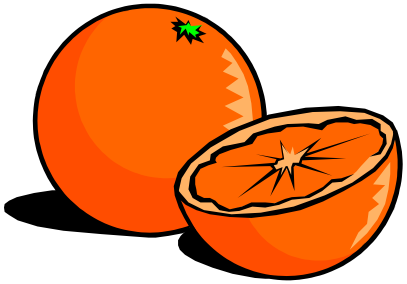

Polymers from Oranges

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Chris Fogle

Josef Dalaeli

Basis for Project

- Alternating Copolymerization of Limonene Oxide and Carbon Dioxide
- Limonene is citrus peel oil
- Combination of renewable resource and consuming excess carbon dioxide
- Polymerization results in a polycarbonate plastic with properties similar to expandable polystyrene

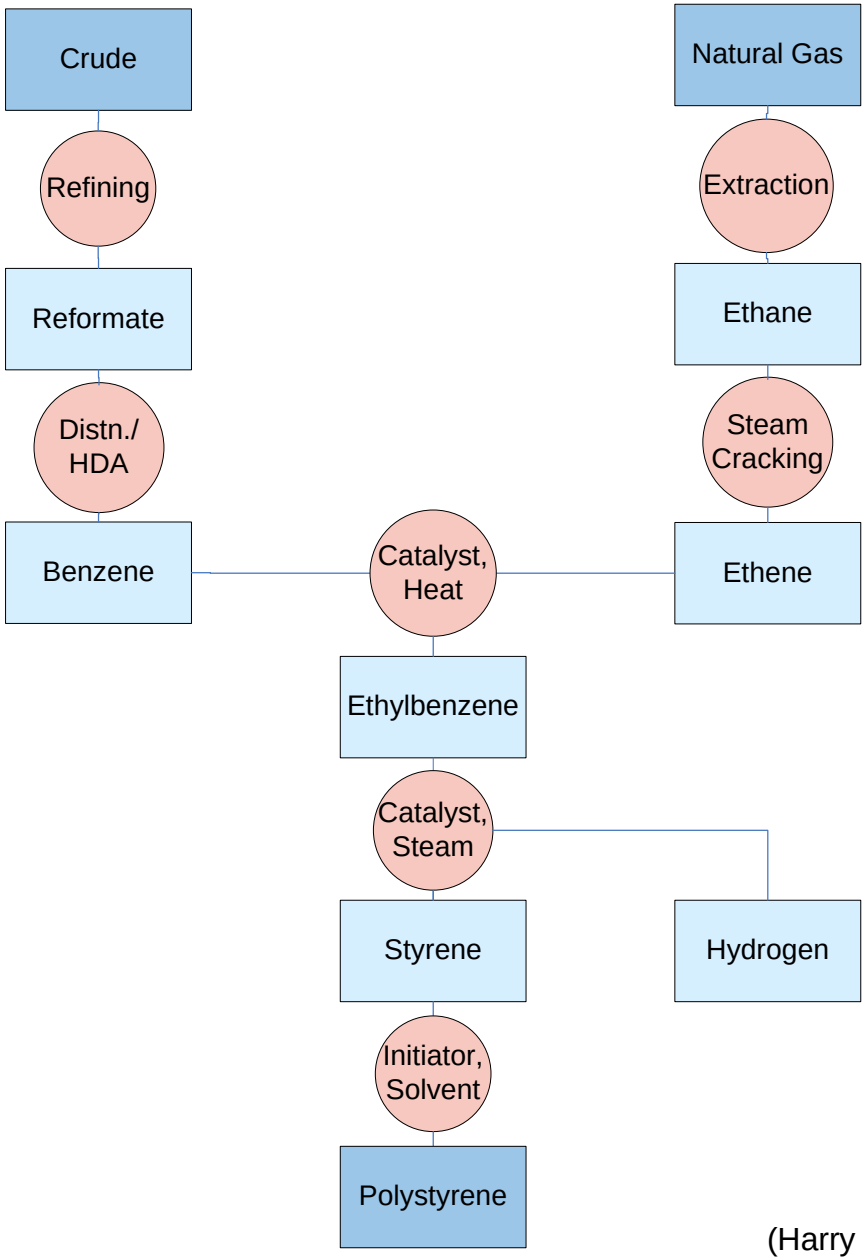
Project Benefits

- Carbon dioxide is a cheap feedstock
- Carbon dioxide is likely to remain cheap or become cheaper as pollution restrictions increase
- Reduces dependence on oil derivatives, the current source of polystyrene
- Reduces dependence on oil market

Current Polystyrene Production Method

- Polystyrene is produced from ethene and benzene.
- Ethene and benzene are first combined to make ethylbenzene.
- Ethylbenzene is dehydrogenated to make styrene.
- Styrene is then used to make polystyrene.

Flowchart of Current Production Method



(Harry Blair Consultants)

Major Risks

- Feedstock depends on varying citrus market, prone to natural disaster
- Industrial scale failure of experimental scale technology
- Introduction of new material technologies that replace polystyrene

