BPSA 2020 Speaker Series

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Plastics Recycling in the '20s: Back to Atoms

Featured Speaker
Dr. William Carroll

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CHEMICAL RECYCLING OF PLASTICS THROUGH SYNTHESIS GAS

William F. Carroll, Jr., Ph.D.

Carroll Applied Science, LLC

RECYCLING IN FOUR EASY STEPS

- Collection
  - Accumulating piles of garbage
- Separation
  - Removing valuable garbage
- Reprocessing
  - Cleaning it up and putting in in shape for…
- Resale
  - Where recycling really happens

THREE ERAS OF PLASTICS RECYCLING

- 1978: First Bottle Bills
  - Wellman steps up to "free" material
- 1987: Mandated recycling rate threats and recycled content demands
  - Procter & Gamble Tide bottles
- 2002-2015
  - Pax Polymericus
- 2017: Ocean plastics and pressure on single-use applications

WHY RECYCLING PLASTICS IS COMPLICATED

- Different chemical identities of materials
- Different melt processing and mechanical properties
- Pigments, dirt, labels, photodegraded material
- Loss of physical properties with reprocessing
- Markets want virgin properties at off-grade prices
- No specific markets for recycled materials
- Being a recycler is to learn the depth, subtlety and universality of Murphy’s Law

RECYCLE PROCESSING: PART I
WHOLE MOLECULES

- Mechanical
  - Collect, separate, grind, wash, pelletize, remold
  - Need large volume of homogenous non-degraded material
  - Works best for non-pigmented single-stream materials
- Solvent Refined
  - Dissolving material in solvent, removing solids, precipitating
  - May not impact organic dyes or other organic additives

SPECULATING ON MARKET SITUATION, 2025

- Situation: Continued dominance of polyolefins in plastics space
- What consumers/government want
  - Virgin-like quality of recycled material
  - Increased recovery rates/recycle content, particularly for single-use items
- What resin producers want
  - Ability to operate monomer and polymer facilities
  - Continue to grow market for plastics
- One way to do this: Back to atoms
  - Recycling polymers as monomer feedstock

RECYCLE PROCESSING: PART 2
BACK TO FRAGMENTS OR ATOMS

- Depolymerization
  - Only works for condensation polymers; requires purification and repolymerization
- Mixed Material Pyrolysis:
  - Yields non-specific oil material; may require liquid purification
- Polyolefin Pyrolysis:
  - Yields hydrocarbon liquid and gas; requires pre-sorting or cleaning
- Conversion to Synthesis Gas: $CO + H_2$
  - Requires gas purification, synthesis of feedstock hydrocarbon

BACKGROUND: HOW WE MAKE PLASTIC

- Oil/Natural Gas → Naphtha, Ethane, NGL
- Ethylene Cracker → Ethylene, Propylene…
- Polymerization → Ethylene → Polyethylene
  - Ethylene + Benzene → Styrene → Polystyrene
  - Ethylene + Cl_2 → PVC
  - Ethylene + O_2 → Ethylene Glycol → PET

THE HIERARCHY

Plastics Processing

Articles + Manufacturing Scrap

Careful Selection

Reuse

Careful Sorting (Milk, Soda, Laundry)

Selected Streams (Grocery Bags)

Mechanical Recycling

<u>The End of the Bale</u>

HDPE High Melt Flow

PP High Melt Flow

PP Fractional Melt

PET Clamshells,
 Specialty Food

LDPE Films

PS Foam

PVC Clamshells

GKW: Carpet, Laundry Baskets, Complex Articles, Electronics…

Maybe in special situations

WHAT DOES THIS ALL MEAN?

- You can't reasonably mechanically recycle everything because there are too many streams…including mixed GKW
- Once you're past the streams that get routinely mechanically recycled today the material is dirty and of low value
- Light and heat wear out polymer molecules in any event
- Any process you propose should be robust and cheap…BUT—
- There are mitigating policy factors:
  - Bans on single use plastics
  - Potential recycle content requirements
  - Europe's Circular Economy Vision, Directives
  - Outrage over ocean plastics
- Plastics waste—the bulk of it--will probably need to be handled differently

SCOPING THE ISSUE

- EU Circular Economy: **All packaging** either reusable or recyclable
- ACC: **All packaging** reused, recovered or recycled by 2040
- How much plastic is packaging?
  - About 35% (per "The Conversation")
  - About 18 of 51.5 MM t produced; About 2.1 MM t recycled, 1.9 MM t incinerated

