

# **Valorization of Waste Plastic for the Synthesis of Sustainable Aviation Fuel (SAF)**

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## Introduction

- ✓ Sustainable aviation fuel
- ✓ Plastic waste
- ✓ Plastic waste to SAF

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## Research Trend

- ✓ Pyrolysis
- ✓ Solvolysis
- ✓ Hydrogenolysis

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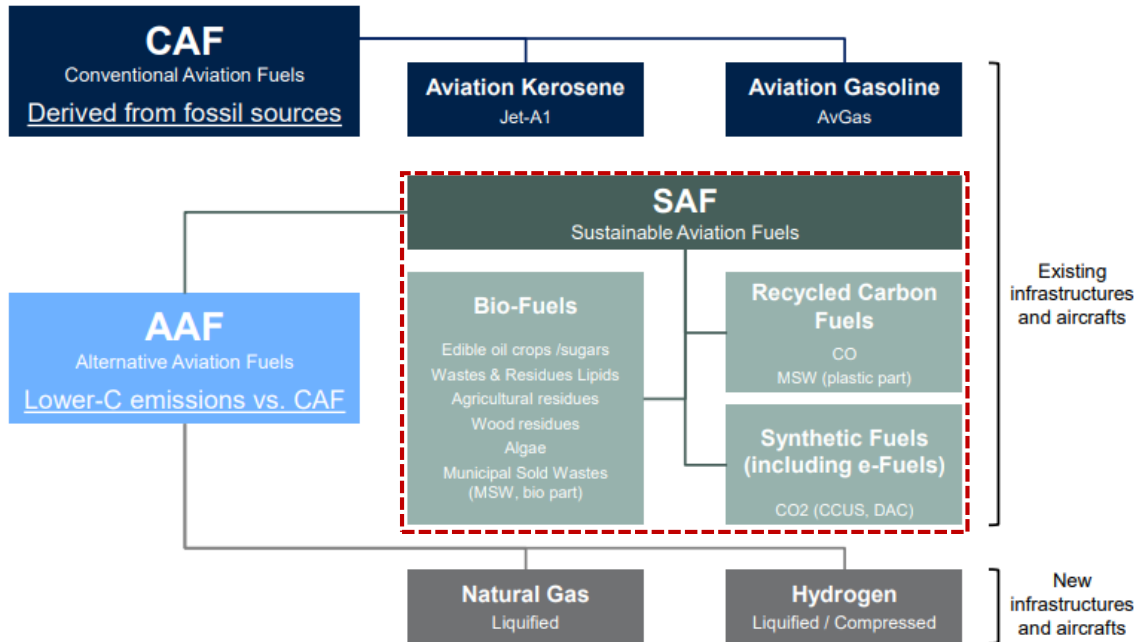
## Ongoing Research

- ✓ Plastic upcycling to SAF
- ✓ Preliminary reaction results
- ✓ Ongoing reactions

4

## Outlooks and Conclusion

# Introduction



## Aviation Industry Goals

GOAL 1	GOAL 2	GOAL 3
PRE-2020 AMBITION	IN LINE WITH THE NEXT UNFCCC COMMITMENT PERIOD	ON THE 2°C PATHWAY
1.5% ANNUAL AVERAGE FUEL EFFICIENCY IMPROVEMENT FROM 2009 TO 2020.	STABILISE NET AVIATION CO <sub>2</sub> EMISSIONS AT 2020 LEVELS WITH CARBON-NEUTRAL GROWTH.	REDUCE AVIATION'S NET CO <sub>2</sub> EMISSIONS TO 50% OF WHAT THEY WERE IN 2005, BY 2050.
TOI	TOI+M	TOI



## Advantages

	1	2	3
Comparison vs fossil kerosene	Battery-electric	H <sub>2</sub> fuel cell	H <sub>2</sub> turbine
Climate impact <sup>1</sup>	100% reduction <sup>2</sup>	75%-90% reduction	50%-75% reduction
Aircraft design	Low-battery density limits ranges to 500km-1,000km	Feasible only for commuter to short-range segments	Feasible for all segments except for flights >10,000km
Aircraft operations	Same or shorter turnaround times	1-2x longer refuelling times for up to short range	2-3x longer refuelling times for medium and long range
Airport infrastructure	Fast-charging or battery exchange system required	LH <sub>2</sub> distribution and storage required	Existing infrastructure can be used

■ Major advantages    ■ Major challenges

Clean Skies for Tomorrow Sustainable Aviation Fuels as a Pathway to Net-Zero Aviation, INSIGHT REPORT NOVEMBER 2020

# SAF Approved Pathways







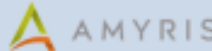











## Summary of technical progress since 2014

Production route	Plant in 2014	Plant in 2018
Alcohol-to-Jet	1. None	2. Several at pilot scale <sup>7</sup> 3. Ekobenz <sup>8</sup> plant in commissioning (23 kt/year) 4. Several other companies including Lanzatech and Gevo planning commercial-scale plant <sup>9</sup>
Gasification + FT	5. 1 plant operational (TRI plant processing black liquor ~20 kt/year) 6. 1 plant planned (UPM, since cancelled)	7. TRI black liquor gasifier shut down 8. Fulcrum <sup>10</sup> and Red Rock <sup>11</sup> have plant under construction (combined 75 kt/year capacity)
Pyrolysis	9. None focusing on aviation fuels	10. Still no pyrolysis plant upgrading to jet 11. Ensyn/Envergent have ability to produce 'green diesel' <sup>12</sup> , but no plant focussing on this 12. IH <sup>2</sup> pilot plant in India <sup>13</sup>
Sugars to hydrocarbons	13. Amyris had operating commercial-scale aerobic fermentation plant (33 kt/year)	15. Amyris plant has since been sold to DSM <sup>14</sup> ; Construction of two other aerobic fermentation plant is ongoing but these are not focused on aviation fuel. <sup>15</sup>
Oil-based processes	15. Many plant globally 16. 2.5 mt/year of HEFA capacity worldwide, and 1.3 mt more planned	17. Over 4.5 mt capacity in dedicated hydro-treating plant 18. Over 2 mt co-processing at refineries
Power-to-liquids: Fischer-Tropsch	19. None	20. Sunfire planning a demonstration facility in Norway (8 kt/year) <sup>16</sup>

SUSTAINABLE AVIATION FUELS ROAD-MAP, Fueling the future of UK aviation

# SAF Approved Pathways

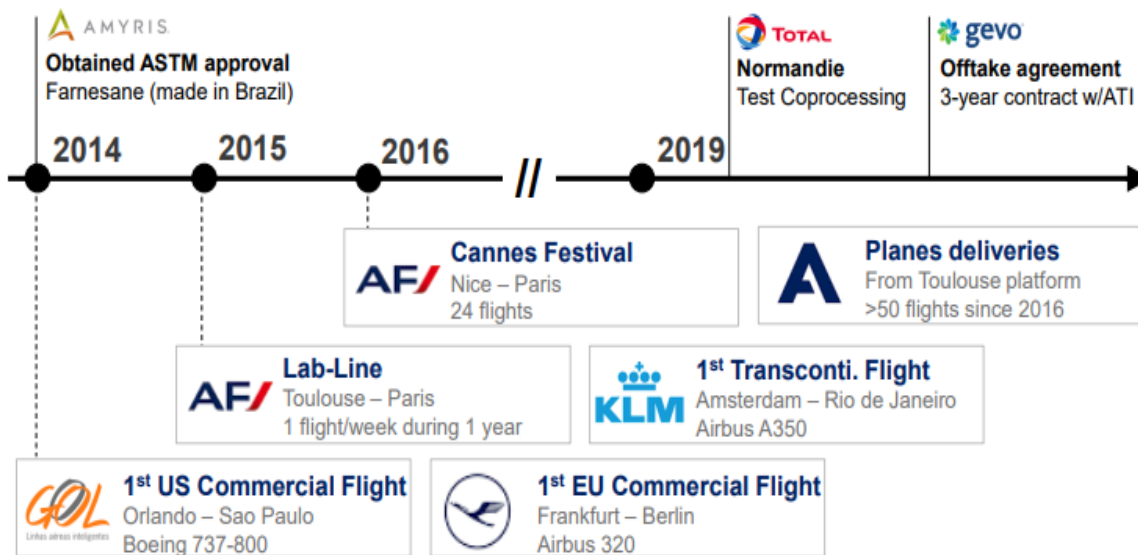
## 7 Technical pathways to date [SAF Approved]

Year approved	Technology pathway	Blend limit	Key players
2009	<b>FT</b> Fischer-Tropsh Synthesized Paraffinic Kerosene (FT-SPK)	50%	  
2011	<b>HEFA</b> Hydroprocessed Esters and Fatty Acids (HEFA-SPK)	50%	  
2014	<b>SIP</b> Hydroprocessed Fermented Sugars Synthesized Isoparaffins (HFS-SIP)	10%	 
2015	<b>FT-A</b> ST SPK with Aromatics (FT-SPK/A)	50%	
2016/18	<b>ATJ</b> Alcohol to Jet Synthesized Paraffinic Kerosene (ATJ-SPK) Isobutanol and Ethanol	50%	 
2020	<b>CHJ</b> Catalytic hydrothermolysis jet fuel (CHJ), a type of synthetic kerosene	50%	 
2020	<b>HHC</b> HHC-SPK: similar to HEFA but utilizes biological derived hydrocarbons from algae	10%	
2018/20	<u>Co processing</u> of renewable content with crude oil-derived middle distillates	5%	    

Sustainable Aviation Fuel Review of Technical Pathways

# Commercialization of SAF

## Successful commercial flights since 2014



Fuel Name	Date certified	Maximum blend level
Fischer-Tropsch - Synthetic paraffinic kerosene (FT-SPK)	2009	50%
Hydroprocessed Esters & Fatty Acids (HEFA) - Synthetic paraffinic kerosene (SPK)	2011	50%
Synthetic Iso-Paraffinic fuels (SIP)	2014	10%
Fischer-Tropsch - Synthetic paraffinic kerosene with added aromatics (FT-SPK/A)	2015	50%
Alcohol-to-jet	2016 (updated 2018 to include more feedstocks and higher blend %)	50%