Project Challenges

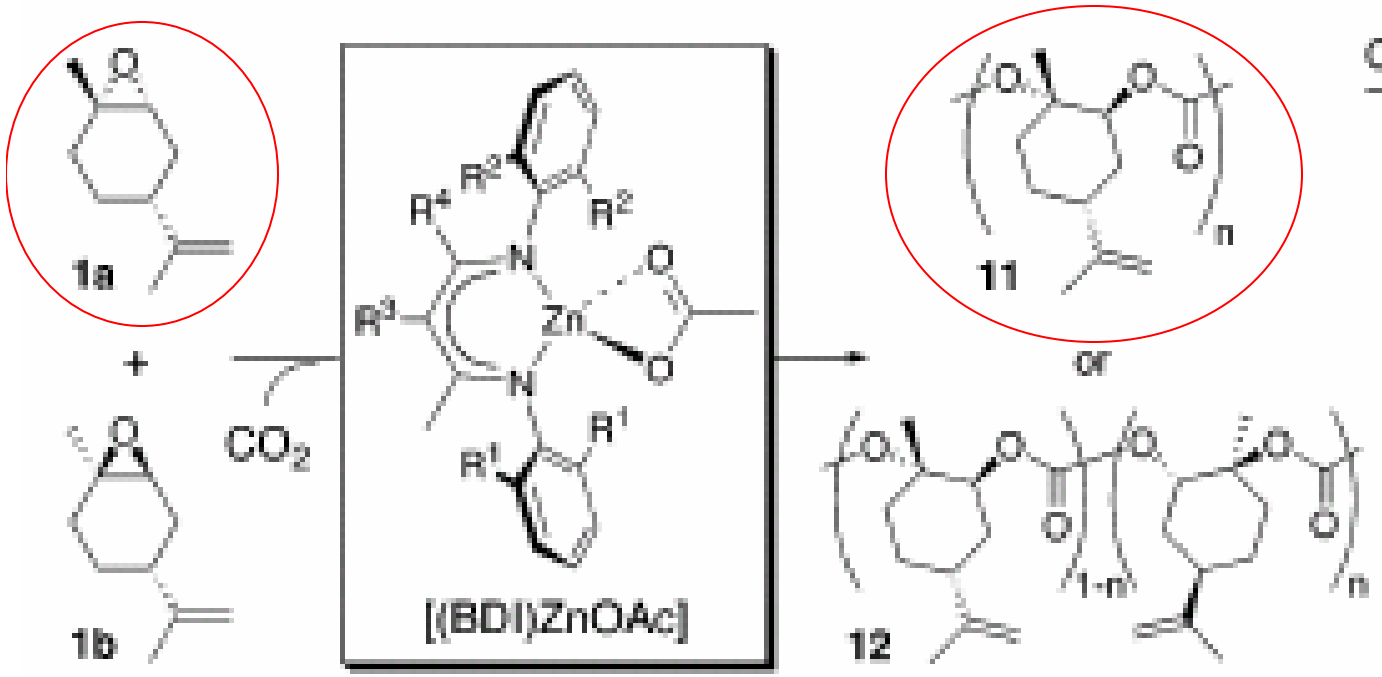
- Based on new technology which has not been thoroughly tested
- Involves different chemistry than oil derivatives, such as stereochemistry
- Uncommon catalyst for industrial use
- Limonene Oxide production versus purchase
- Product will vary slightly from conventional polystyrene in an unknown manner

Process Details

- Reaction involves:
  - R-enantiomer of limonene oxide
  - Carbon dioxide at 100 psi
  - Beta-diiminate zinc complex catalyst
  - Nearly ambient temperature (25^0C)
  - Methanol wash to remove catalyst and unreacted limonene oxide

Process Reaction

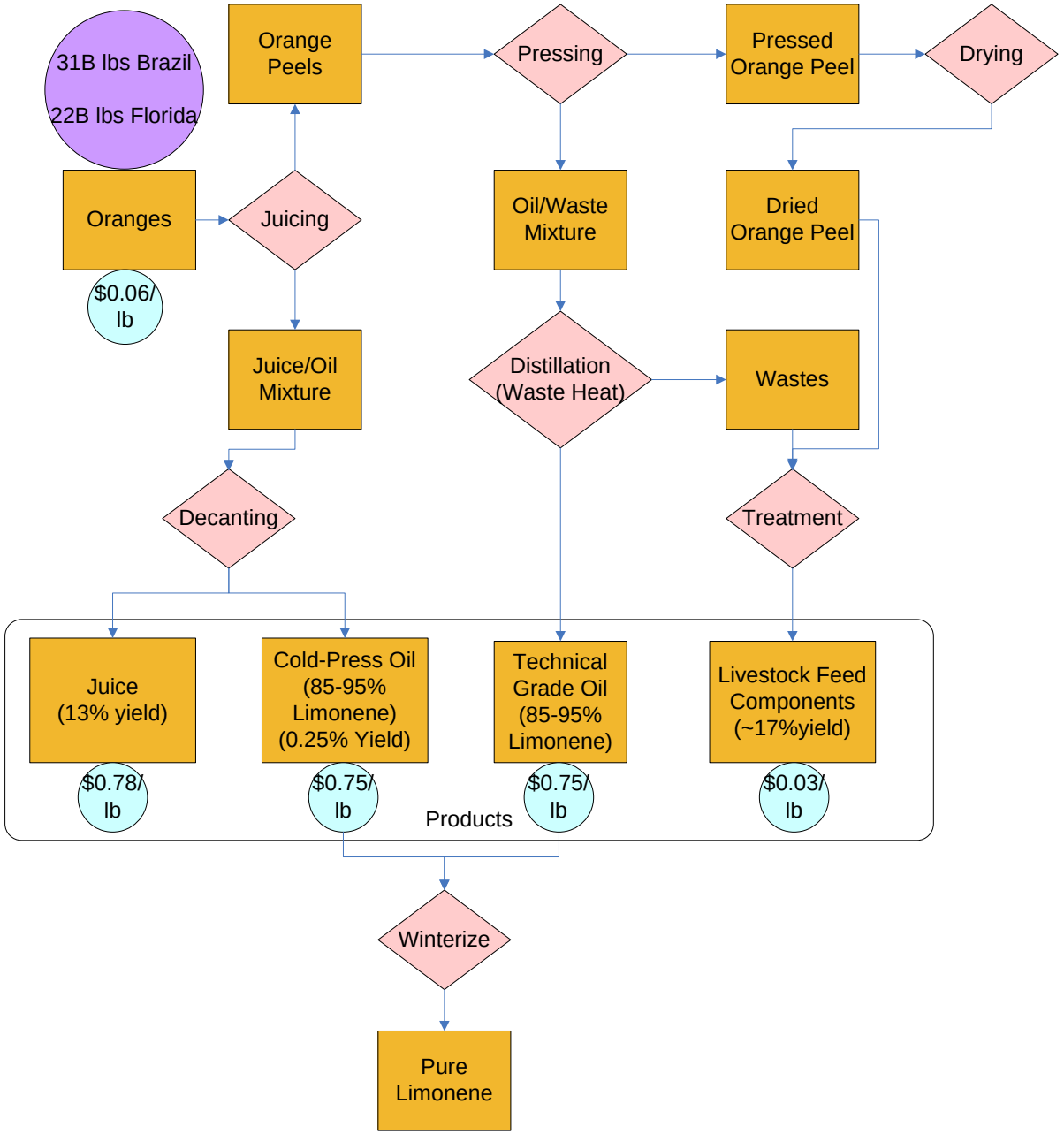
Scheme 1. Copolymerization of *trans*- (1a) and *cis*-(*R*)-Limonene Oxide (1b) and CO_2 using β-Diiminate Zinc Acetate Complexes