BY THE NUMBERS

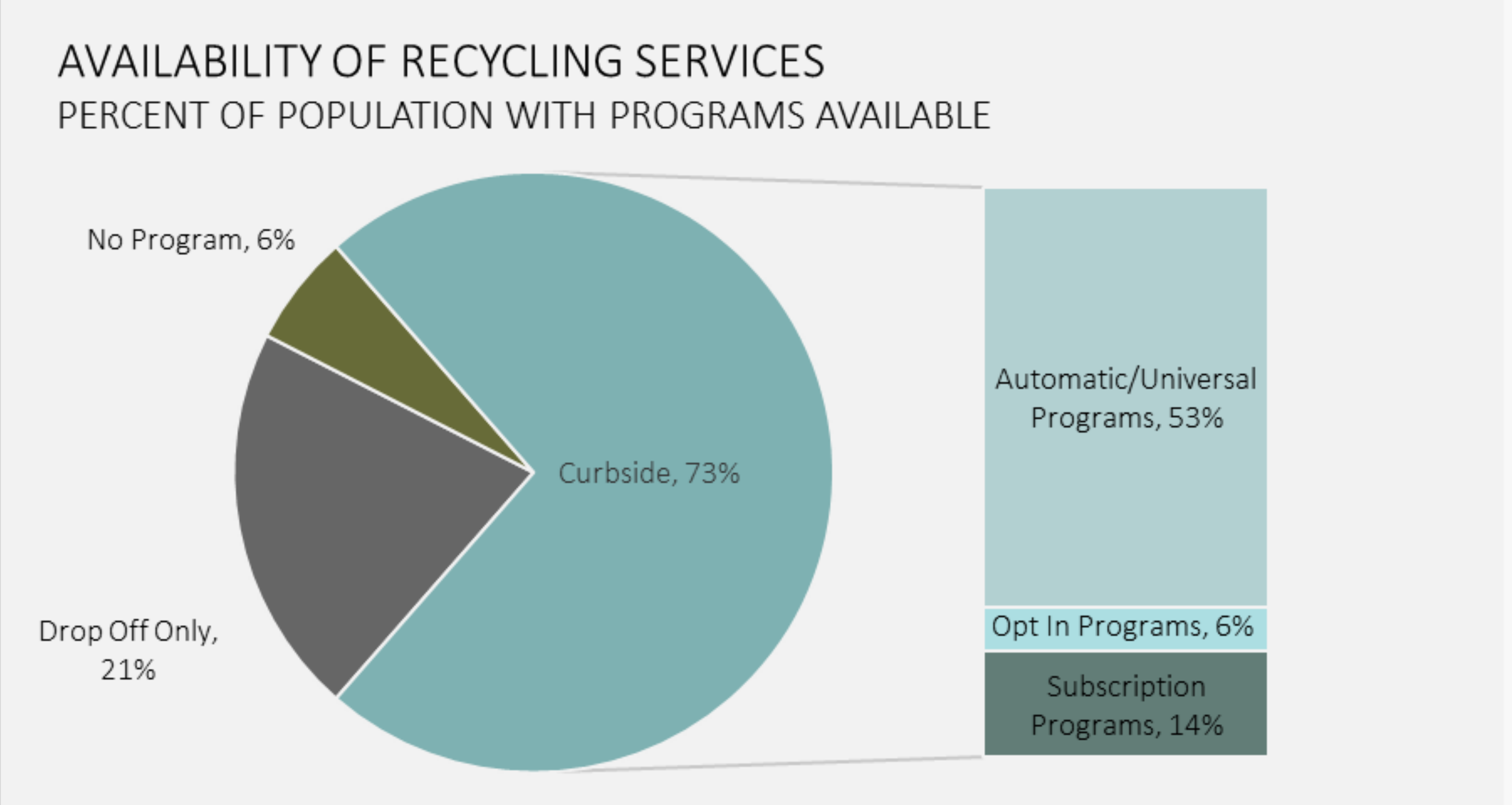
EPA
ACC
Ratioed

MM t	Production	Recycle	Incineration	Landfill
Total Plastics	51.4	3.1	5.4	26.1
Polyolefin	26.5	1.92	2.87	13.7
PET	3.2	0.91	0.32	0.84
Other (PS, PVC, Nylon…)	21.7	0.27	2.2	11.7

Plastic waste generated per capita: ca. 235 lb (2015)
Population of US with automatic curbside recycling: 53% (465 cities)
Average total collection of recyclables: 357 lb/HH/yr (ca 40% of theoretical)

Sources: US EPA, American Chemistry Council, The Recycling Coalition

A BIT MORE ABOUT COLLECTION



Source: Resource Recycling Systems

Carroll Applied Science, LLC

AN ILLUSTRATION

AND SO,

- To recover all packaging you need to collect another 14 MM t
- Impossible to mechanically recycle that stuff
- If you did, you would obsolete 35% of monomer and polymer capacity—ca $200 B capital
- Only way to continue to run the current system while recovering ALL PACKAGING is to make an ethylene precursor from waste

RETURNING TO THE FOUR STEPS

- Automatic curbside collection yield: 40%
  - How do you drive both yield and collection coverage?
- Separation: How pure must your feedstock be?
  - Do you need a polyolefin stream? If so, preprocessing by float-sink might be necessary
  - Greater yield if all materials could be included in the process of generating hydrocarbon
- Reprocessing: Technology will have to be chosen, implemented (paid for) and operated

