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CLiCC Webinar Series
Life-Cycle Inventory Module

September 14, 2016

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CHEMICAL LiFE CYCLE COLLABORATIVE

CLiCC Webinar Series

- **Webinar 1, September 14th, 10am - 11am PDT.**
  Title: *CLiCC Life-Cycle Inventory module*

- **Webinar 2, September 30th, 10am - 11am PDT.**
  Title: *CLiCC QSAR, Release, and Fate & Transport modules*

- **Webinar 3, October 7th, 10am - 11am PDT.**
  Title: *CLiCC Predictive Life Cycle Impact Assessment, Exposure, Toxicity, and Uncertainty modules*

All of the webinars will be recorded

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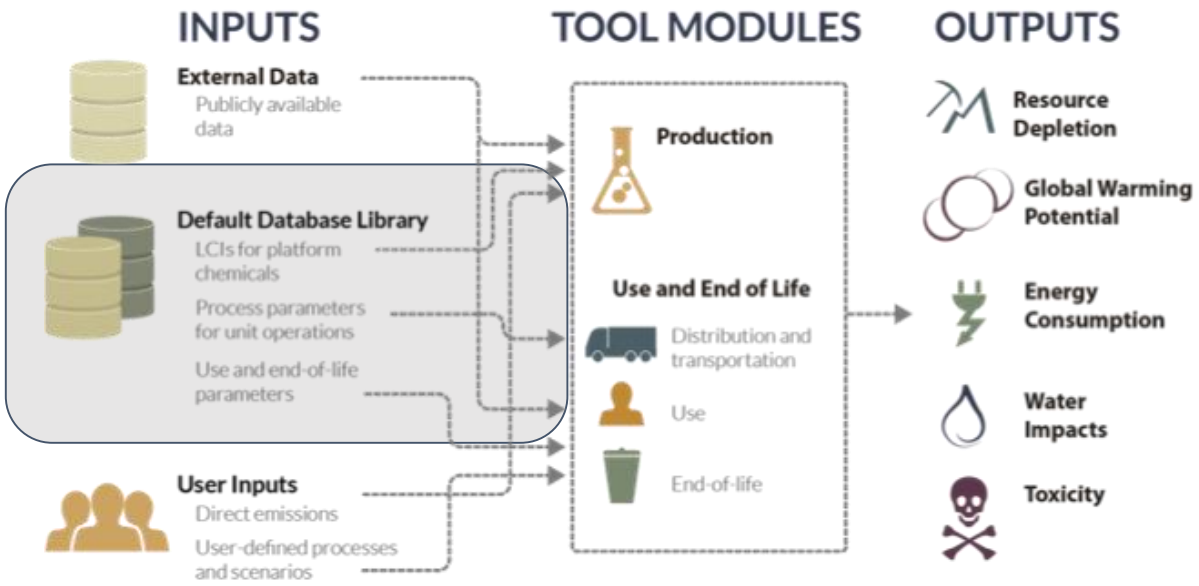
The CLiCC Project at UCSB

U.S. EPA funded UCSB to develop a tool that can ***rapidly*** estimate the environmental impacts of a chemical ***life-cycle*** based on ***limited information***.



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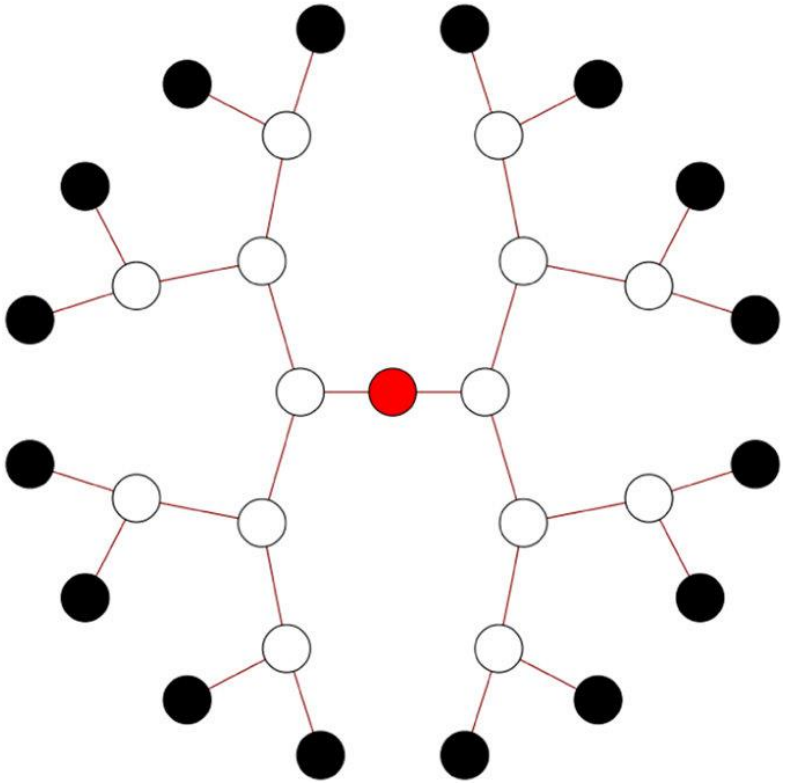
What is Life Cycle Inventory?