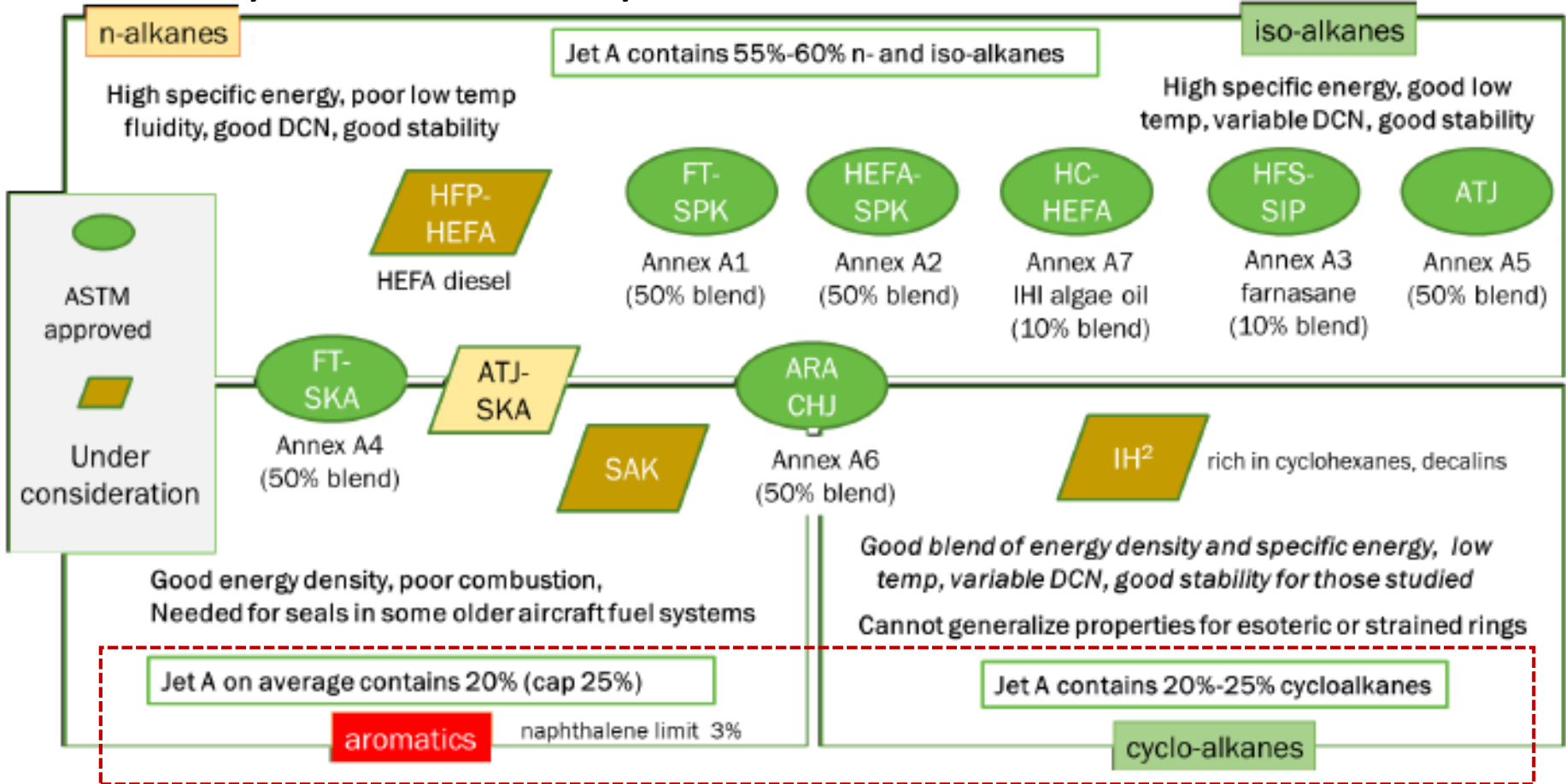
# SAF in D4054 Qualification Process

ASTM Progress	Pathway	Feedstock	Task Force Lead
Phase 2 Testing	Hydro-deoxygenation Synthetic Kerosene (HDO-SK)	Sugars and cellulotics	Virent
	Catalytic Hydrothermolysis Synthetic Kerosene (CH-SK)	Renewable fats oils and greases FOG	ARA
Phase 1 OEM Review	High Freeze Point Hydroprocessed Esters and Fatty Acids Synthetic Kerosene (HFP HEFA-SK)	Renewable fats oils and greases	Boeing
Phase 1 Research Report	Hydro-deoxygenation Synthetic Aromatic Kerosene (HDO-SAK)	Sugars and cellulotics	Virent
Phase 1 Testing	Alcohol-to-Jet Synthetic Kerosene with Aromatics (ATJ-SKA)	Sugars and lignocellulosics	Byogy, Swedish Biofuels
	Integrated Hydropyrolysis and Hydroconversion (IH <sup>2</sup> )	Multiple	Shell
	Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK)	Hydrocarbon-rich algae oil	IHI

*Sustainable Aviation Fuel Review of Technical Pathways*

# Hydrocarbons for SAF

## Summary of four classes of SAF hydrocarbons



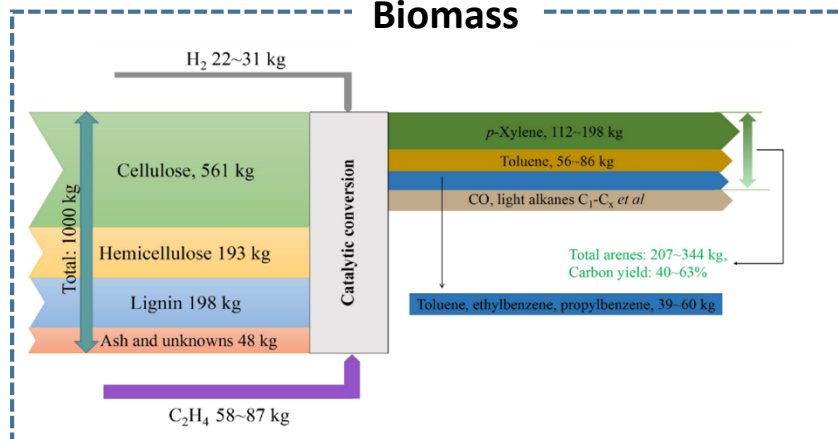
Can be obtained from

1. Biomass
2. Carbon dioxide
3. Waste Plastic

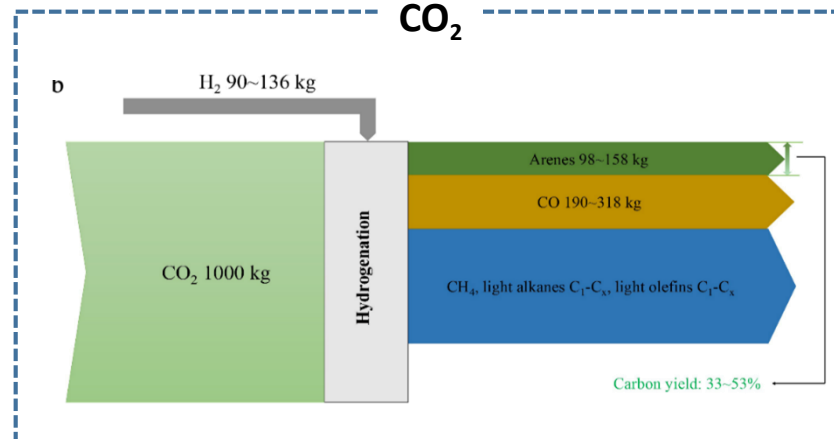


# Aromatics and Cyclo-alkanes for SAF

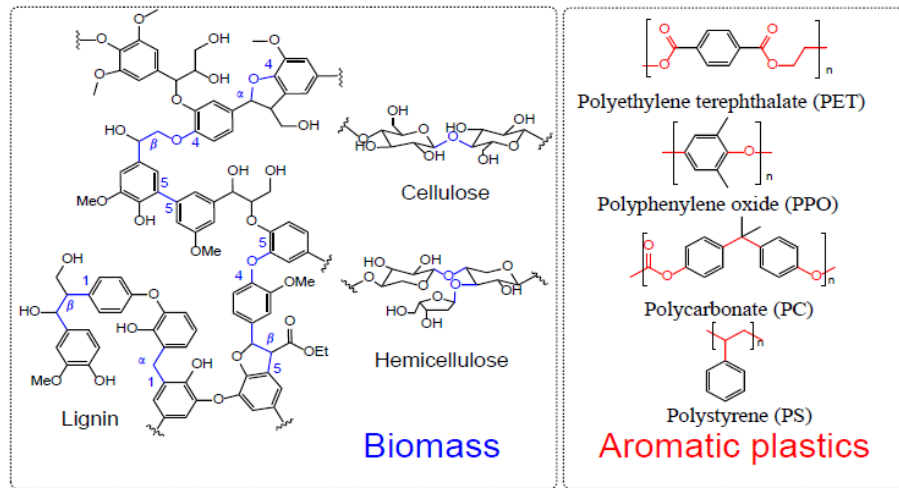
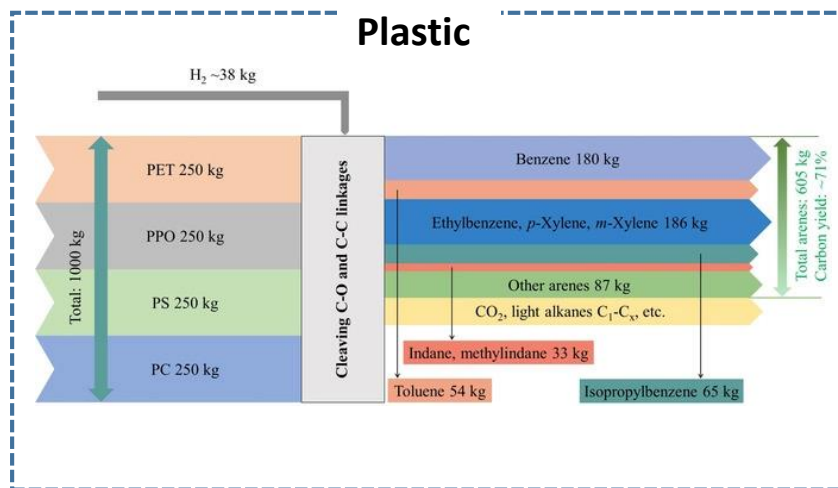
## Biomass



## CO<sub>2</sub>



## Plastic



Compared to biomass and CO<sub>2</sub>, aromatic plastic waste has prominent advantages

- ❖ Simpler molecular structure contrasting the complexity of biomass
- ❖ Much lower oxygen contents
- ❖ Abundant aromatic functionality
- ❖ Selective production jet fuels

Angew. Chem. Int. Ed. 10.1002/anie.202011063

# Solving Two Problems at One

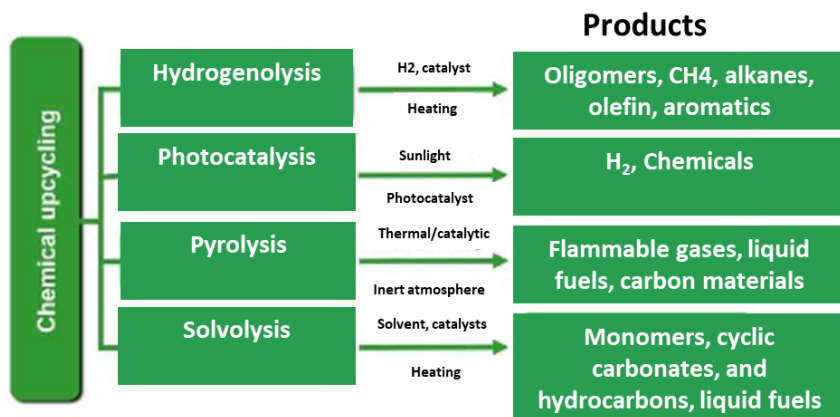
1960–2018 Data on Plastics in MSW by Weight (in thousands of U.S. tons)

Management Pathway	1960	1970	1980	1990	2000	2005	2010	2015	2017	2018
<b>Generation</b>	390	2,900	6,830	17,130	25,550	29,380	31,400	34,480	35,410	35,680
<b>Recycled</b>	-	-	20	370	1,480	1,780	2,500	3,120	3,000	3,090
<b>Composted</b>	-	-	-	-	-	-	-	-	-	-
<b>Combustion with Energy Recovery</b>	-	-	140	2,980	4,120	4,330	4,530	5,330	5,590	5,620
<b>Landfilled</b>	390	2,900	6,670	13,780	19,950	23,270	24,370	26,030	26,820	26,970

- Only ~ 7 % of the generated plastics are being recycled to date
  - **Incineration:** combustion of organic substances contained in waste materials; converts the waste into ash, flue gas, and heat
  - **Landfill:** plastic wastes are buried under the ground
  - **Mechanical Recycling:** processing of plastic waste into secondary raw material or products without significantly changing the chemical structure of the material

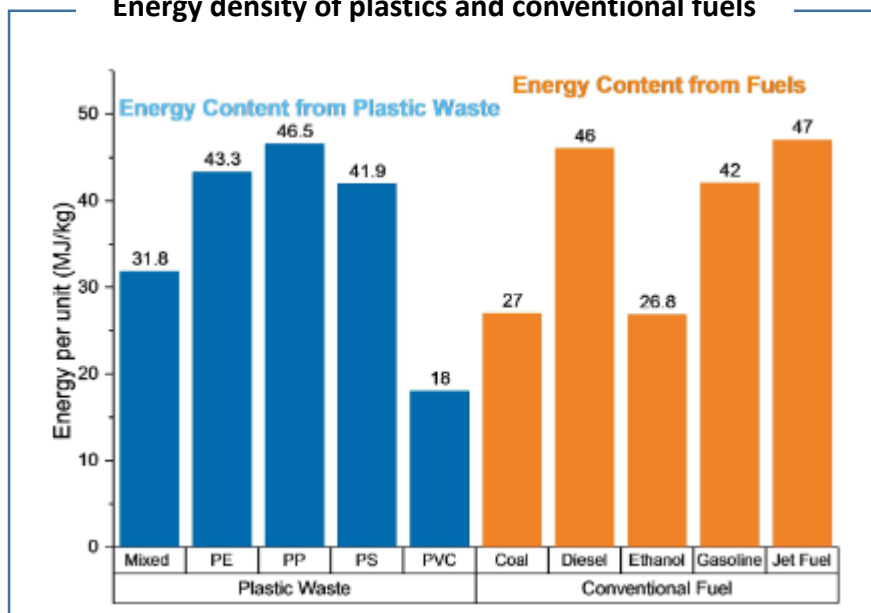
# Plastic to SAF Technologies

## Existing pathways for plastic waste recycling

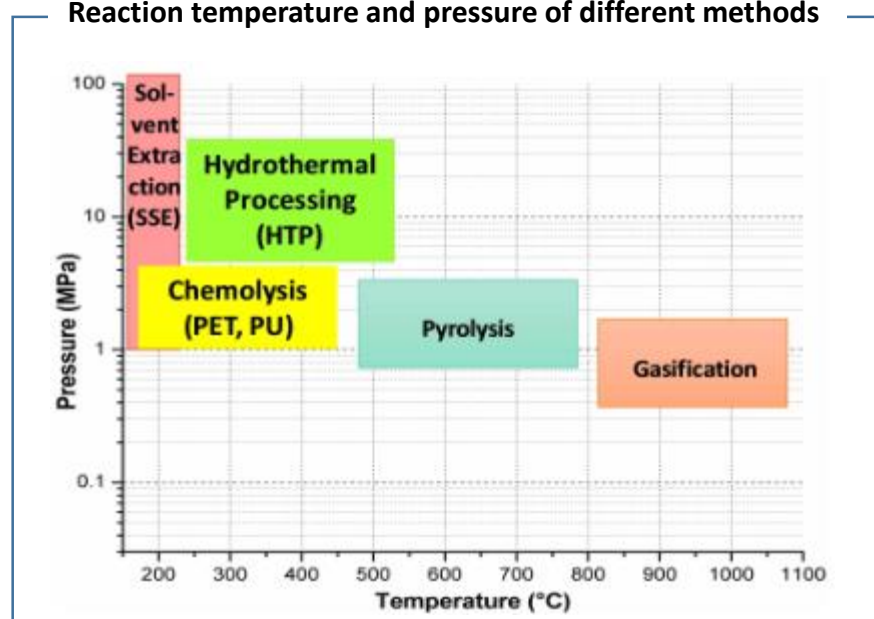


- ❖ **Chemical degradation** → pyrolysis → allows to handle relatively mixed plastic waste streams → poor selectivity
- ❖ **Alternative strategies** → hydrolysis, alcoholysis, hydrogenation and aminolysis → have been developed to handle specific aromatic plastics in particular PET → sorting as a prerequisite