Complex	R^1	R^2	R^3	R^4
2	Et	Et	H	CH_3
3	^{i}Pr	^{i}Pr	H	CH_3
4	Me	Me	H	CH_3
5	Et	^{i}Pr	H	CH_3
6	Et	Et	H	CF_3
7	^{i}Pr	Et	H	CF_3
8	Et	^{i}Pr	H	CF_3
9	Et	Et	CN	CH_3
10	^{i}Pr	Me	CN	CH_3

(Byrne)

Limonene Extraction

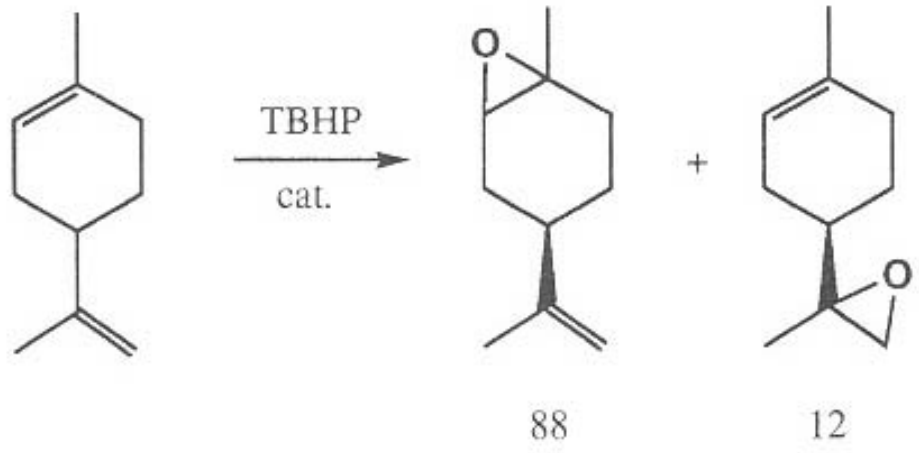


Limonene Supply

- Because limonene is produced both during the juicing process and the peel treatment process, peels cannot be purchased to obtain limonene.
- Juice and orange prices fluctuate greatly (over past twenty years the prices have doubled and halved).
- Because of unstable product prices and relatively low limonene yield in the process (0.5%), breaking into the orange market is not advisable for an internal source of limonene.

Limonene Oxide

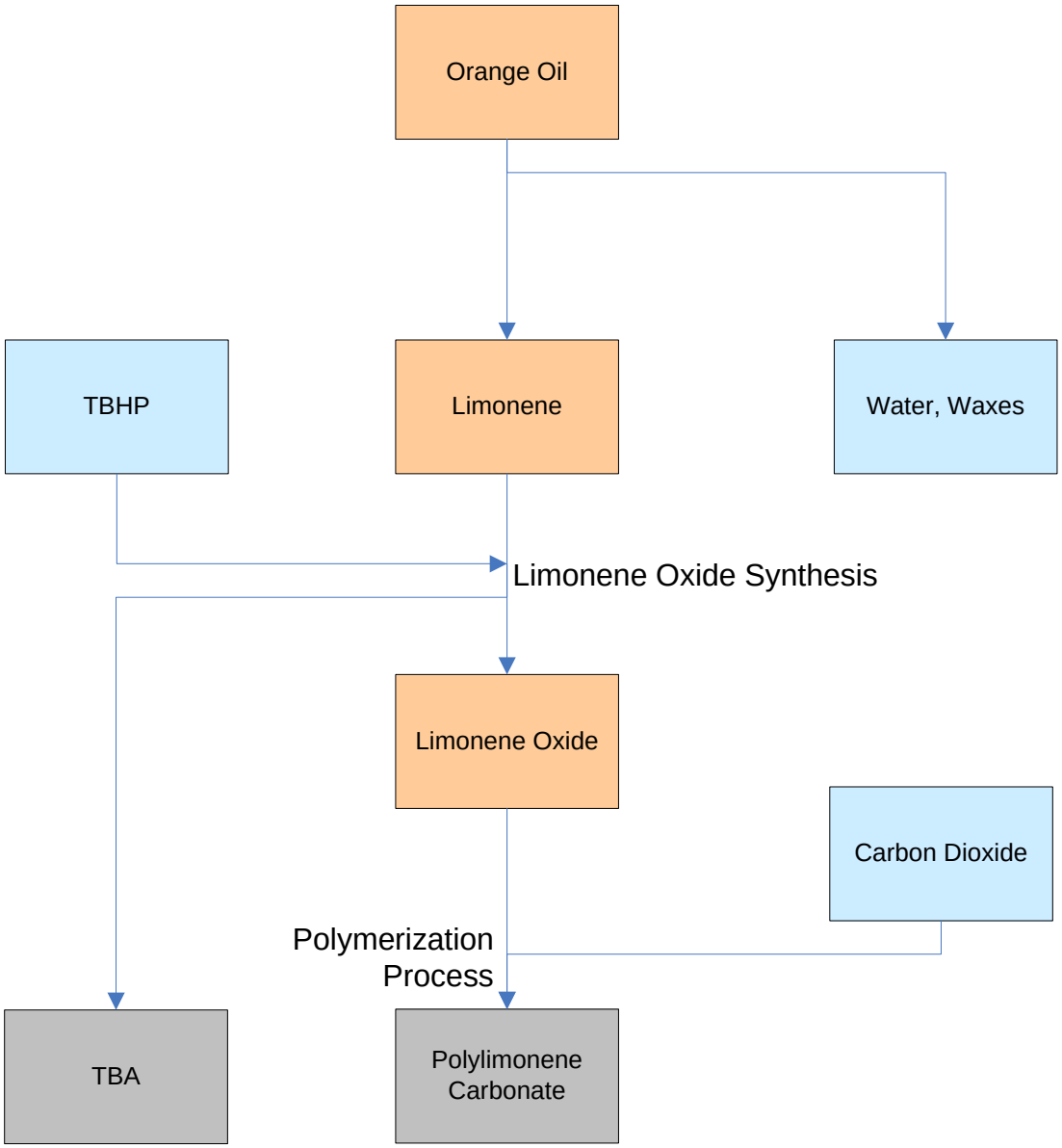
- Limonene oxide can be synthesized by a titanium catalytic reaction of TBHP and limonene.