- Building block for LCA
- Tracking each inputs/outputs for each process
- Need to cut-off at some point



LCI grows as tree

Why We Create Our Database

- *Number of chemicals is limited*
  - Less than 300 chemicals;
- *Highly uncertain assumptions are applied*
  - Default selectivity for every chemical;
  - Averaged heat requirement for every chemical;
- *Can't provided enough information for the rest of the modules in CLiCC*
  - Also most of the databases are for commercial use

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Major Components in Chemical LCI

Raw material

Energy requirements

Other

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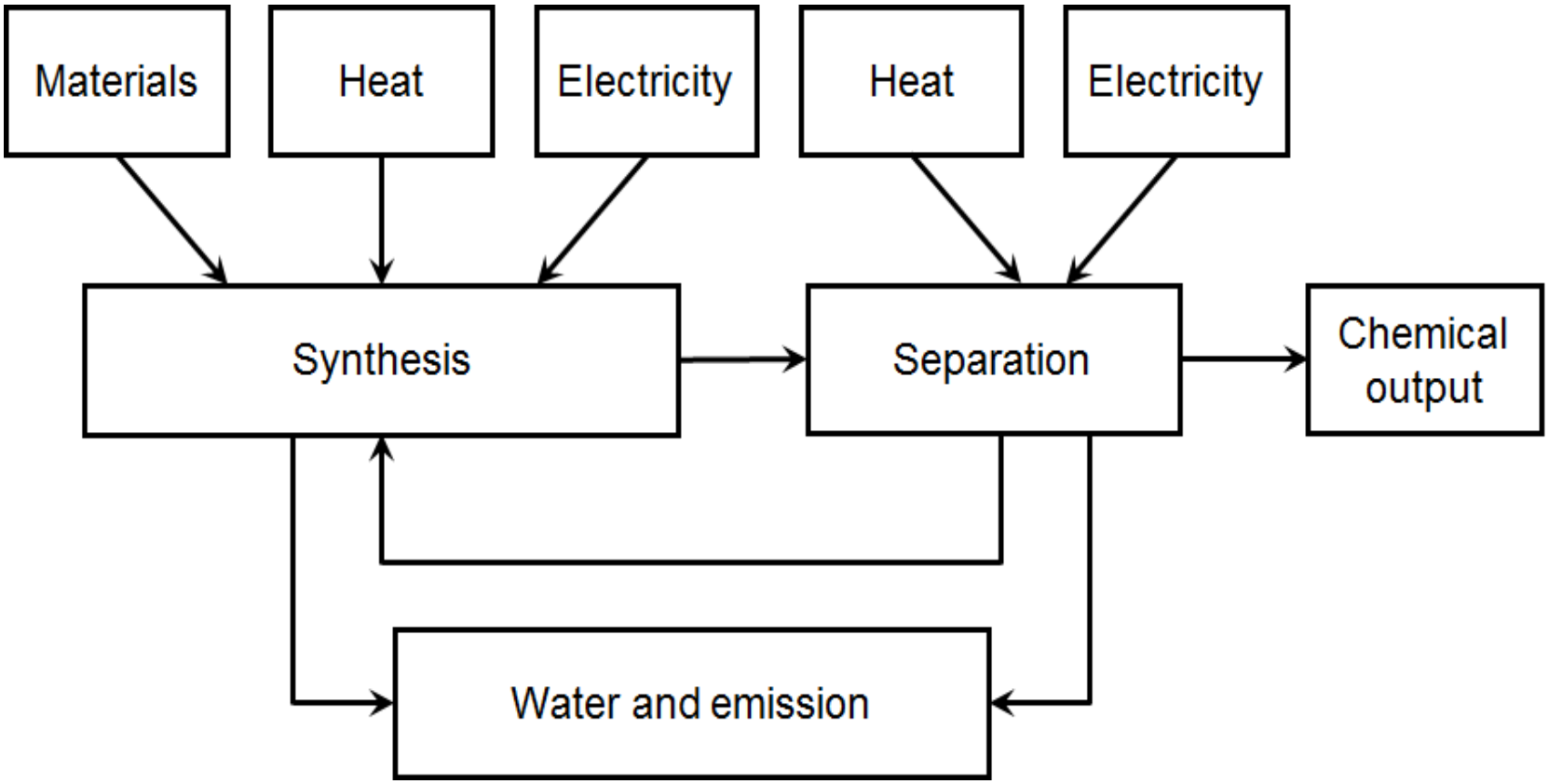
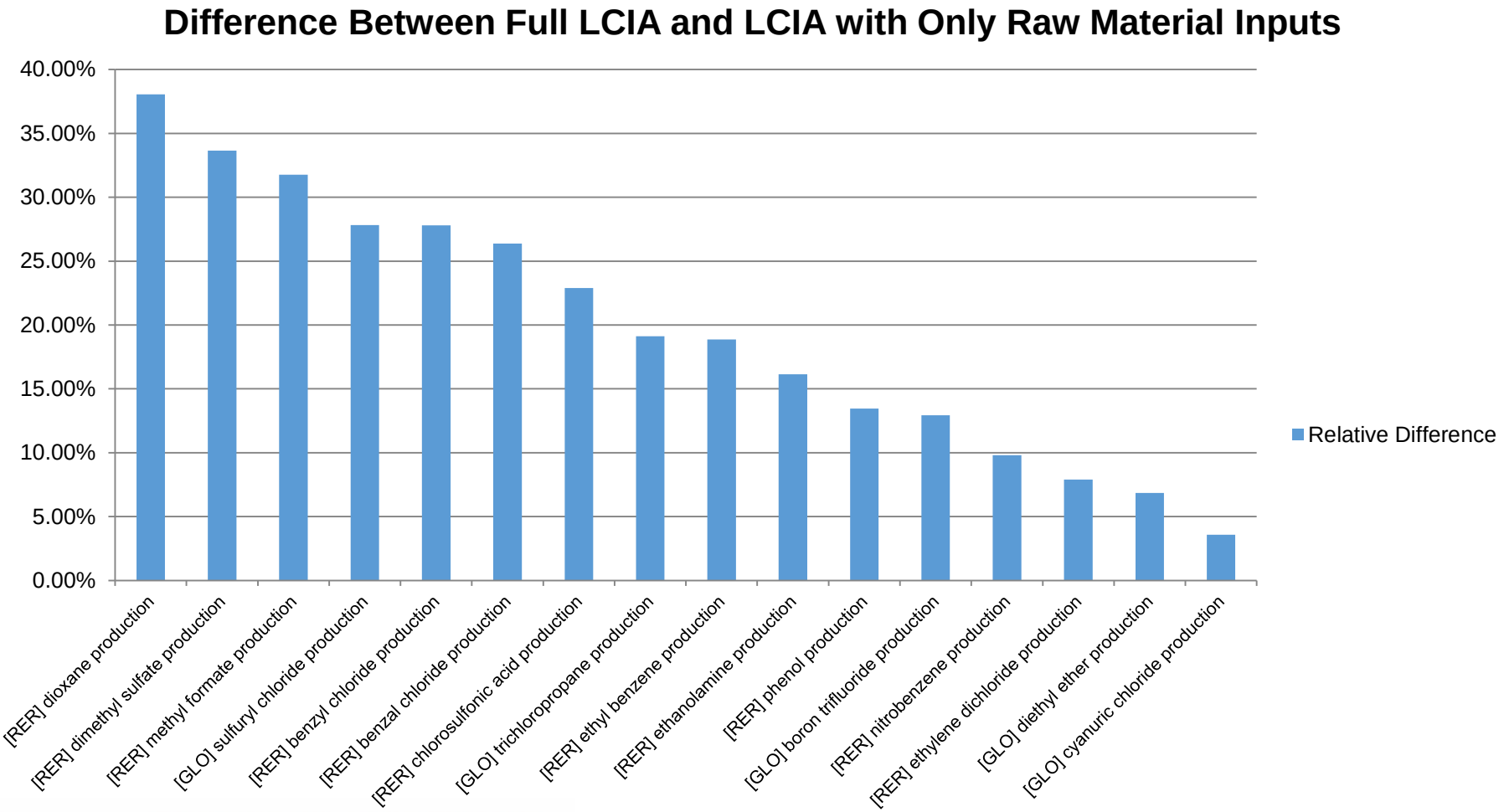
LCI Modeling Framework