## Energy density of plastics and conventional fuels



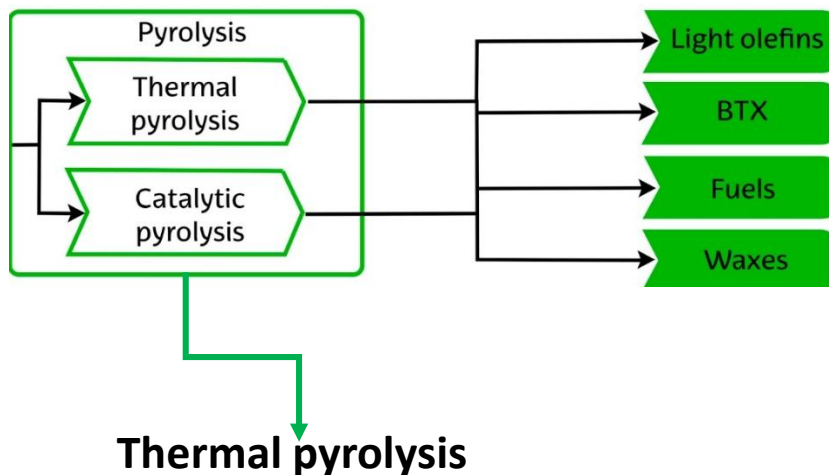
## Reaction temperature and pressure of different methods



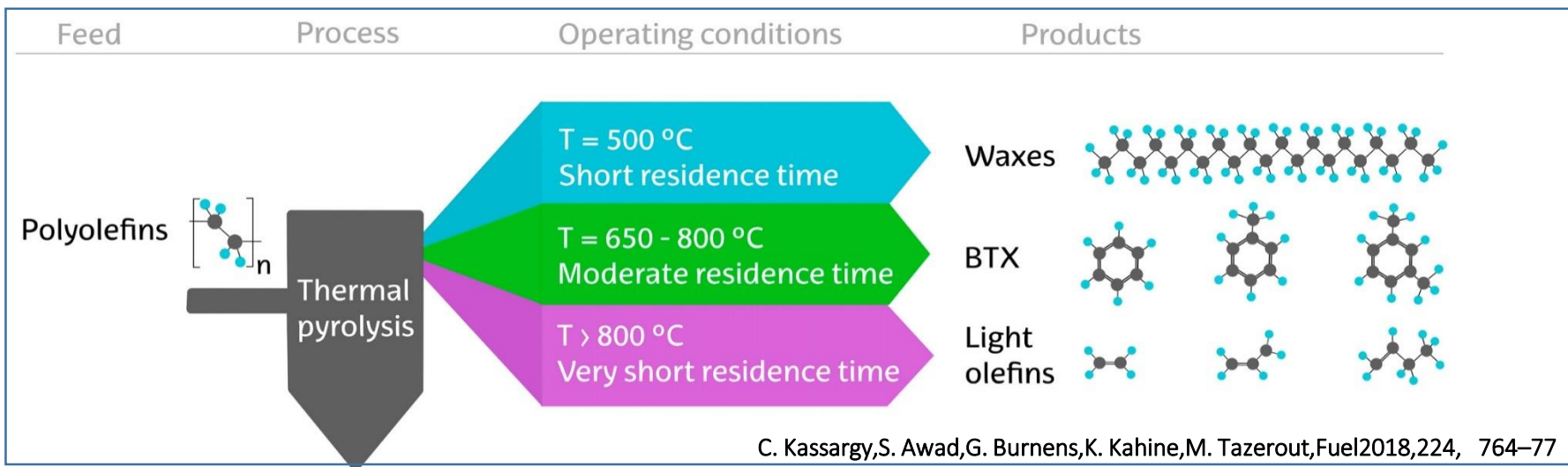
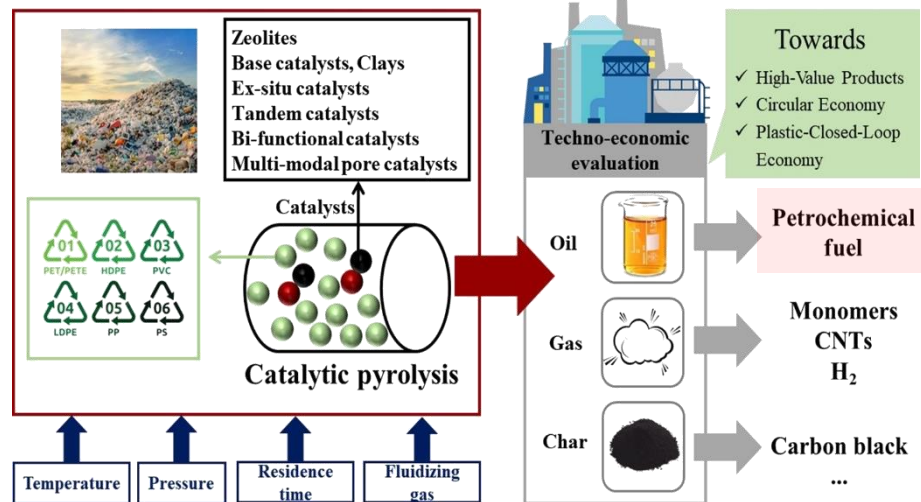
Energy Conversion and Management 254 (2022) 115243

# Pyrolysis

- Pyrolysis generally refers to the thermal processes to degrade polymers at relatively high temperatures under an inert atmosphere into gases, liquid products, and solid chars.



## Catalytic pyrolysis



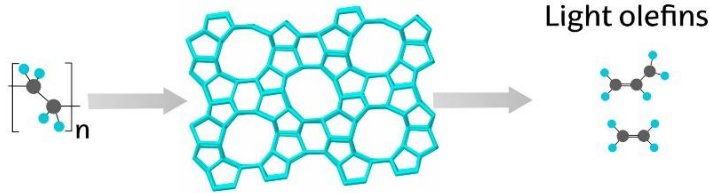
C. Kassargy, S. Awad, G. Burnens, K. Kahine, M. Tazerout, Fuel 2018, 224, 764–77

# Pyrolysis Reactors and Product Yield

## Zeolites

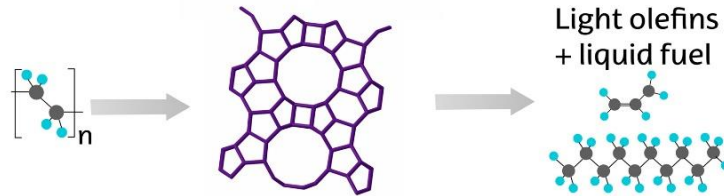
HZSM-5

↑↑↑ acidity



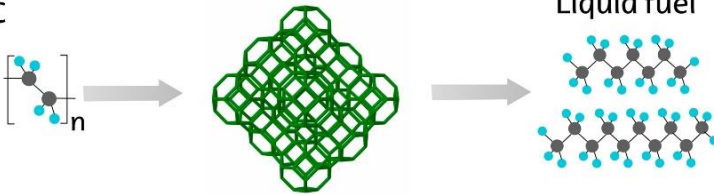
H $\beta$

↑↑ acidity



HY / USY / FCC

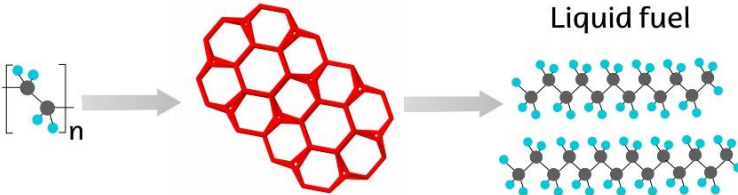
↑ acidity



## Mesoporous catalysts

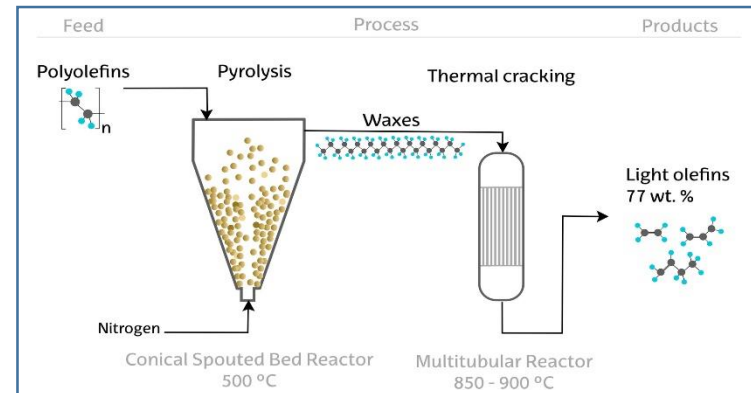
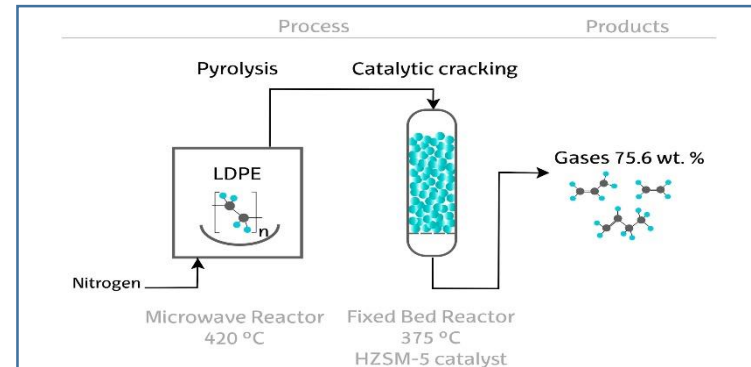
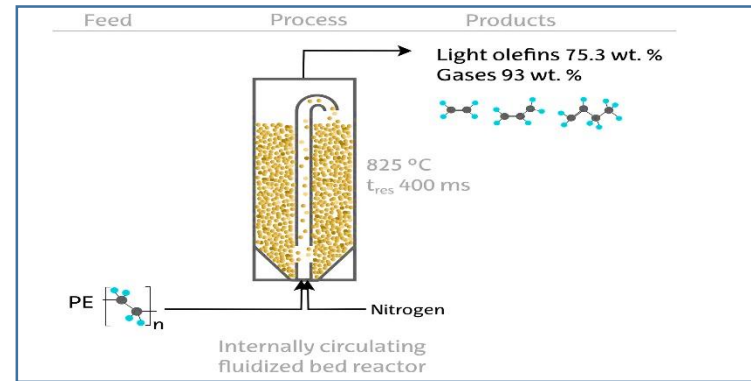
MCM-41