Scheme 2.

(Cativiela)

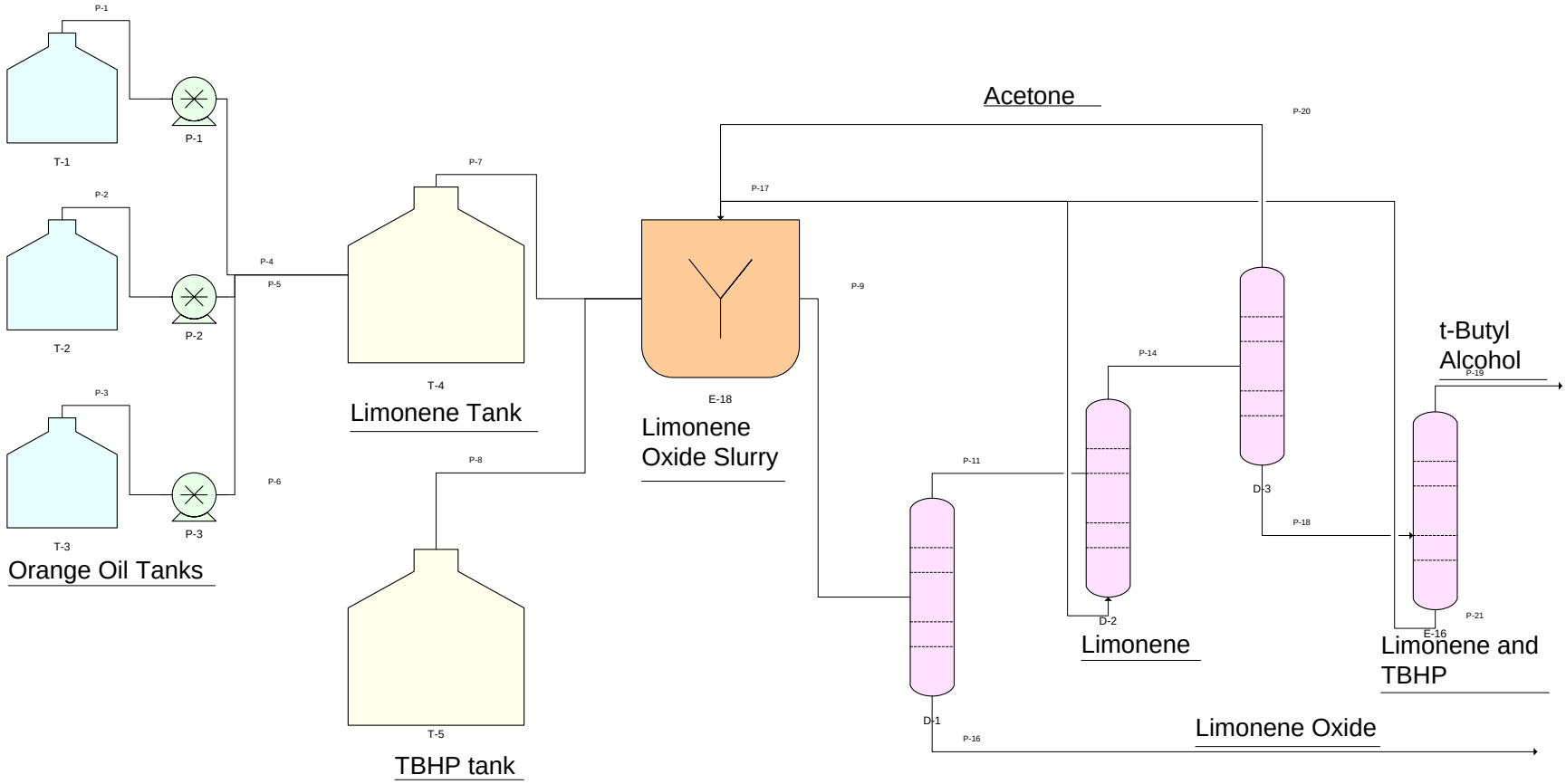
Process Flowchart



Major Pieces of Equipment

- Storage for limonene oxide, polymer, and carbon dioxide
- Continuous Stirred Tank Reactors for limonene oxide synthesis and polymerization
- Methanol Wash Mixing Tanks
- Distillation Columns
- Rotary Vacuum Filters and Dryer