Raw Materials Take the Major Part



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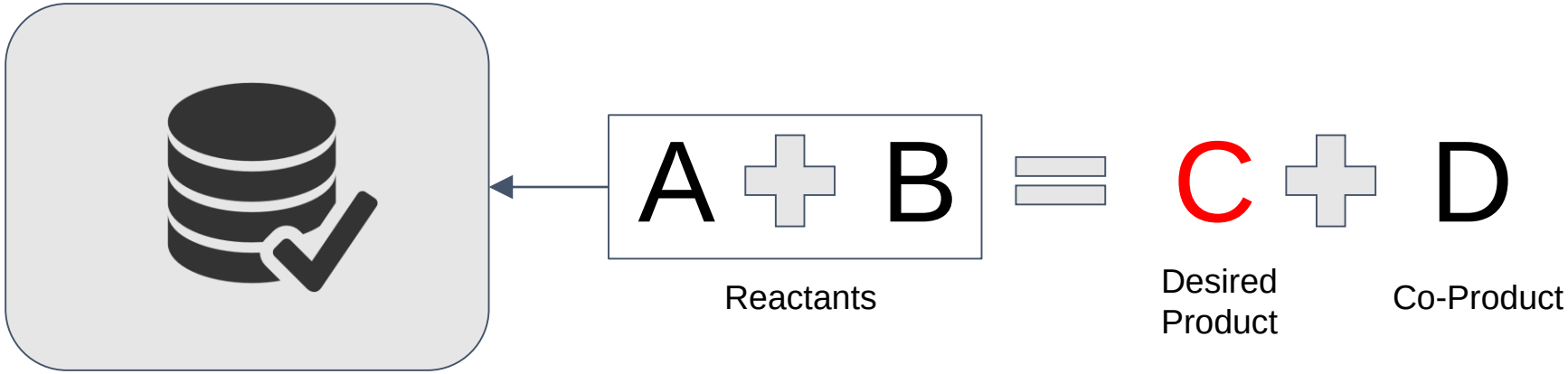
Building Unit Process Information

Developing a database that contains manufacturing information for thousands of chemicals