↓ acidity



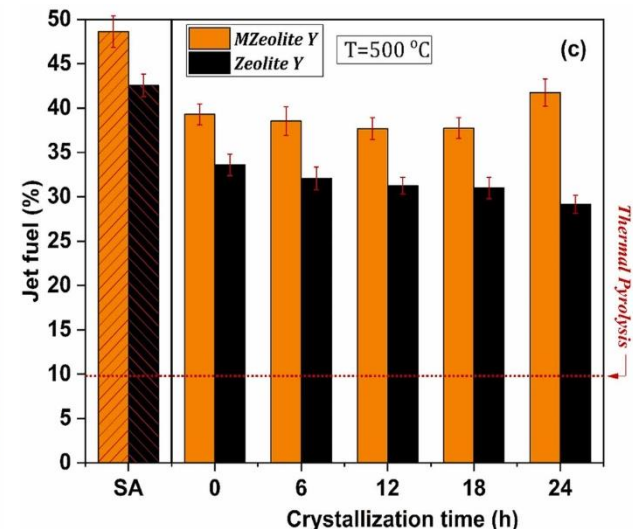
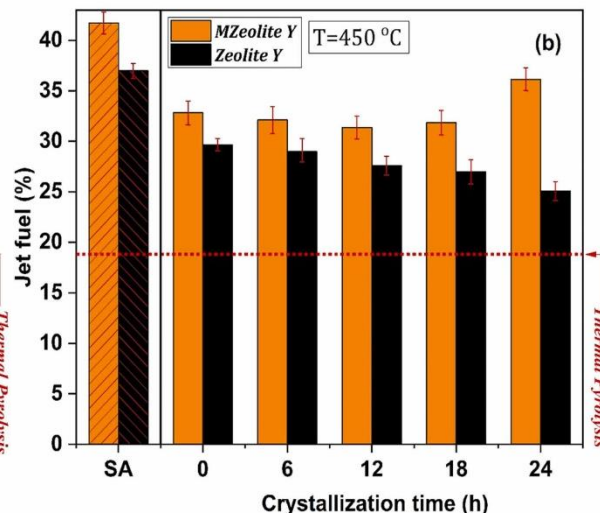
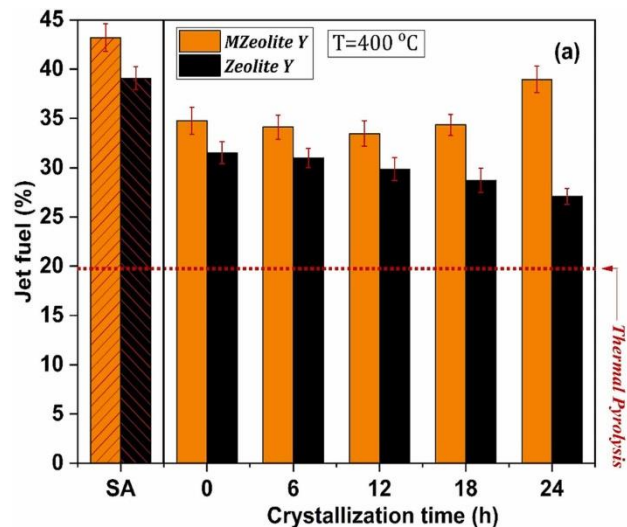
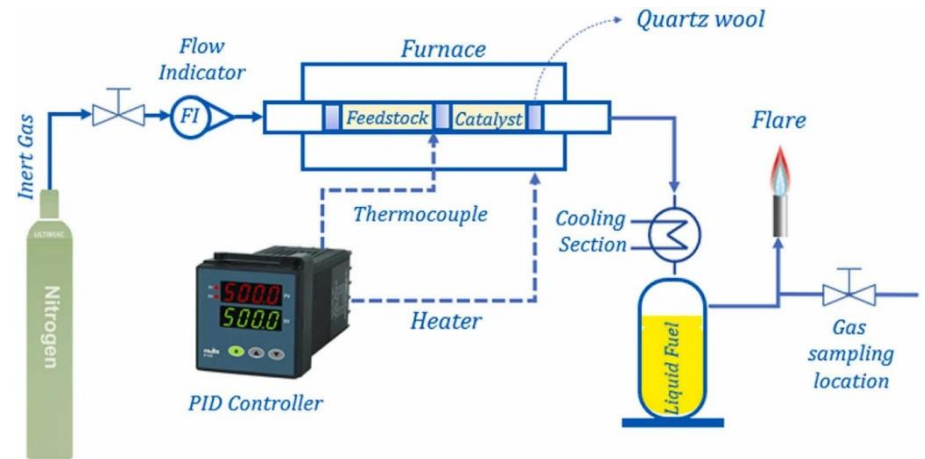
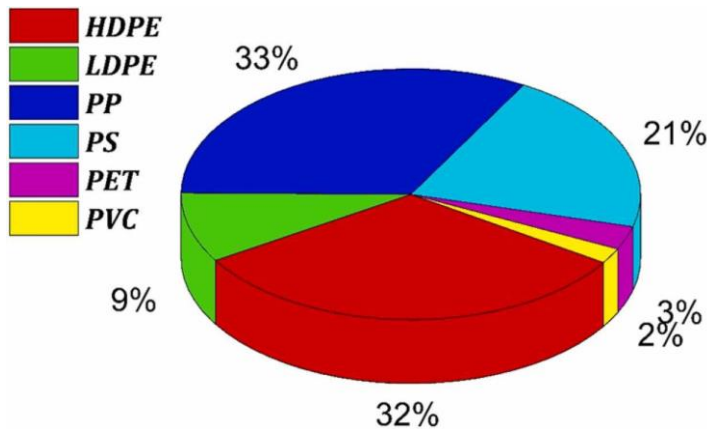
SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

↕ acidity



Renewable and Sustainable Energy Reviews 73 (2017) 346–368354

# Catalytic Pyrolysis of Mixed Plastic

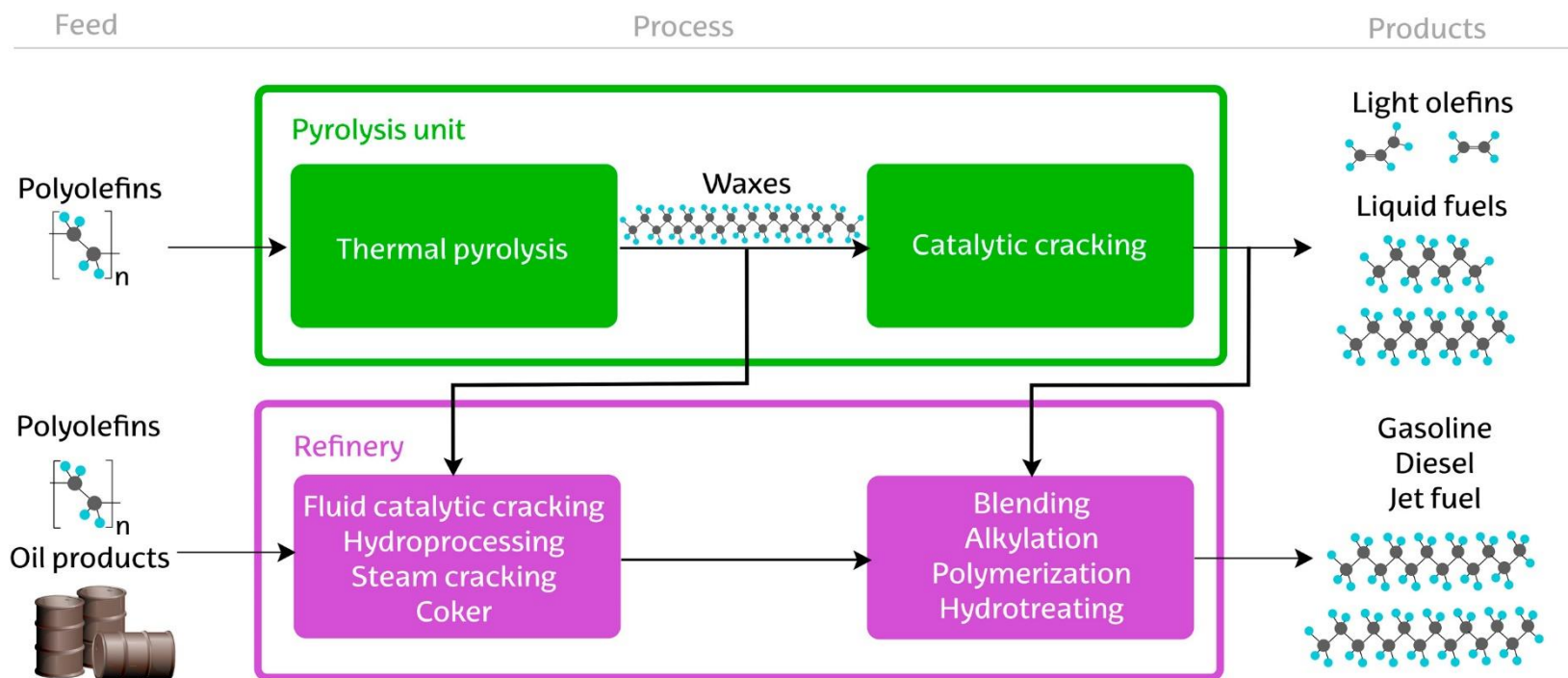


pyrolysis of municipal polymer waste at (a) 400 °C, (b) 450 °C, and (c) 500 °C for different catalysts and their comparison with thermal pyrolysis.

*Process Safety and Environmental Protection 164 (2022) 449–467*

# Co-Pyrolysis

- The co-pyrolysis of plastic furnishes a beneficial strategy to possibly improve the quality of gas or liquid fuels, attenuate carbon emissions, and aid the waste management
- The synergistic effect has enabled fast heating rate and rapid process time.

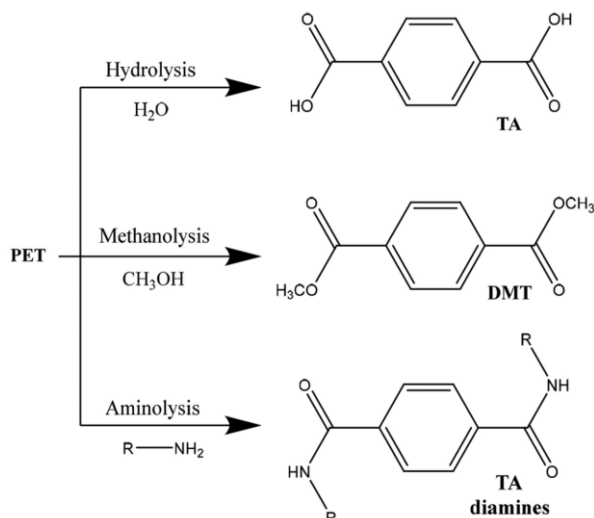


## Limitations of pyrolysis

- Energy-intensive process
- Low selectivity to SAF
- Environment problem (environmental emission standard)

# Solvolytic

- Chemical depolymerization (solvolytic) involves using a reagent to decompose the polymer matrix.
- The name of the technique depends on the reagent used: hydrolytic when the reagent is water, alcoholysis when it is an alcohol, and glycolysis when glycol is used.



Feedstock	Particle size [mm]	Solvent	Reaction conditions (T, P, t)	Solid content <sup>[a]</sup> [wt%]	Plastic/water	Yield or conv. [%]	Major product
polyolefins PE, PP	N/A	water	450 °C 2 MPa 45 min	8	0.57 (1:2)	87 (PP) 50 (PP/PE)	C <sub>4</sub> -C <sub>25</sub>
HDPE, PP	N/A	water	450 °C 1.55-23 MPa 45-60 min	8	0.57 (1:1.75) 2.35 (1:2)	87	C <sub>6</sub> -C <sub>7</sub>
HDPE + sugarcane bagasse	N/A	ethanol	280 °C 75 min	15	0.05 (1:20)	69.54	hydrocarbons phenols naphtha
PP	N/A	water	380-500 °C	3	0.25 (1:4)	91	
PBT, PC, PET, PLA, PMMA, POM, PPO, PVA, SB	3	distilled water	400 °C 25 MPa 15 min	4	0.1 (1:10)	95 (PC)	toluene isopropyl phenol isopropenyl phenol
PP, PC, PS, PET	0.02	pure water	350-450 °C 25 MPa 0.5-1 h	3	0.35 (1:3)	86 (PS) 60 (PC)	terephthalic acid ethylene glycol bisphenol methylene
ABS, HDPE, LDPE, PA6, PA66, PET, PC, PP, PS, PU, PVC	2	water	350 °C 14-20 min	3	0.058 (1:17)	80 (PC)	bisphenol-A ethylene glycol benzoic acid
PS	2-5	ethanol	250-375 °C 15-75 min	2	4 (1:0.25) 0.25 (1:4)	85 (at 0.5:1)	α methyl-styrene aromatics alkenes

S. Ügdüler, K. M. Van Geem, R. Denolf, M. Roosen, N. Mys, K. Ragaert, S. De Meester, *GreenChem.* 2020, 22, 5376-5394

## Limitations of Solvolytic

- Developed to handle specific aromatic plastics in a particular PET
- Sorting as a prerequisite
- Not applicable for aliphatic plastics

*J Polym Sci.* 2020;58:1347-1364.