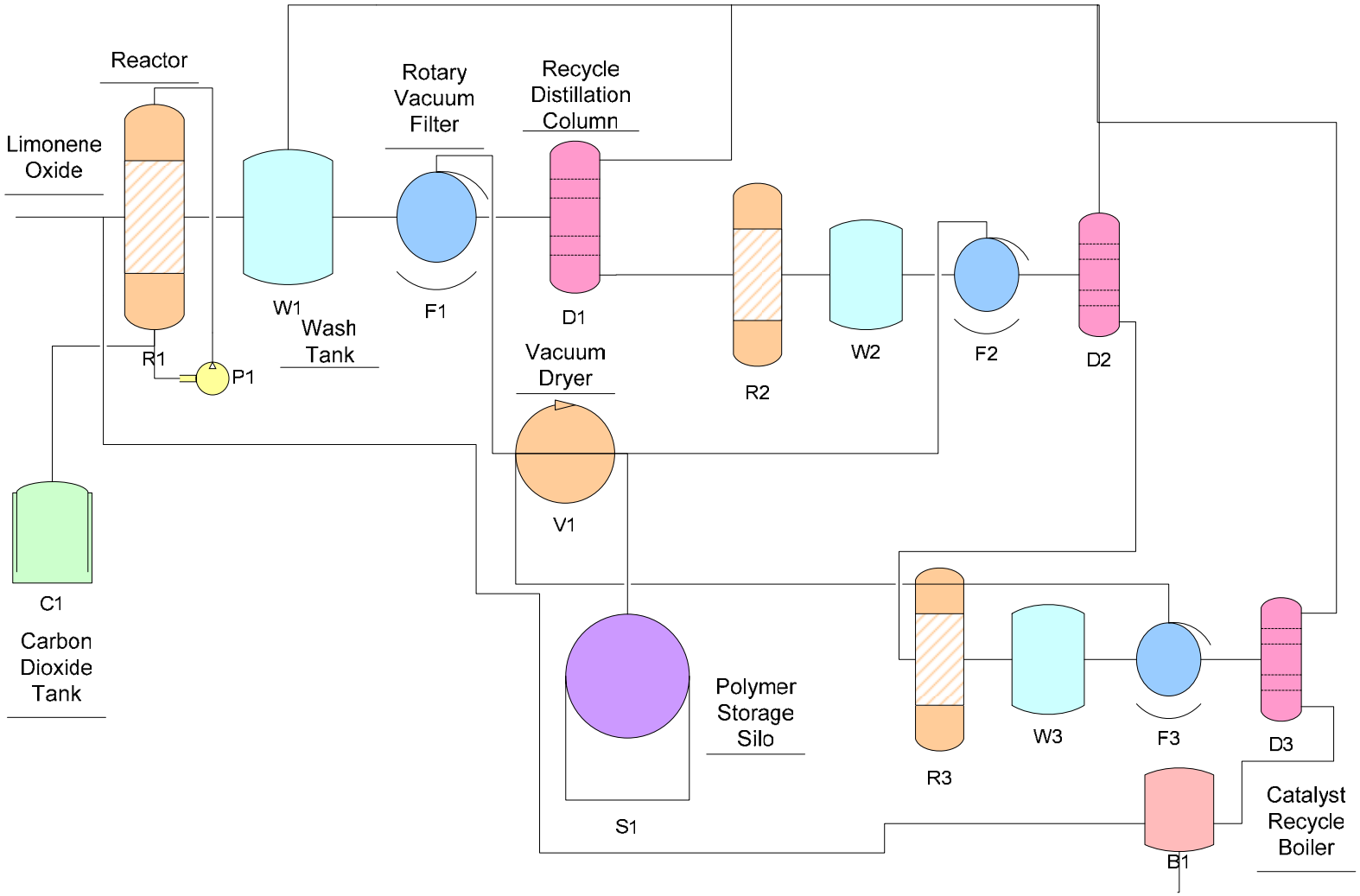
PFD
Limonene Oxide Production



Equipment-Limonene Oxide Production

Limonene Oxide Process Equipment Costs				
Displayed Text	***Description***	***Size***	***Cost (1997)***	***Cost (2005)***
D1	Distillation Column 1	0.5 m dia., 10 trays	$13,400	$14,458
D2	Distillation Column 2	0.5 m dia., 4 trays	$5,400	$5,826
D3	Distillation Column 3	0.5 m dia., 13 trays	$17,500	$18,882
D4	Distillation Column 4	0.5 m dia., 13 trays	$17,500	$18,882
R1	Slurry Reactor	3000gal	$25,000	$26,974
T1	Orange Oil Tank 1	2.3E4gal	$77,000	$83,079
T2	Orange Oil Tank 2	2.3E4gal	$77,000	$83,079
T3	Orange Oil Tank 3	2.3E4gal	$77,000	$83,079
T4	Limonene Tank	9E3gal	$57,000	$61,500
T5	TBHP Tank	9E3gal	$57,000	$61,500
			Total Polymerization Equipment Cost	$457,258