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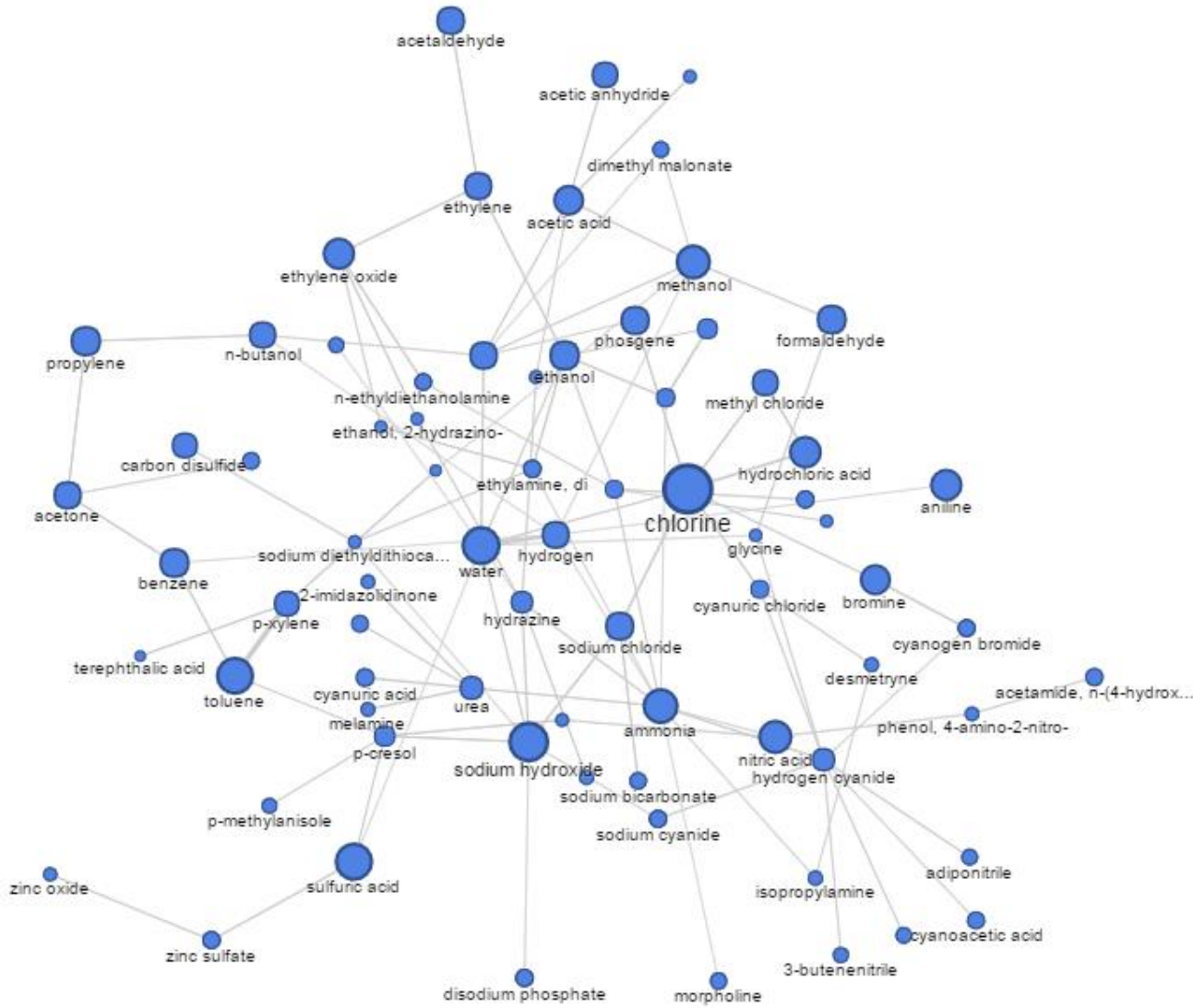
Link to Cradle-to-Gate LCI

- Users would only able to input ***unit process information***.
- We build a background database to generate chemical LCI.
- More than ***1,000 common chemicals*** unit process information are collected and linked.
- Cutted off at basic ‘building block’ chemicals where we have accurate LCI
- LCIs are calculated under ***three different*** scenarios according to user’s inputs



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Methods to Generate LCI

- Available methods depend on user knowledge
- Detailed process knowledge
  - Most favorable option
  - Calculate LCI from material flows
- Knowledge of kinetics for chemistry of interest
  - Kinetics-Based Approach
  - Second-most favorable option
  - Use methodology to find best-case LCI
- Knowledge of chemistry of interest only
  - Stoichiometry-Based Approach
  - Use assumptions about efficiency of raw materials consumption

Cradle-to-Gate LCI

- Methods listed for LCI generate Gate to Gate LCI
  - Only considers direct inputs and outputs of production
- We desire Cradle to Gate LCI
  - Need LCI of process inputs
- Possibly many steps upstream of production of desired chemical
  - Gathering all required information is daunting
- Developing a database of chemistry, kinetics, and LCI
  - Makes Cradle to Gate LCI a feasible task

The Stoichiometric Approach

- Stoichiometry is molecular accounting in chemical reactions
- We know how much product we wan
  - Calculate requirements of other species
- Consider the following chemistry

$$A + 2B \rightarrow C + 3D$$

- To make 1 molecule of C:
  - We need: 1 molecule of A and 2 molecules of B
  - Also must make 3 molecules of D
- Calculate mass from molecules

A More Complicated Example

- In general, chemistries are more complex

$$A + B \rightarrow C \qquad A + C \rightarrow D$$

- We want to make C
  - How much A and B do we need?
  - How much D to we produce?

- Need information about reaction selectivity
  - Like a "reaction efficiency"

$$\text{Selectivity of Product} = \frac{\text{Molecules of Desired Product Formed}}{\text{Molecules of Limiting Reactant Consumed}}$$

- Assume S=0.95 in lieu of other information

A More Complicated Example

$$A + B \rightarrow C \qquad A + C \rightarrow D$$

specify

$$\text{raw materials req'd} = \frac{\text{production rate of product}}{\text{selecitivity of product}}$$

Assume S=0.95

specify

Obtain from S=0.95 assumption

$$\text{amount of byproduct or waste generated} = \frac{(\text{production rate of product})(\text{selectivity of byproduct})}{\text{selectivity of product}}$$

S=0.95

We can calculate all material flows into and out of the process using only stoichiometry and an assumption about selectivity.