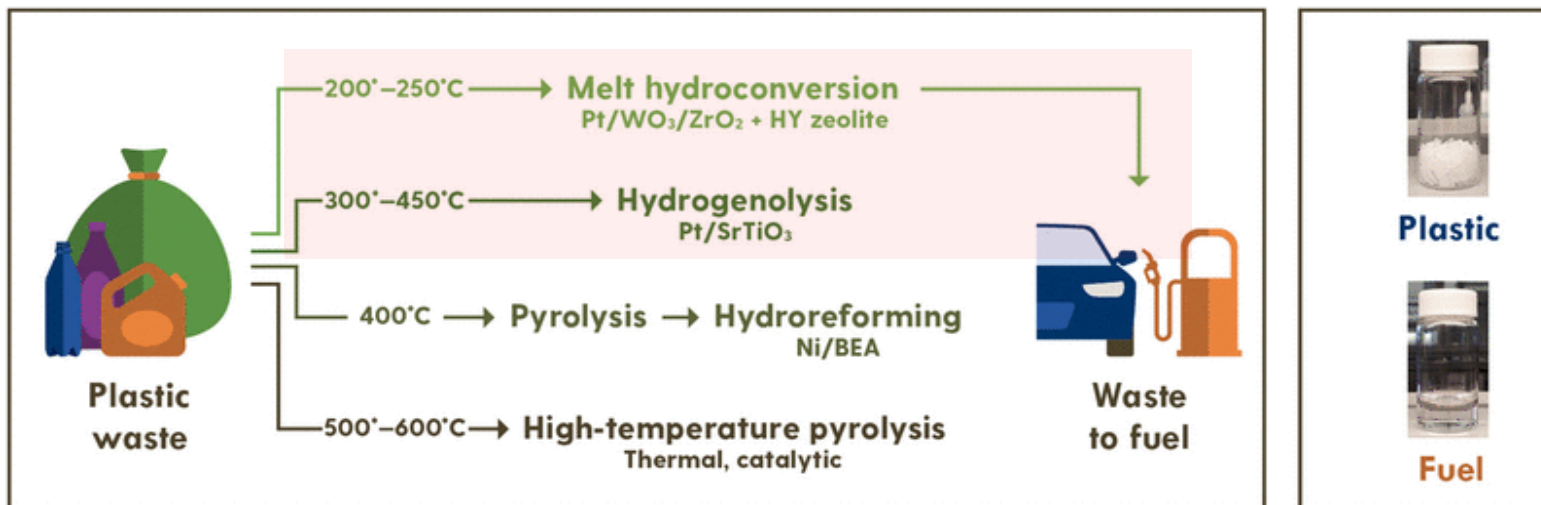


# Hydrogenolysis

- Hydrogenolysis is a catalytic chemical method to break down the CC bond or C heteroatom bonds such as CO (hydrodeoxygenation, HDO) in the feedstock by using  $H_2$ .
- Although thermochemical conversion is promising for handling mixed plastic waste, it typically occurs at high temperatures (300–800°C).

## Advantages

- Mild reaction temperature
- Highly selective
- Ease of product separation
- Adaptable to a number of plastics
- Wide range of C catalyst selection and design



# Solvent-assisted Hydrogenolysis

## Effect of solvent

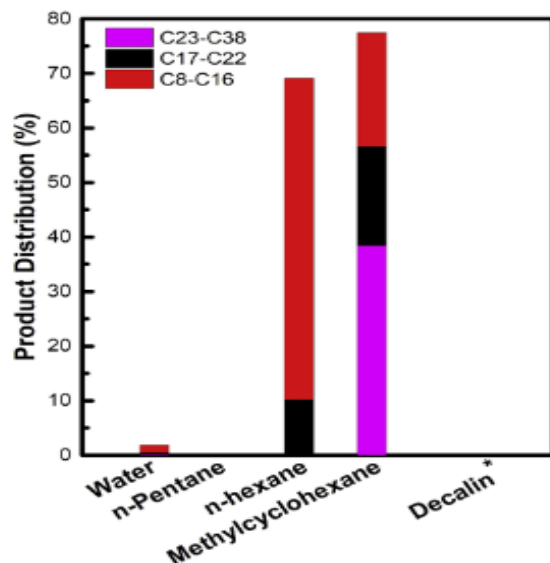
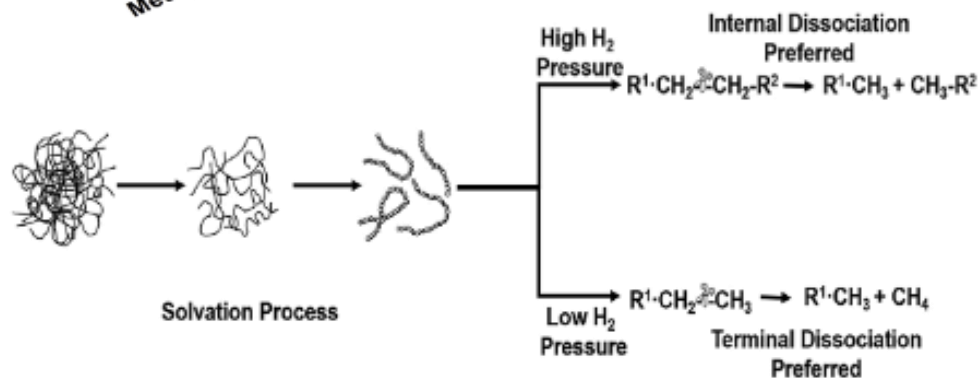


Table 2. Performance of the screened catalysts in the depolymerization of HDPE

Entry	Feedstock	Catalyst	Temperature (°C)	Time (h)	C8-C16 (wt %)	C17-C22 (wt %)	C23-C38 (wt %)
1	HDPE	5% Cu/C	220	1	0	0	0
2	HDPE	5% Fe/C	220	1	0	0	0
3	HDPE	5% Ni/C	220	1	0	0	0
4	HDPE	5% Pt/C	220	1	0	0	0
5	HDPE	5% Pd/C	220	1	0	0	0
6	HDPE	5% Rh/C	220	1	0	0	0
7	HDPE	5% Ru/C	220	1	60.8	14.1	0
8	HDPE	5% Pt/C	250	6	0.2	0.16	0.23
9	HDPE	5% Pd/C	280	1	0.29	0.01	0.1
10	HDPE	5% Pt/C	280	1	0.28	0.37	0.42
11	HDPE	5% Rh/C	280	1	21.7	20.2	33.4

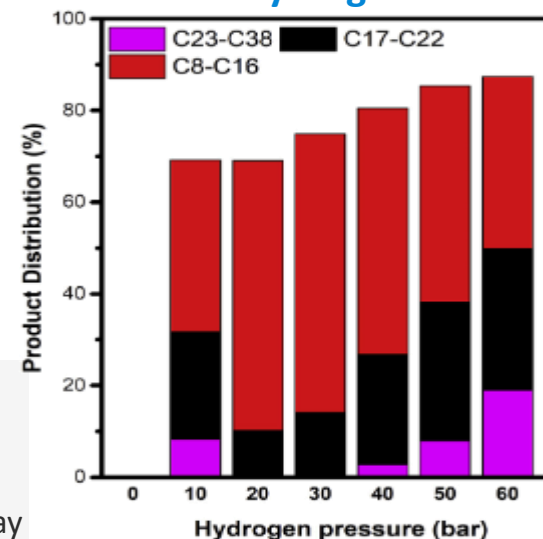
Reaction conditions: 0.1 g HDPE, 0.05 g catalyst, 25 mL n-hexane, p(H<sub>2</sub>) 30 bar, 700 rpm.



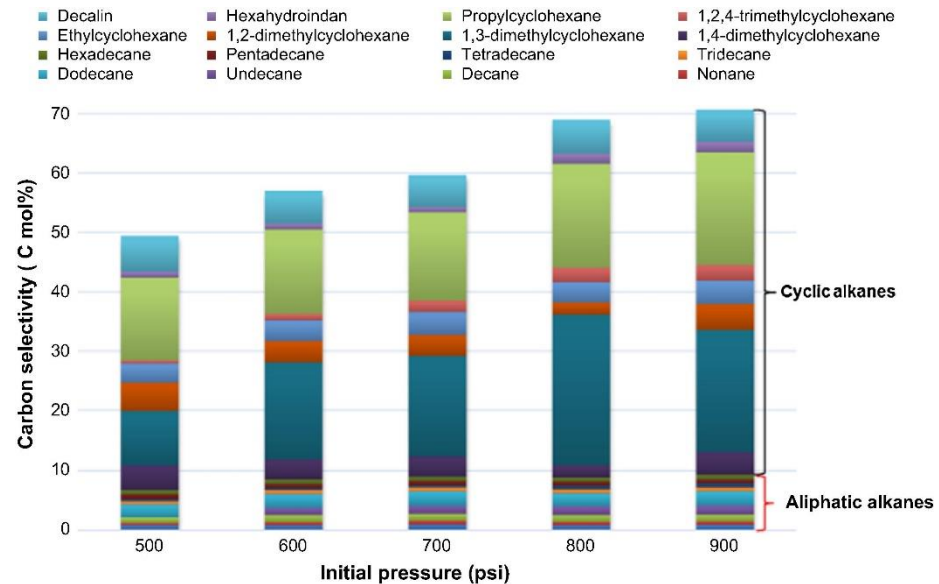
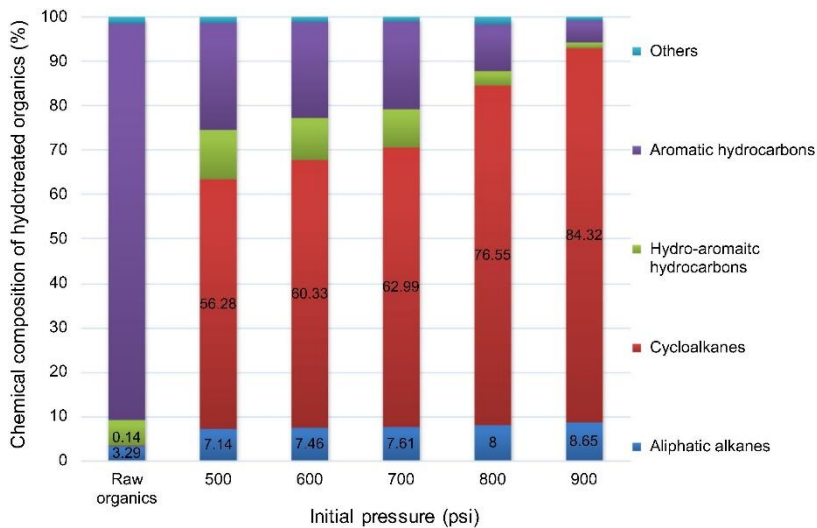
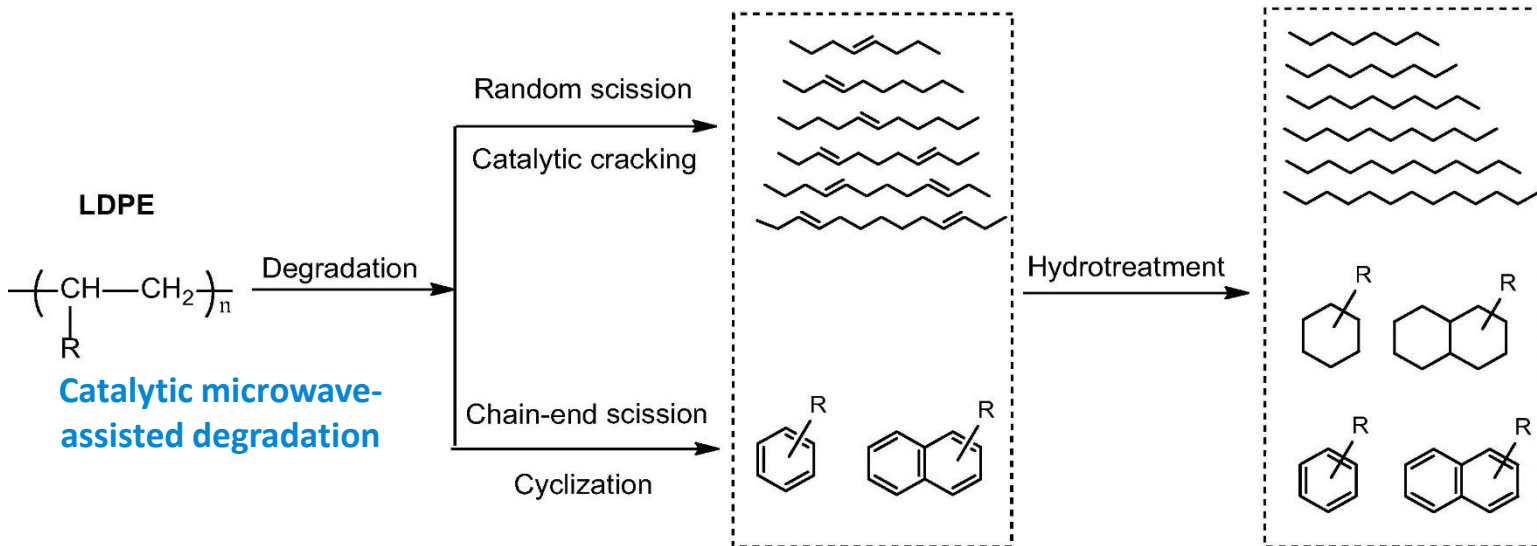
- Ru/C was a highly active catalyst for the liquid-phase hydrogenolysis of HDPE
- Solvent effects were prominent in the depolymerization of HDPE
- H<sub>2</sub> partial pressure played a significant role in the HDPE depolymerization pathway

