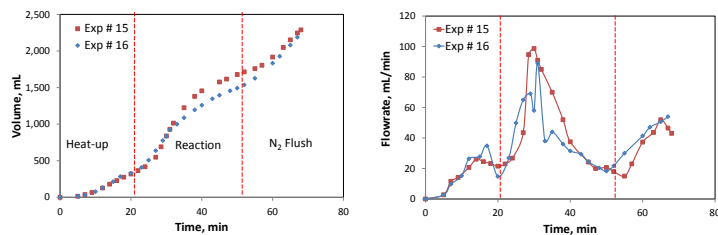
Propene and CO₂ yields from decarboxylation of CA

Thermal depolymerization and decarboxylation of polyhydroxybutyrate to propene in a flow-through reactor

Schematic of a flow-through reactor



Gas (Propene and CO₂) production in a flow-through experiment



Propene and CO₂ yields from decarboxylation of CA in flow-through experiments

Tube	Coil	N ₂ Flowrate	Residence time, min	Yield		Unreacted CA	
				Propene %	CO ₂ %	g	%
340	375	10	15.5	79.1	78.8	0.37	18.5
340	375	10	15.5	70.5	68.8	0.53	26.5
375	375	10	15.5	60.2	61.6	0.73	36.5

Conclusions

- This work has shown that in a batch reactor both the depolymerization of PHB to CA and the decarboxylation of CA can be described with first-order reaction kinetics.
- Decarboxylation is the rate limiting step; the CA decarboxylation rate is 500-900 times slower than the PHB depolymerization reaction depending on temperature.
- Thermal decarboxylation of crotonic acid was achieved in a flow-through reactor.
- Decarboxylation of crotonic acid in a flow-through reactor under optimized conditions resulted in greater than 75% yields of propene at 375°C.