Obtaining Realistic LCI Data

- Reaction selectivity is required for true LCI data
  - Don't know selectivity until after you design the plant
- No two chemical plants are the same
- Multiple potential synthesis routes
- Can't obtain information before design
  - Difficult to conduct life cycle analysis early
- Difficult to re-design if selectivity or life cycle results are unfavorable
- Want more accuracy than assuming S=0.95
  - Don't want to design a plant

Chemical Process Design Module

- Strategy for obtaining upper bound on selectivity
  - Use to obtain realistic production numbers for early life-cycle analysis
  - Provides benchmark during process design

Inputs

- Components and reactions
- Reaction kinetics
- Physical properties
- Process constraints

Outputs

- Target selectivities
- Amount of raw materials required
- Amount of by-products, co-products, and wastes formed
- How much waste is avoidable

Feinberg's CFSTR Equivalence Principle

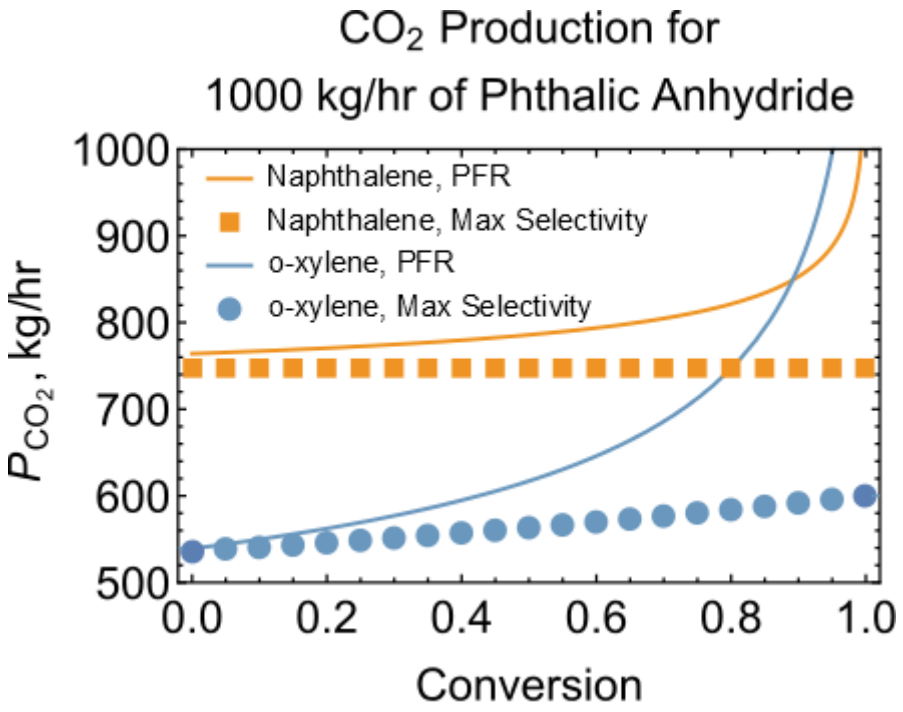
- Allows us to represent any arbitrary process using a single model
- Uses a small number of "basis" reactors and perfect separations
- This model encompasses all possible plant designs
  - Even those which cannot be imaged
- Obtain an upper bound on selectivity
  - Use selectivity bound to calculate LCI
- Can impose "practical process constraints"

Feinberg, M; Ellison, P. *Ind. Eng. Chem. Res.* **2001**, *40*, 3181-2194.

A Target Upper Bound on Reaction Selectivity via Feinberg's CFSTR Equivalence Principle. Manuscript in preparation.

Comparison of Synthesis Routes

$$P_{CO_2} = \frac{S_{CO_2} P_{PA}}{S_{PA}}$$



CO_2 Production for 75MM pounds of Phthalic Anhydride (millions of pounds per year)		
	o-Xylene	Naphthalene
PFR	137	122
Feinberg Limit	80	100

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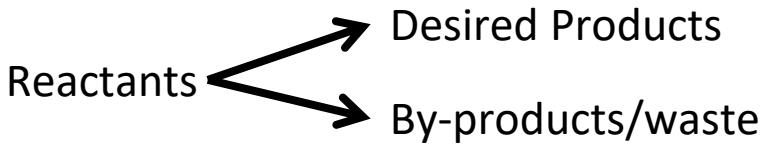
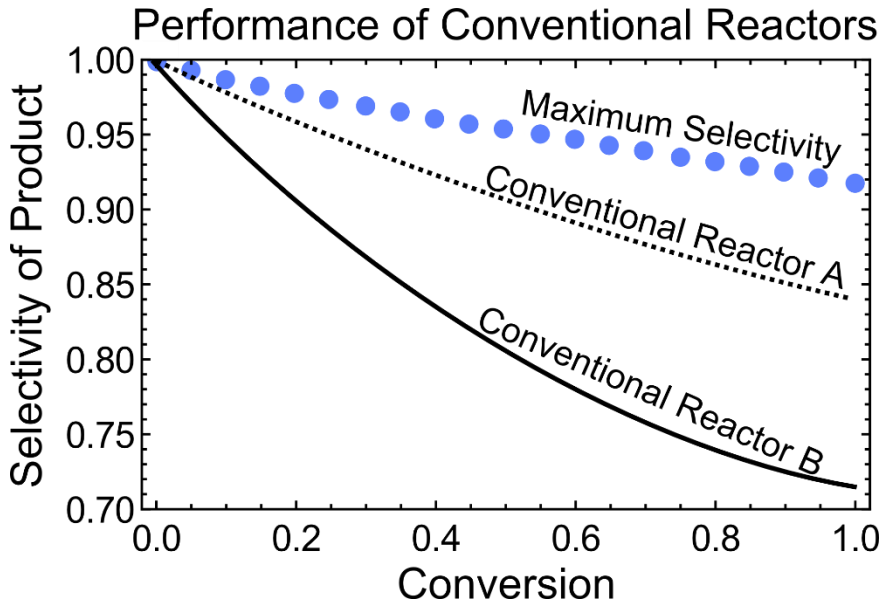
A Target Upper Bound on Reaction Selectivity via Feinberg's CFSTR Equivalence Principle. Manuscript in preparation.