*Chem Catalysis* 1, 437–455, July 15, 2021

## Effect of Hydrogen Pressure



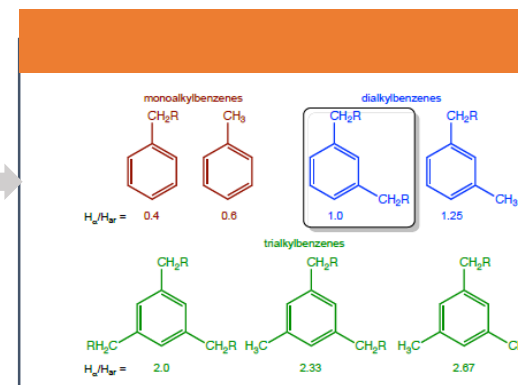
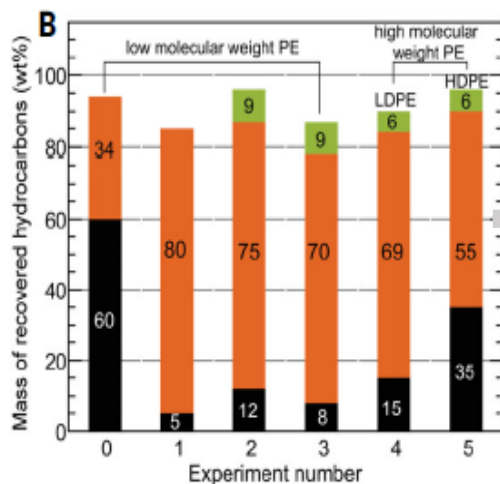
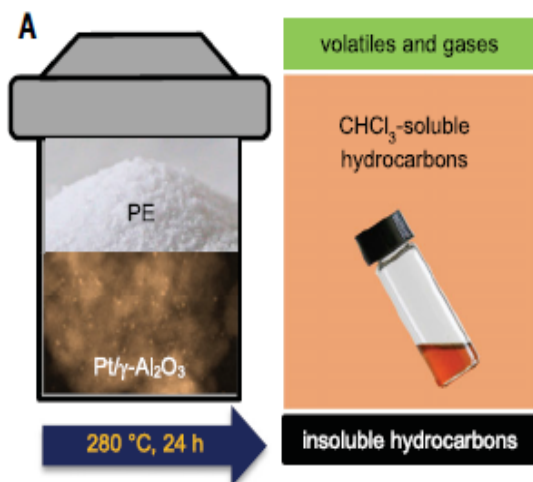
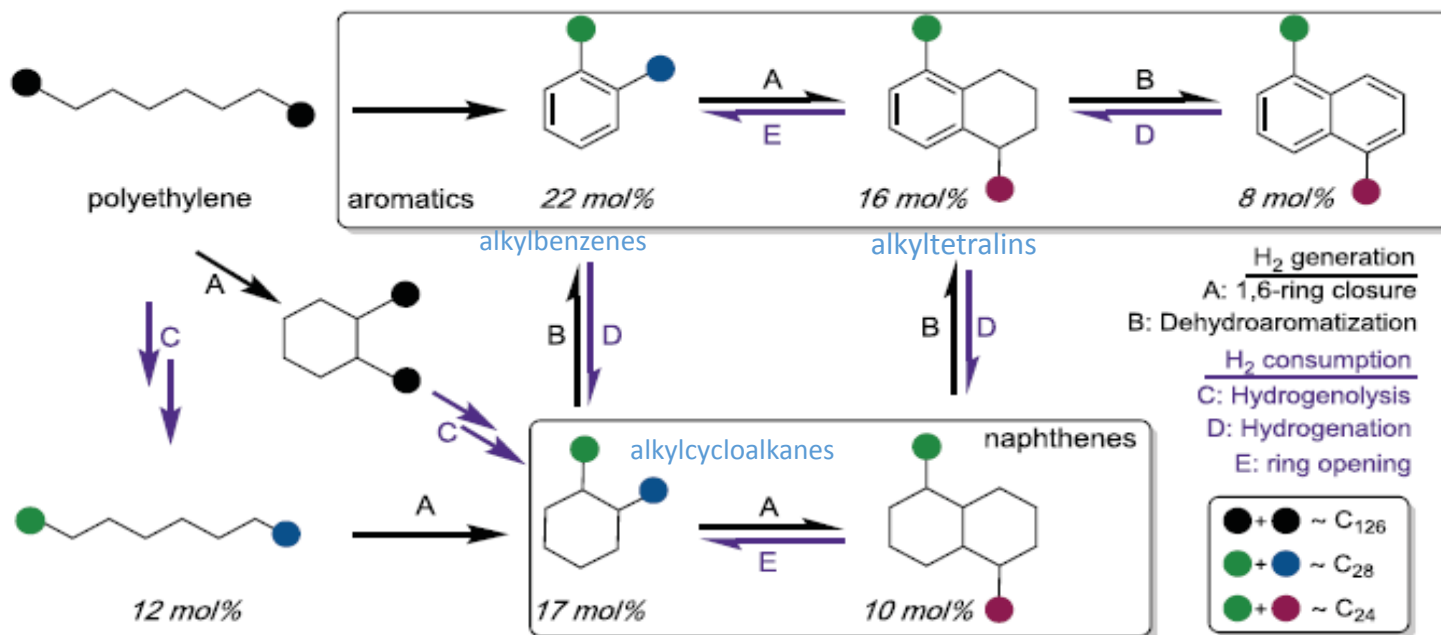
# Degradation/Hydrogenation



Reactant: raw organics from catalytic microwave degradation of LDPE over 20 wt% ZSM-5 catalyst; reaction temperature, 200 °C; Raney Ni 4200 catalyst, 10 wt% with respect to reactant mass; reaction time, 2 h.

X. Zhang et al. / Fuel 188 (2017) 28–38 29

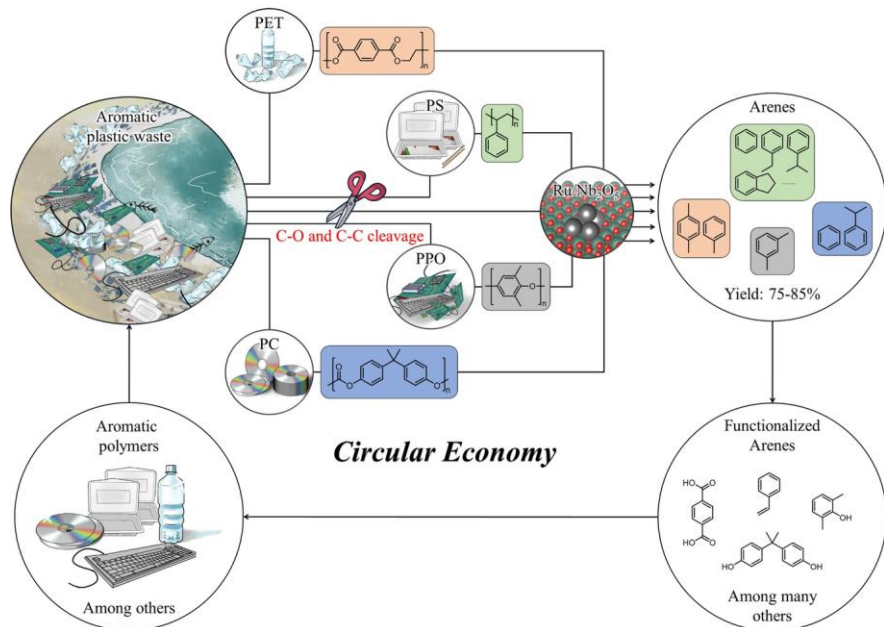
# Tandem Hydrogenolysis/Aromatization



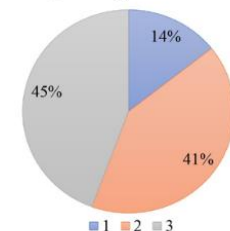
Solvent-free disassembly of polyethylene catalyzed by Pt/g-Al<sub>2</sub>O<sub>3</sub> in an unstirred mini-autoclave reactor at 280°C.

Zhang et al., *Science* 370, 437–441 (2020)

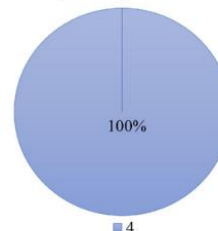
# Upgrading of Mixed Plastic in Octane



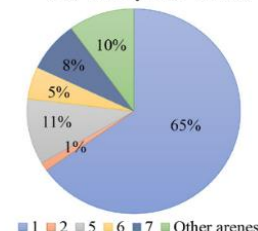
PET, Total yield: 83.6%<sup>a</sup>



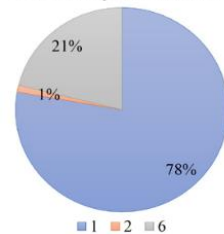
PPO, Total yield: 85.0%<sup>b</sup>



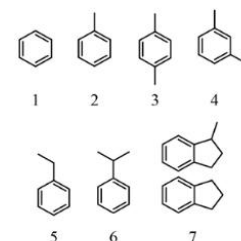
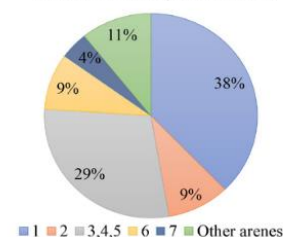
PS, Total yield: 75.9%<sup>c</sup>



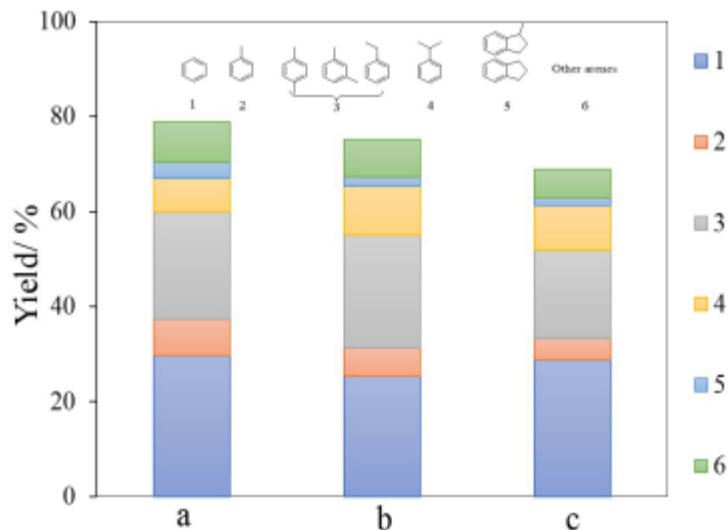
PC, Total yield: 83.3%<sup>d</sup>



Mixture, Total yield: 78.9%<sup>e</sup>



Reaction conditions: 15 mg PET, 15 mg PC, 15 mg PS, 15 mg PPO, 60 mg  $Ru/Nb_2O_5$ , 4 g octane, 0.5 MPa  $H_2$ , 320 °C, 16 h.