PFD
Polymerization



Equipment-Limonene Oxide Production

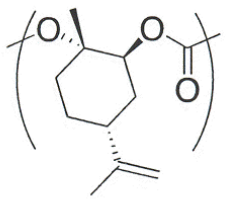
Displayed Text	***Description***	***Size***	***Cost (1997)***	***Cost (2005)***
D1	Distillation Column	2 trays, 0.5 m diameter	$2,500	$2,697
D2	Distillation Column	2 trays, 0.5 m diameter	$2,500	$2,697
D3	Distillation Column	2 trays, 0.5 m diameter	$2,500	$2,697
F1	Rotary Vacuum Filter	0.5 m^2	$30,000	$32,368
F2	Rotary Vacuum Filter	0.5 m^2	$30,000	$32,368
F3	Rotary Vacuum Filter	0.5 m^2	$30,000	$32,368
R1	PFR	12.872 m^3	$115,500	$124,618
R2	PFR	5.024 m^3	$70,000	$75,526
R3	PFR	2.392 m^3	$47,000	$50,711
S1	Polymer Silo	47 m^3	$15,000	$16,184
W1	Wash Mixing Tank	0.3 m^3	$6,000	$6,474
W2	Wash Mixing Tank	0.3 m^3	$6,000	$6,474
W3	Wash Mixing Tank	0.3 m^3	$6,000	$6,474
B1	Flash Tank	0.15 m^3	$2,000	$2,158
V1	Rotary Dryer	4.65 m^2, 3.73 kW	$75,000	$80,921
			Total Polymerization Equipment Cost	$474,737

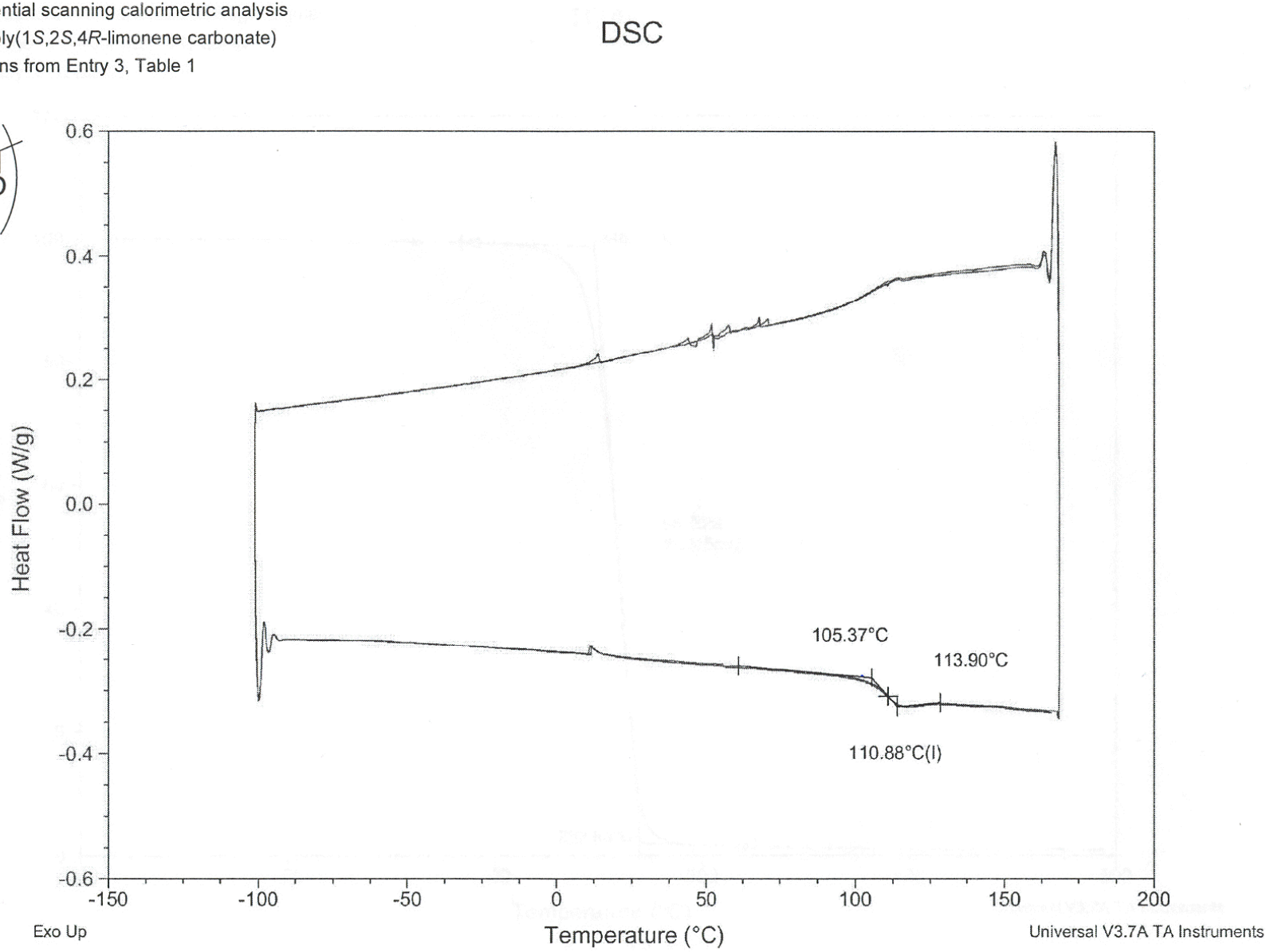
Characterization Analysis of Polymer

- DSC shows high likelihood of polymer being amorphous
  - Glass point transition with no melting point
- Because the polymer is amorphous, it is more similar to expandable PS than crystalline PS

DSC

Figure S8. Differential scanning calorimetric analysis of Regioregular Poly(1*S*,2*S*,4*R*-limonene carbonate) (**11**) using conditions from Entry 3, Table 1





(Byrne)

Production Rates

- Most polystyrene plants produce more than 100 million pounds per year.
- Several plants produce more than 500 million pounds per year.
- These plants are owned by chemical companies like Dow and most major oil companies.
- Production rate was chosen as 33Mlb/yr by assuming the maximum possible amount of limonene available in Florida without disturbing the limonene market

Material Costs

- Orange Oil (90% Limonene)
  - Florida $0.77/lb
  - Brazil $0.45/lb
- Carbon Dioxide
  - Florida $0.10/lb
  - Brazil $0.15/lb (estimate)
- Polystyrene (conventional) $0.90/lb
- Methanol $0.14/lb
- t-Butyl Alcohol $0.67/lb

One pound of polymer will require 0.78 lb limonene oxide and 0.22 lb carbon dioxide.