Perfect Selectivity is Unachievable

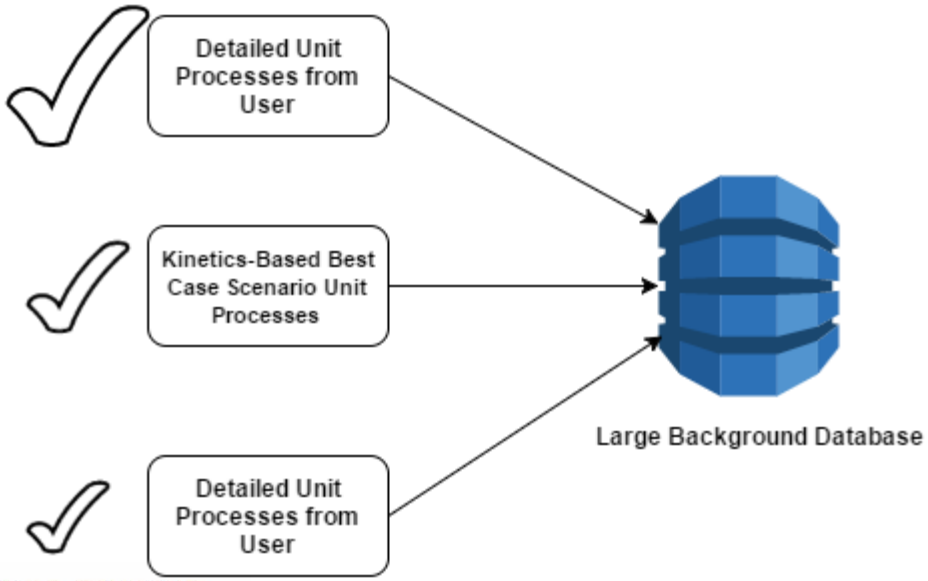
- By-products/ waste is inevitable
- Some reactors are close to the maximum possible selectivity and some are not
- Can determine how much waste is avoidable
- Compare different technologies





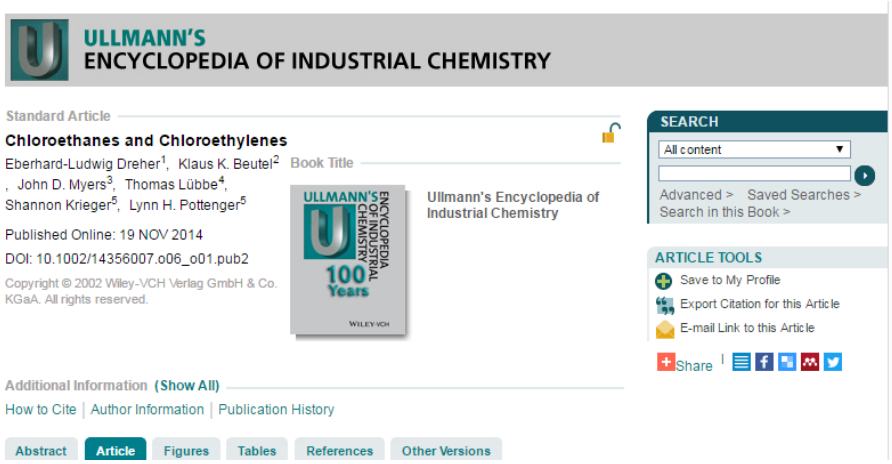
Building the LCI Database

- All of the three scenarios need the support of a background database
- We collected chemical production information from industry report, and filled in numbers using chemical stoichiometry.



Data Mining Project

- Source: Ullmann's encyclopedia of industrial chemistry



2.4.3 *Production*

The production of trichloroethylene is mainly based on acetylene or ethylene.

The acetylene route comprises acetylene chlorination to 1,1,2,2-tetrachloroethane (see Section Production) followed by dehydrochlorination to trichloroethylene.

In the ethylene-based processes, ethylene or ethylene-based chlorohydrocarbons, preferably 1,2-dichloroethane, are chlorinated or oxychlorinated and dehydrochlorinated in the same reactor. Tetrachloroethylene is obtained as a byproduct in substantial amounts.

Some production is based on the catalytic hydrogenation of tetrachloroethylene coming from the chlorinolysis of C_1 to C_3 chlorohydrocarbons.

Trichloroethylene from Acetylene via Tetrachloroethane. 1,1,2,2-Tetrachloroethane derived from acetylene chlorination can be dehydrochlorinated in the liquid or gas phase.