BEGIN WITH THE END IN MIND

- Cracker feedstock: Ethane or naphtha (hydrocarbon)
- Garbage: C, H, O, N, S, Cl, Br, F, Metals, Minerals
- Two choices: clean up the thermolysis feed or clean up the thermolysis product

BACKGROUND: HOW WE MAKE PLASTIC

- ~~Oil/Natural Gas → Naphtha, Ethane, NGL~~
- Thermolysis Product → Ethylene Cracker → Ethylene, Propylene…
- Polymerization → Ethylene → Polyethylene
  - Ethylene + Benzene → Styrene → Polystyrene
  - Ethylene + Cl_2 → PVC
  - Ethylene + O_2 → Ethylene Glycol → PET

THREE DIFFERENT APPROACHES

- Case 1 Goal: "Pure" polyethylene and polypropylene thermolysis feedstock
  - Hand sort, auto sort, recovered film
  - Grind, float-sink?
- Case 2 Goal: "Pure" liquid hydrocarbon product
  - Thermolyze general plastics stream
  - Treat liquid to spec for cracker feed—remove acid gases, solids
- Case 3 Goal: "Pure" gaseous stream
  - Combination of thermolysis and cracking to yield C_1-C_4
  - Synthesis gas—$CO + H_2$

SYNTHESIS GAS

- $CO + H_2$
- Derived from natural gas or coal by steam reforming

$$C + H_2O \longrightarrow CO + H_2$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$2CH_4 + O_2 \xrightarrow{Zn} 2\,CO + 4H_2 \quad \text{(Sasol GTL Technology)}$$

- Normal industrial source for H_2
- Virtually any source of C, H and O can be a feedstock
- Gaseous materials relatively easy to clear of contaminants

FISCHER-TROPSCH HISTORY

- World War II
  - Germany: Developed 1920s, commercialized 1930s, 10% of war fuel, 25% of motor fuel
- Late 20th/Early 21st Century
  - South Africa: Sasol 1: 1954; Sasol 2: 1980
  - Sasol licensure as "coal to chemicals"
  - Sasol 3: 2020--Natural gas to diesel fuel

FISCHER-TROPSCH AND METHANOL TO OLEFINS (MTO)

- Fischer-Tropsch Synthesis
  - $(2n)H_2 + nCO \longrightarrow n(CH_2) + nH_2O$ Fe, Ru, Co catalyst
  - Biomass-to-Liquid (BTL), Gas-to-Liquid (GTL) or Coal-to-Liquid (CTL) process
  - Produces Synthetic Diesel Fuel (C_9-C_{25})
- Methanol to Olefins (MTO)
  - Methanol currently made from synthesis gas
  - Zeolite or other shape-sensitive catalyst, Cu
  - Produces ethylene and propylene

GENERAL PROCESS CONSIDERATION: GETTING FROM WASTE TO SYN GAS

- British Gas/Lurgi process (ca. 2000 deg C): coal or "garbage" to synthesis gas; waste to vitreous slag
- Easiest with relatively clean but mixed olefins stream
  - Films, pigmented bottles, PP tubs, injection mold HDPE…
  - High Temperature to slag out inorganics
- Gas vs. liquid purification step
- In principle, could use mixed plastic material feed

WHAT ABOUT THE ENERGY

- 1 bbl crude oil ~ 6 MM BTU
- 1,000 cu ft Natural Gas ~ 1 MM BTU
  - Note: traditionally ratio of price of oil/price of gas ~ 7
- From Sasol:
  - 10,000 cu ft Natural Gas to produce 1 bbl diesel

    Oil at $60; Gas at $3.50: still makes money
- Synthesis gas is a very energetic fuel; raw material can also power the process

SOME ISSUES

- How pure does a hydrocarbon thermal product have to be to go back into a cracker? Hard to say.
- Where will you make this stuff? Relatively huge capital cost and insurmountable local siting barriers—probably must be done at plant sites
- Operating cost could be partially offset by heat value of input material, but could still be on the order of \$0.02-\$0.05/lb
- Technology is less of an issue than logistics, especially sorting, baling and transportation

THE MOST VEXING ISSUE: SCALE

- What do you need?
  - Expanded MRF capacity in 450 cities+
  - Capital for pyrolysis units: ca. $1000/t/yr SWAG: ca. $14 B
- Transportation
  - Bales by rail to megasite: 950,000-1,000,000 intermodal containers
  - Or trucks of liquid from local units: 400,000
- Outlet for slag & other waste

SO, WHERE IS THIS GOING?

- Collection and transportation is still an issue even if sorting isn't
- Will probably be driven by political exigencies rather than cost
  - Perception of plastics waste
  - Peril to single-use plastics markets
  - Potential for recycle content requirements
  - Huge investment in monomer and polymer production
- Vexing issues of scale
- Doable under the right set of circumstances
- Might be the only technology that scales

Coming Up in the Summit Speaker Series…

- The role of Single-Use Technologies in **vaccine production and industry capacities**;
- **Integrity Assurance** BPSA guidance and case studies;
- **Cell and Gene Therapy E&L Guide** (pending June publication).