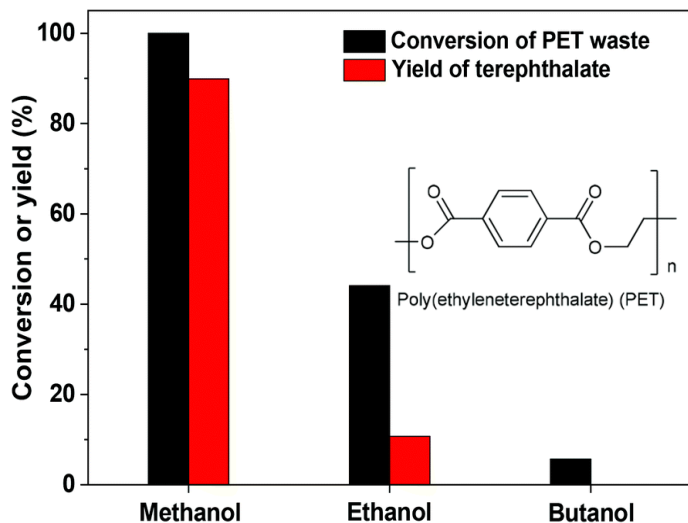


- They reported one-pot hydrogenation of mixed plastic waste to arenes
- $Ru/Nb_2O_5$  catalyst plays two roles in the selective cleavage of C–O/C–C bonds in aromatic plastic waste into arenes:
- (a) 60 mg  $Ru/Nb_2O_5$ , 4 g octane, (b) 60 mg  $Ru/Nb_2O_5$ , 2 g octane; (c) 30 mg  $Ru/Nb_2O_5$ , 4 g octane.

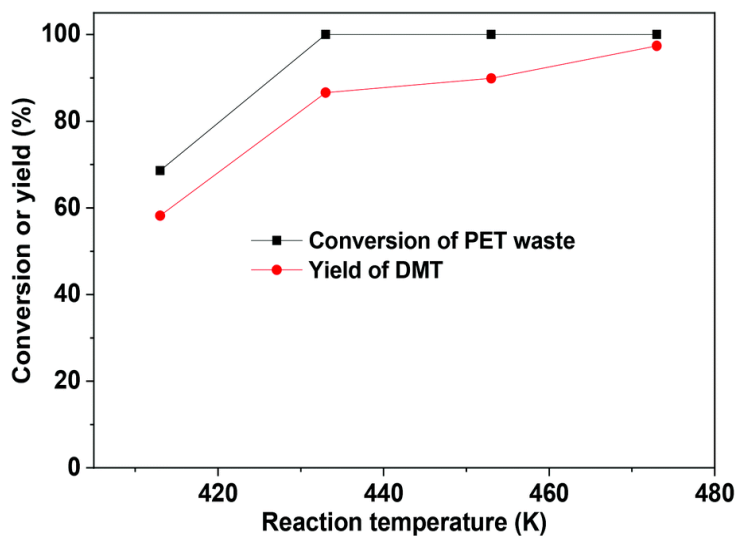
Angew. Chem. Int. Ed. 10.1002/anie.202011063

# Alcoholysis/Solvent-free Hydrogenation

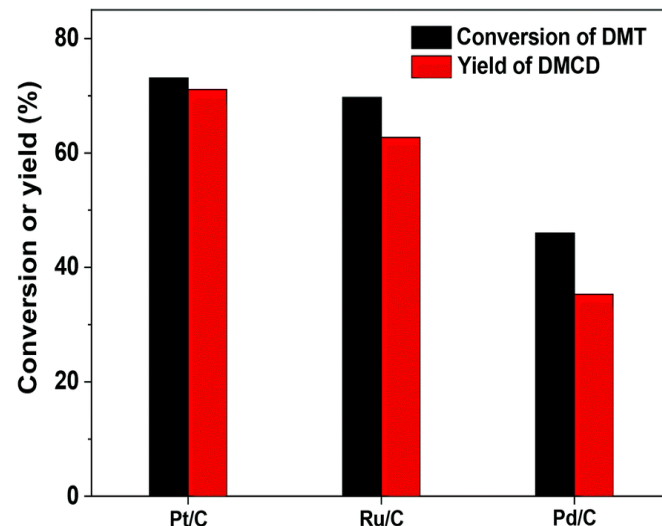
## Alcoholysis of PET waste



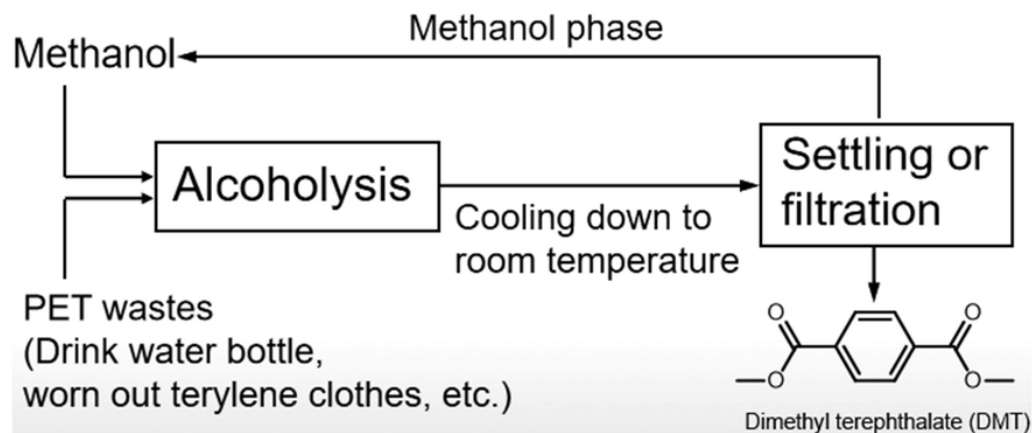
453 K, 3.5 h; 1 g PET waste and 40 mL alcohol



## Hydrogenation of DMT

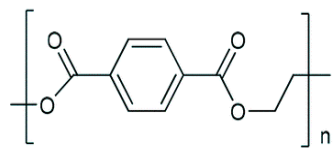


373 K, 5 MPa H<sub>2</sub>, 7 h; 30 g DMT and 1 g catalyst



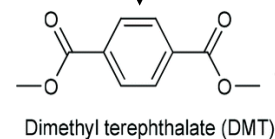
*Green Chem.*, 2019, 21, 2709–2719

# Alcoholysis/Solvent-free Hydrogenation



Poly(ethyleneterephthalate) (PET)

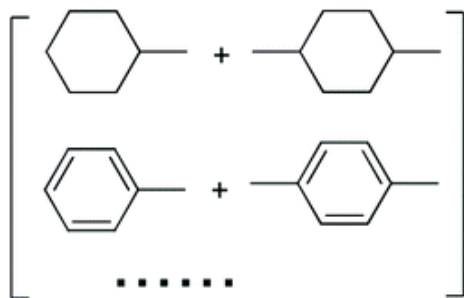
Alcoholysis



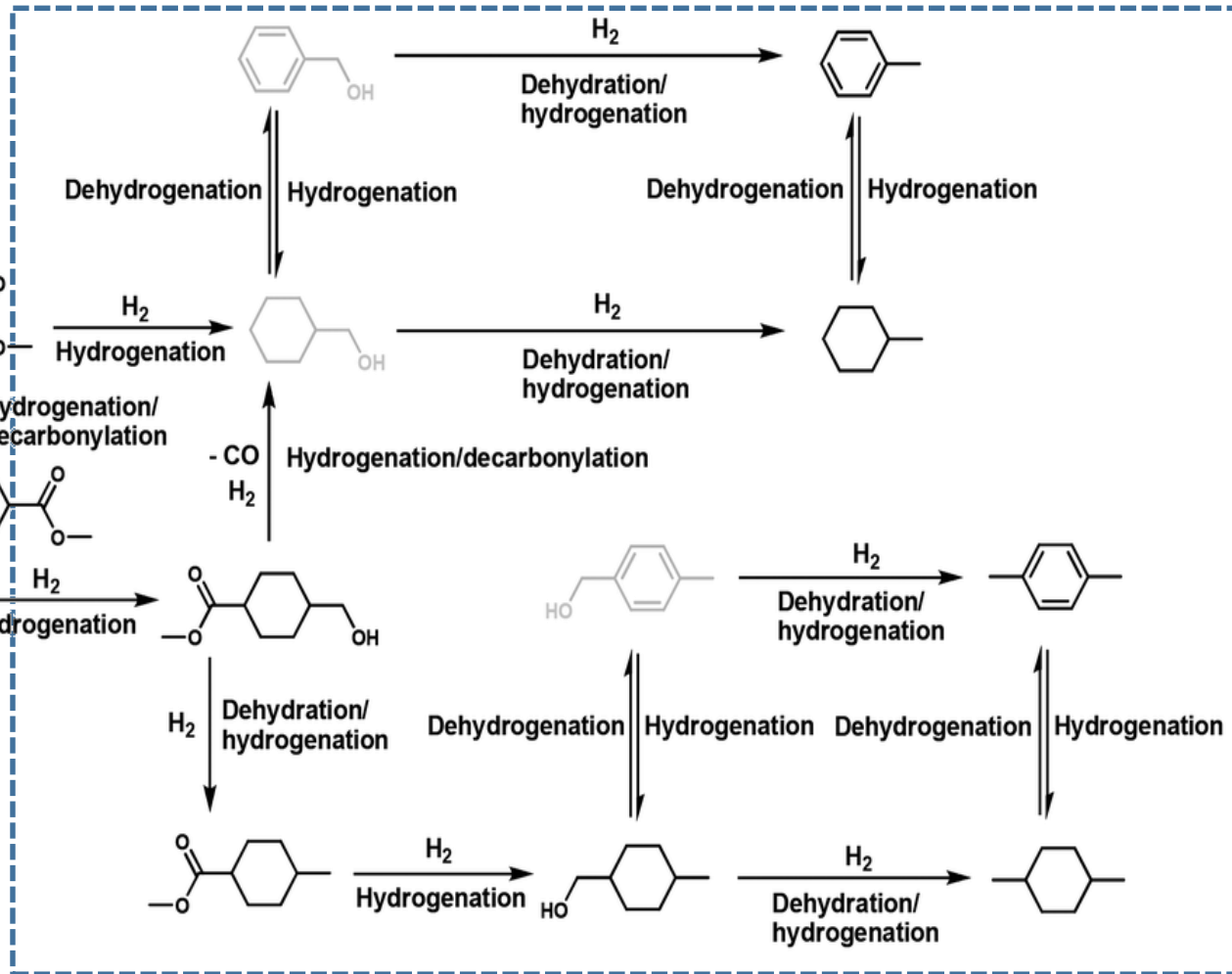
Dimethyl terephthalate (DMT)



Final products



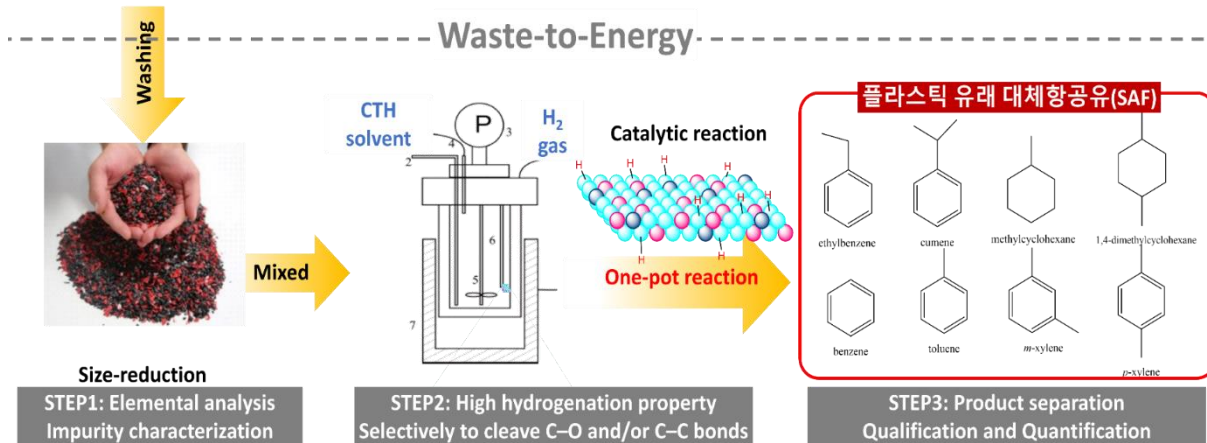
Gasoline and jet fuel range  
C<sub>7</sub>-C<sub>8</sub> cyclic hydrocarbons



Detailed reaction pathways

# MCREL Approach

## One-pot catalytic conversion of aromatic plastic waste back to arenes for aviation fuels



The selective degradation of aromatic plastic waste into target arenes is exceedingly rare

- Identify a catalyst that enables the selective cleavage of C–O and/or C–C bonds while **preserving the aromatic rings**