The liquid-phase process uses diluted aqueous calcium hydroxide (10–20%) for cracking [395].

$$2CHCl_2 - CHCl_2 + Ca(OH)_2 \rightarrow 2CCl_2 = CHCl + CaCl_2 + 2H_2O$$

The use of sodium hydroxide is not recommended because explosive dichloroacetylene could be formed. The heat of the highly exothermic reaction can be used for overhead distillation of the trichloroethylene as an aqueous azeotrope. The calcium chloride solution is continuously withdrawn from the bottom of the reactor and can be further purified from the remaining organics by steam or vacuum stripping. This process can be carried out with high selectivity, but has the disadvantage that chlorine is lost by calcium chloride formation. In plants using carbide-derived acetylene, however, it offers an outlet for the calcium hydroxide obtained from carbide decomposition.

Gas-phase dehydrochlorination of 1,1,2,2-tetrachloroethane is an endothermic reaction in which the chlorine is recovered as hydrogen chloride, which can be used in other chemical processes.

$$CHCl_2 - CHCl_2 \rightarrow CHCl = CCl_2 + HCl \quad \Delta H^0_{298} = +61 kJ/mol$$

It can be carried out as a pure thermal reaction at temperatures between 300–600 °C in tubular reactors similar to the conversion of 1,2-

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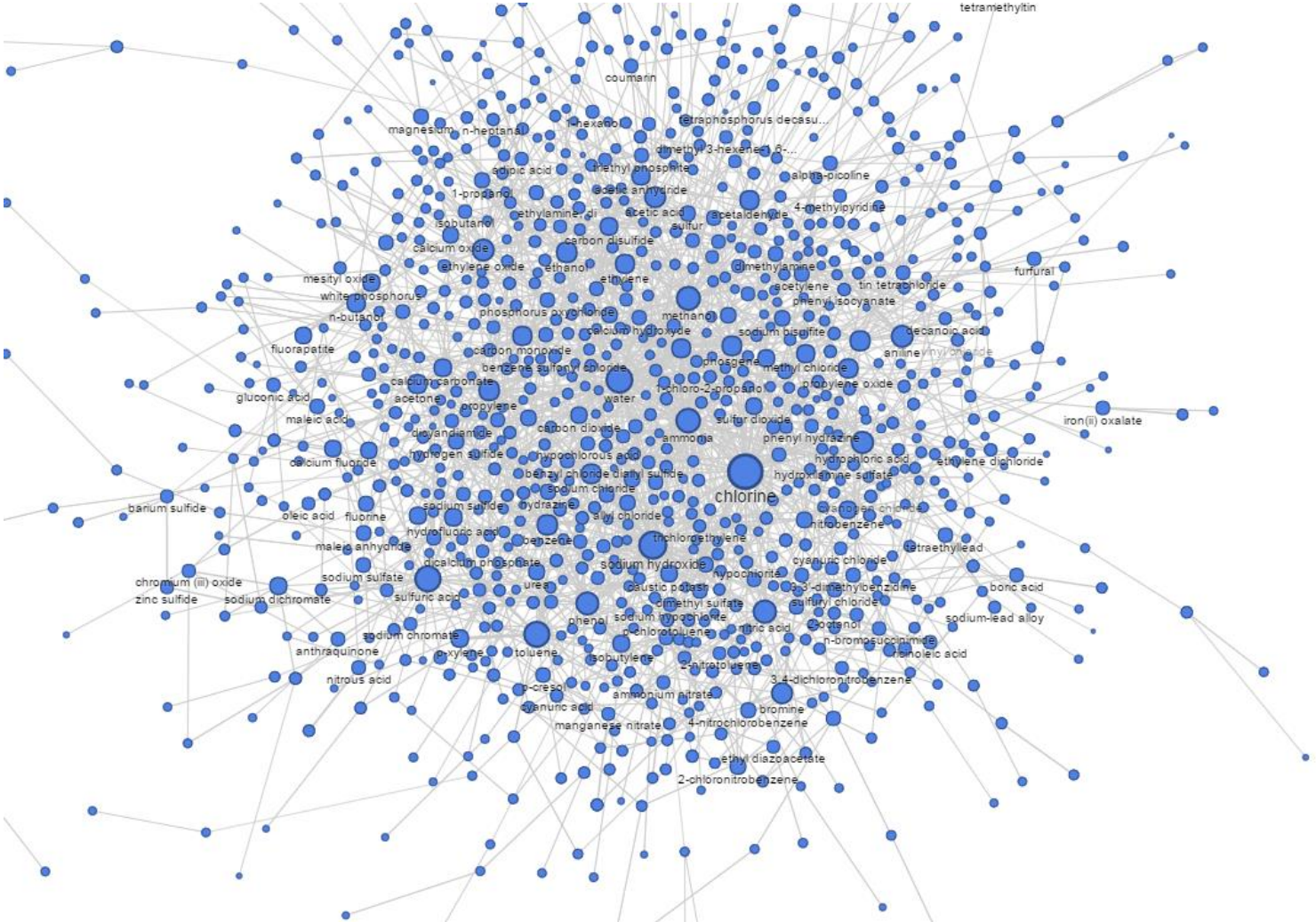
LCI database

- Current database size: 1100 chemicals
  - Contains petrochemicals, chlorine chemicals, ICIS global trading chemicals, European large volume chemicals, ecoinvent chemicals, USETox chemicals and many others…

LCI database



https://fusiontables.google.com/DataSource?docid=1wPHTTrcs2vwDZ5sOUfPOwRetDRzn_PNDmxZht-9_#chartnew:id=6