Markets

- The polystyrene market is currently strong and expected to continue growing for a few years
- The limonene market is vulnerable to natural disasters but is currently stable
- Key end-use markets include packaging, appliances, electronics, consumer products, information technology, and sheet

Process FCI

Estimation of Capital Investment Cost

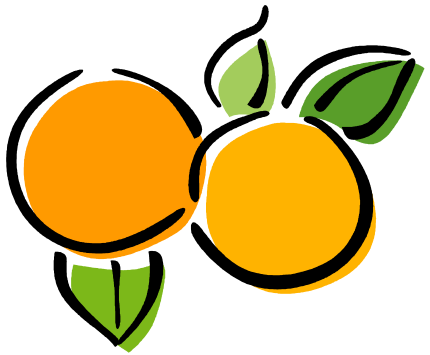
Component	Percent of Delivered Equipment Cost	Estimated Cost
Direct Costs		
Purchased Equipment	Based on Equipment Sizes	$931,995
Delivery	10% of Purchased Equiment	$93,199
Subtotal: Delivered Equipment	100	$1,025,194
Total Direct Cost		$4,715,888
Indirect Costs		
Engineering and Supervision	33	$338,310
Construction Expense	41	$420,330
Legal Expense	4	$41,010
Contractor's Fee	22	$225,540
Contingency	44	$451,090
Total Indirect Cost		$1,476,280
Fixed Capital Investment	Direct Cost + Indirect Cost	$6,192,170
Working Capital	15% of TCI	$1,092,740
Total Capital Investment		$7,284,900

First-Year, Annual Total Product Cost

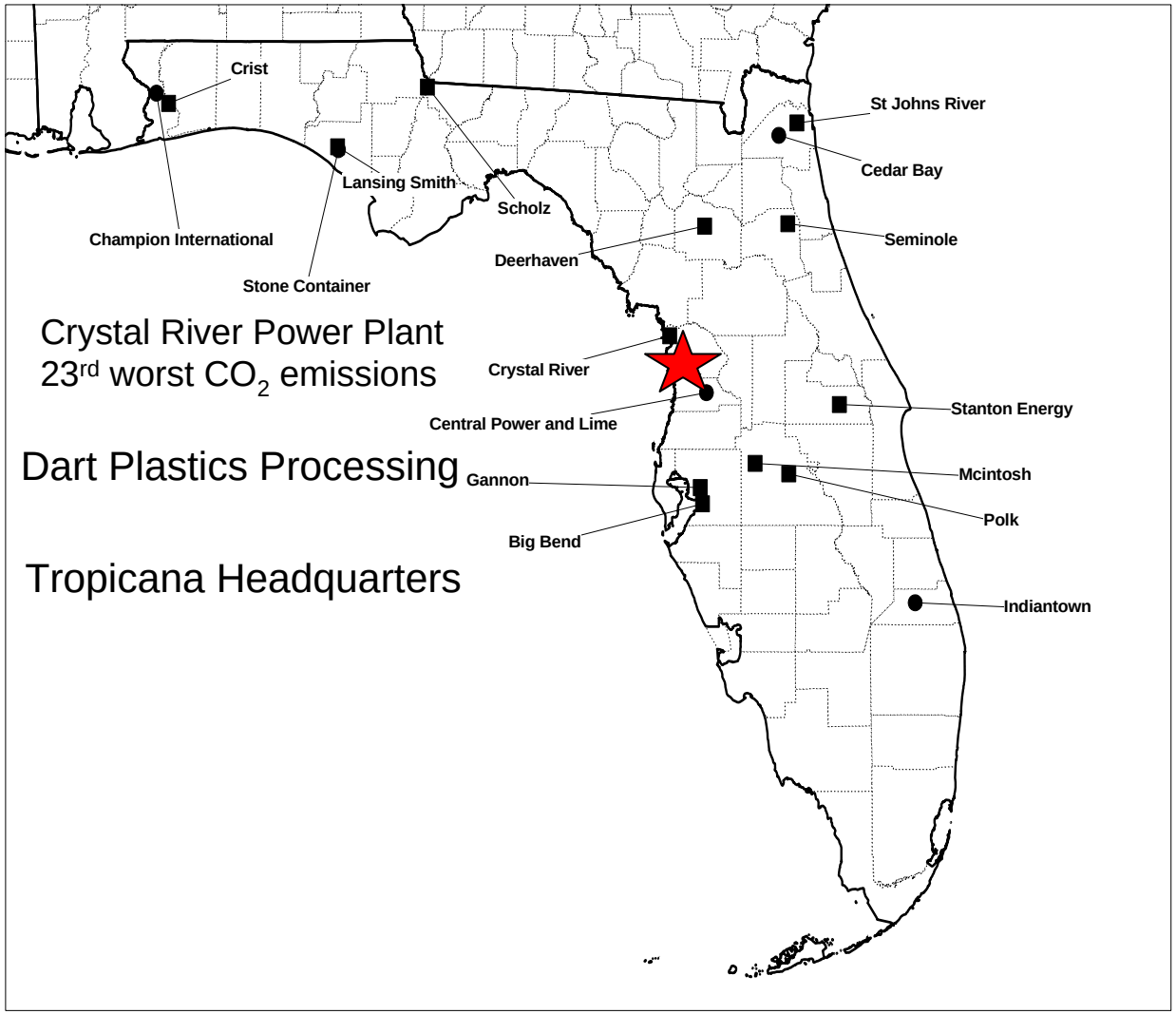
Component	Basis for Estimate	Cost
I. Manufacturing Cost		
A. Direct Production Costs		
1. Raw Materials (Values for Subsequent Years Shown in Table Y)		
Orange Oil	$0.77/lb X 3333 lb/hr X 8760 hr/year	$25,105,634
TBHP	$0.70 X 2025 lb/hr X 8760 hr/year	$12,417,300
Carbon Dioxide	$0.10/lb X 6E6 lb/year	$600,000
Acetone	$0.37/lb X 5025 lb/year	$1,859
Methanol	$0.14/lb X 5000lb/year	$700
Subtotal		$46,587,310
B. Fixed Charges		
1. Depreciation (Calculated Separately in Table X)		
2. Property Taxes	2% of Fixed Capital Investment	$123,840
3. Insurance	1% of Fixed Capital Investment	$61,920
Subtotal (Without Depreciation)		$185,760
C. Overhead costs	50% of operating labor, supervision, and maintenance	$782,042
Total Manufacturing Cost		$47,555,112
II. General Expenses		
Total General Expenses		$2,106,690
Total Product Cost (Without Depreciation)		$47,751,744