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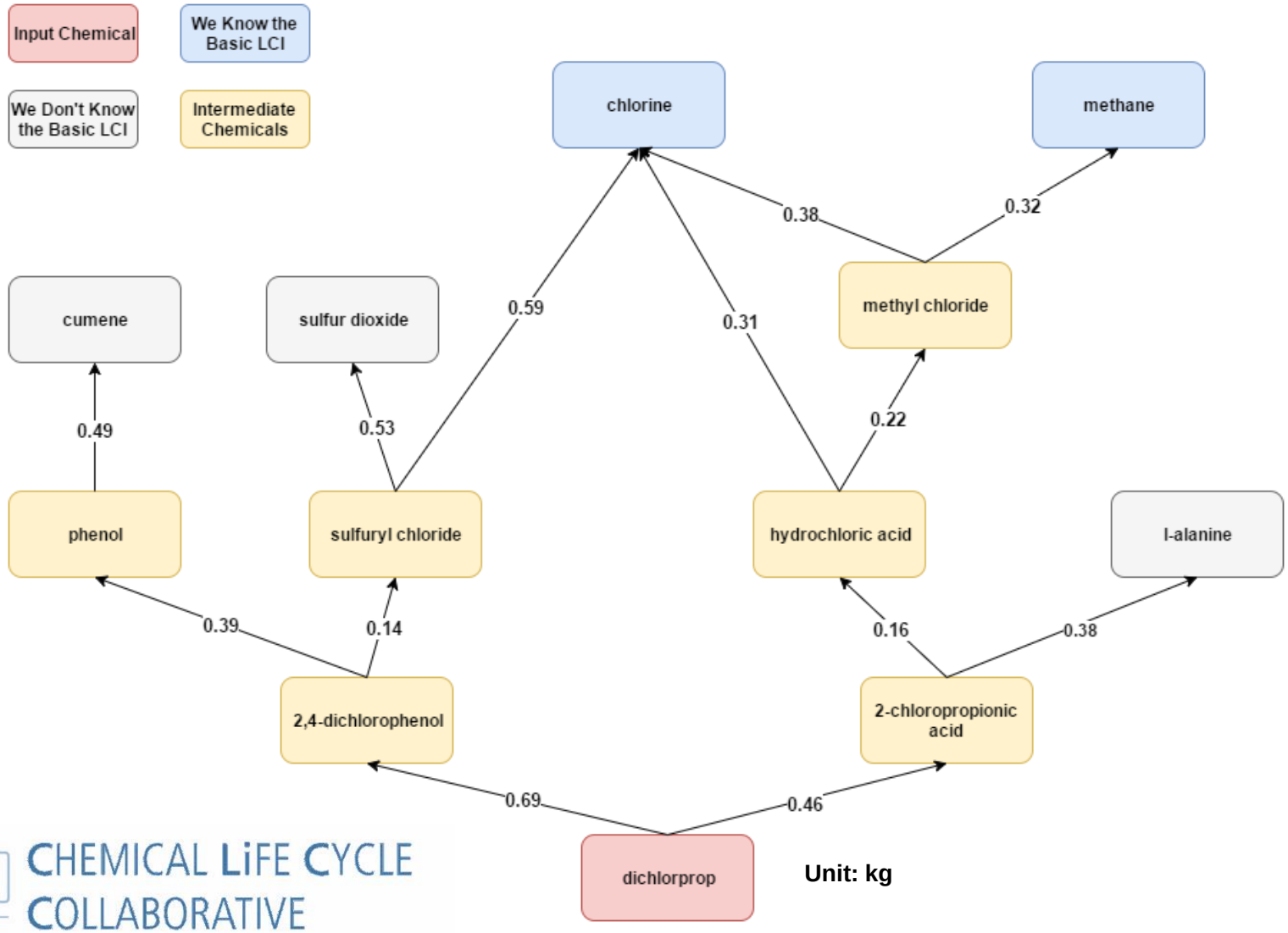
Database Demo

Dichlorprop (herbicide)



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Future Steps

- Clean up the chemicals that are not connecting with ‘building blocks’
- Fill in heat requirement information and other necessary parts of LCI into the database.
- Create the matrix that contains the emission infomration.

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Conclusion

- We are able to generate chemical LCI with different levels of accuracy based on users input data quality.
- Stoichiometric approach shows good results in terms of modeling quantity for raw material inputs.
- The output of the LCI module would support other modules in the CLiCC project.








And specially thanks to our undergraduate interns this summer for helping us collecting data:
David Alvarez, Devon O'Regan, Hean Xuexuan He, Isaac Robledo, Izabella Araujo, Gabriela Volpato, Jacob Canney, Karla Bernardo, Sean Garner, Sihan Zhu, Zhong Zhang

Got questions?

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Back up

	A	B	C	D	E	F	G
1		**Benzene**	**Cumene**	**Oxygen**	**Phenol**	**Propan**	**Propylene**
2	**Benzene**		0,68	0	0	0	0
3	**Cumene**	0		0	1,34	0	0
4	**Oxygen**	0	0		0,36	0	0
5	**Phenol**	0	0	0		0	0
6	**Propan**	0	0	0	0		1,11
7	**Propylene**	0	0,37	0	0	0	
8	...						
9	...						

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Three scenarios of the level of knowing process knowledge

1. Know the detailed process knowledge, so the manufacturer should have the LCI already.
2. Have some of the knowledge about the kinetics. Use kinetics to calculate the best case scenario of LCI.
3. Only know the stoichiometry and use our assumptions to calculate LCI.

Chemical Process Design Module

- Difficult to re-design if selectivity or life cycle results are unfavorable
- Don't know how good the selectivity might have been
- Want more accuracy than assuming S=0.95
  - Don't want to design a plant
- Strategy for obtaining upper bound on selectivity
  - Use to obtain realistic production numbers for early life-cycle analysis
  - Provides benchmark during process design