Plant Location

- Location should offer both access to citrus chemicals and areas of heavy industrialization where carbon dioxide wastes are abundant
- Both Florida and the Brazilian state of Sao Paulo would offer enough carbon dioxide and orange oil for our plant capacity
- Chemical costs and carbon dioxide costs would be higher in Brazil
- Florida also offers access to plastic processing facilities

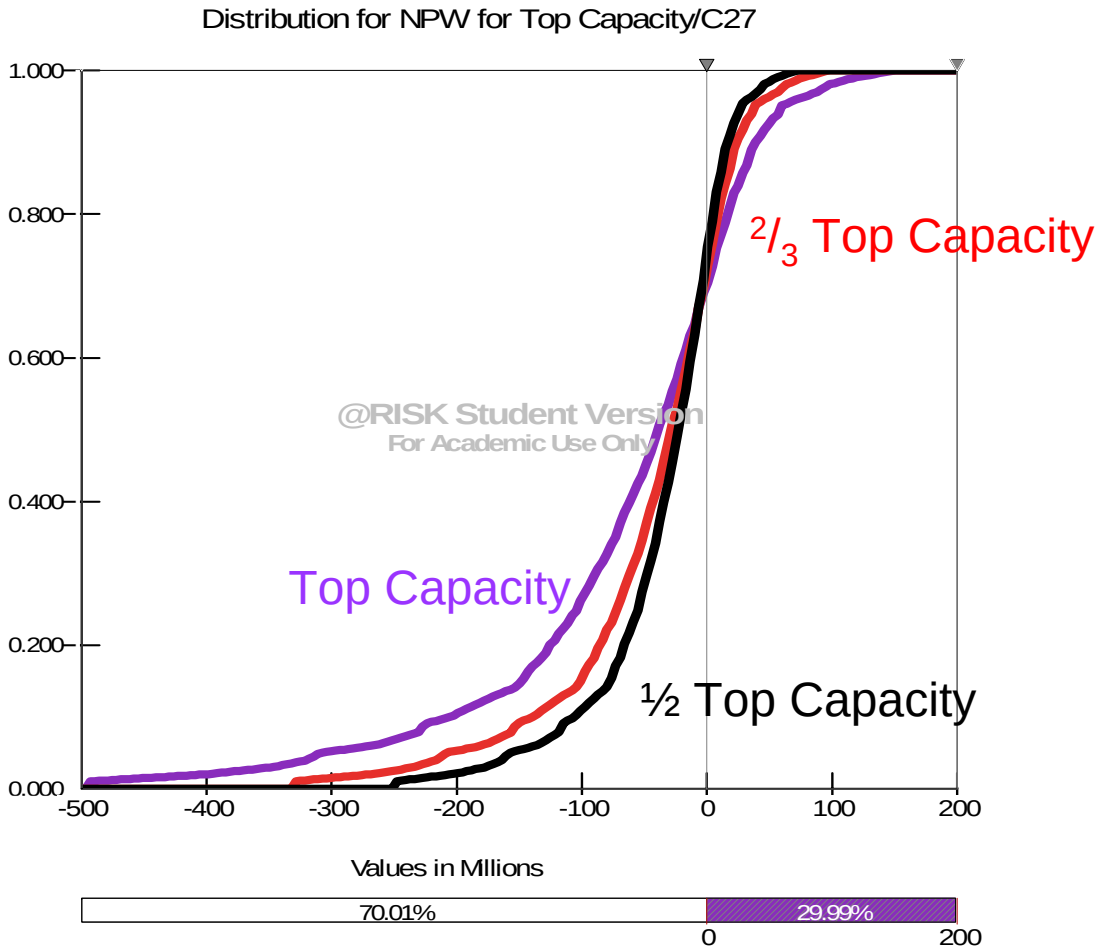


Plant Location



Profitability

Economic Simulations			
ROI	0.1	0.15	0.2
Price of Polymer	$1.18	$1.19	$1.19



Recommendations

- Further plastic analysis by interested companies
- The process will only be profitable if:
  - properties warrant higher prices than polystyrene price
  - oil prices increase the price of polystyrene
- Companies that should be most interested:
  - Orange processing companies
  - Fossil fuel power plants that have high CO_2 emissions

Questions/Comments

Thank you for your time

Have a Nice Day