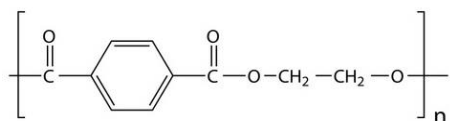
From C–O/C–C activation chemistry,

- Combination of metal sites with high hydrogenation property and acidic sites with the strong ability to activate C–O/C–C bonds is required

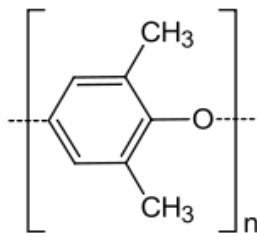


# Raw Material

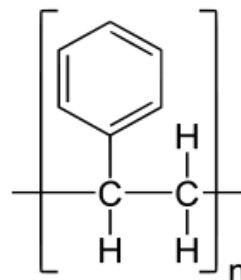
PET



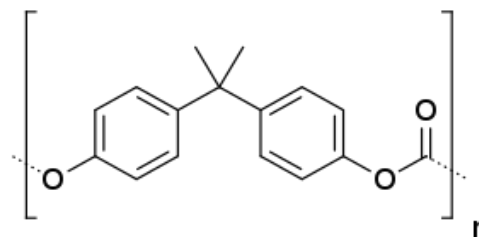
PPO



PS



PC



## Why?

Constructed from aromatic monomers by interunit C–O and/or C–C linkages

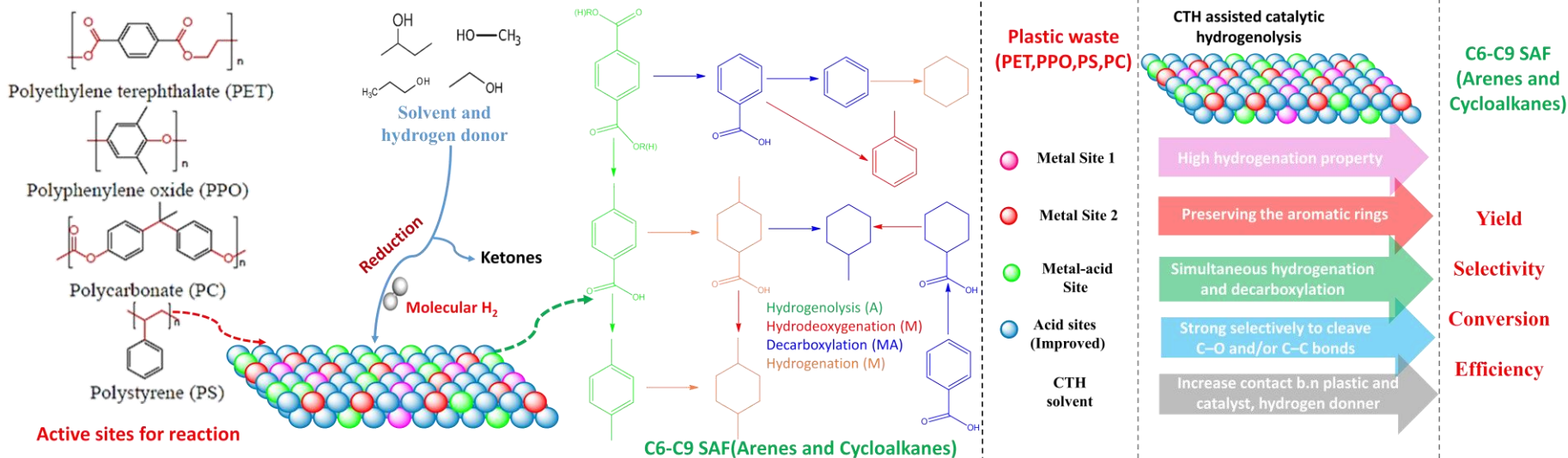
### Many widely used plastics

- Polyethylene terephthalate (PET)
- Polystyrene (PS)
- Polycarbonate (PC)
- Polyphenylene oxide (PPO)

They comprise all common types of linkages in aromatic plastics

- Ester linkage
- Ether linkage,
- C–C
- combinations of C–O and C–C linkages

# Reaction Mechanism



## For C-O bond cleavage,

- Lewis acid sites (support) enable the selective adsorption and activation of C-O bond
- Then, with the help of dissociated H species over Ru, the cleavage of C-O bonds in aromatic plastics is efficiently achieved

## For C-C bond cleavage,

- The benzene ring is first adsorbed on Lewis acid sites
- Then the adsorbed benzene ring is protonated by Brønsted acid sites to proceed the activation of the C-C bond
- Following that, the dissociated H species on metal clusters attack the weakened C-C bond to break it

# Reaction Results



Recycled plastic



Size reduction, reaction mixture preparation



Product separation using ethyl acetate as organic solvent

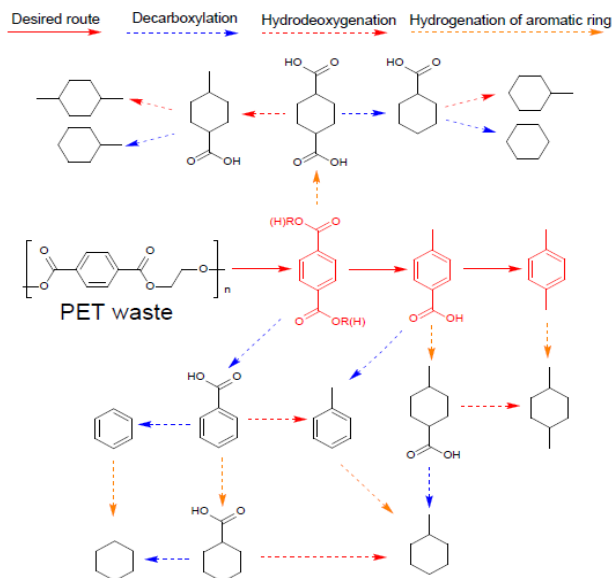
## Water as a solvent

- Polar solvent that binds reasonably strongly with polar functionalities in PET thus, weakening the inter-chain interactions
- Does not react with hydrogen over metal-solid acid catalysts at the reaction temperature

# Reaction Results

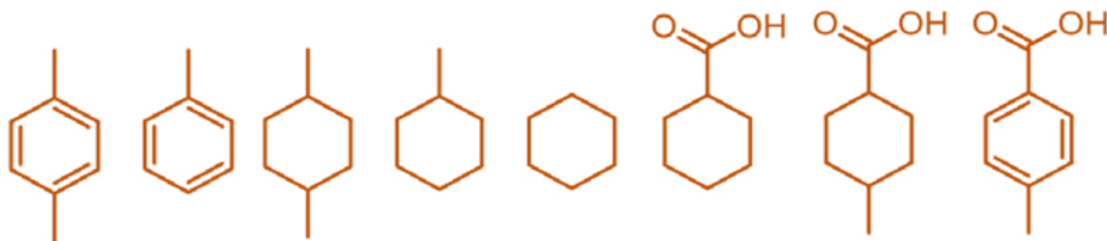
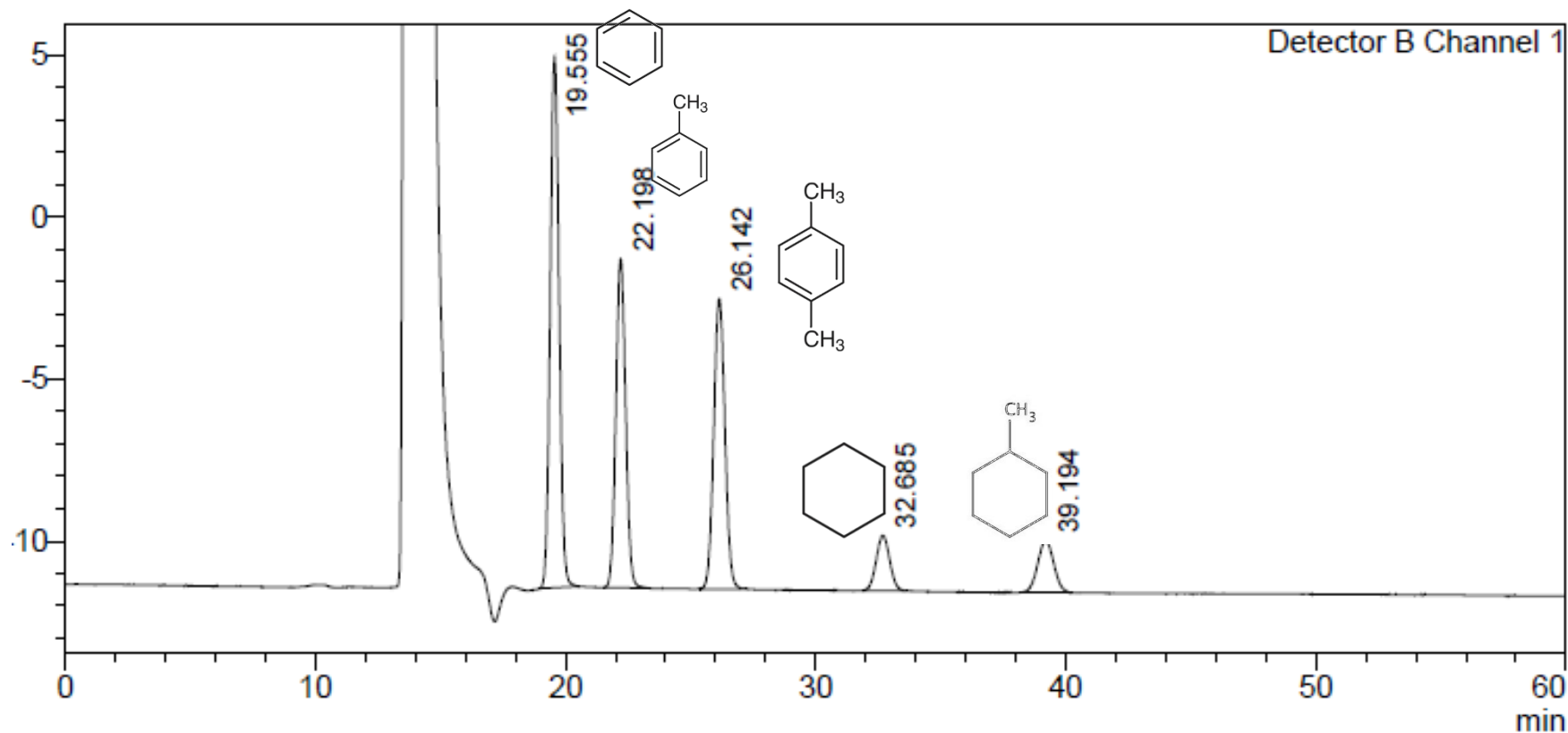
Catalysts	PET conversion (%)	P-xylene S (%)	Toluene S (%)	m-Cyclohexane S (%)	Others
Ru/SNb <sub>2</sub> O <sub>5</sub>	<b>72.0</b>	<b>53.2</b>	<b>19.2</b>	<b>4.10 (MCH+CH)</b>	<b>23.5</b>
Pd/SNb <sub>2</sub> O <sub>5</sub>	57.1	6.3	4.5	8.7 (MCH+CH)	80.4
Ru/ZSM-5	81.0	5.7	7.1	32.1 (MCH+CH)	55.1
Pd/ZSM-5	62.0	1.9	1.6	24.9 (MCH+CH)	71.5
Ru/ZrO	56.3	11.1	13.2	16.8 (MCH+CH)	58.9
Pd/ZrO	37.3	4.2	2.7	20.5 (MCH+CH)	72.6

Reaction conditions: 0.2 g PET, 0.2 g catalyst, 20 g H<sub>2</sub>O, 240 °C, 12 h, 40 bar H<sub>2</sub>



1. Lewis acid sites (NbOx species) enable the selective adsorption and activation of C-O bond
2. For C-C bond cleavage, benzene ring is first adsorbed on Lewis acid sites (NbOx species) of Nb<sub>2</sub>O<sub>5</sub>
3. Then the adsorbed benzene ring is protonated by Brønsted acid sites on Nb<sub>2</sub>O<sub>5</sub>
4. Following that, the dissociated H species on Ru attack the weakened Csp<sup>2</sup>-Csp<sup>3</sup> bond to break it.

# HPLC Chromatogram of the Product Mixture



# Reaction Results



Substrates	Structures	Theoretical contents in pure plastic (wt %)		Elemental analysis (wt %)	
		C	H	C	H
Coca-Cola bottle		62.50	4.17	61.94	4.16

Catalysts	CCB conversion (%)	P-xylene S (%)	Toluene S (%)	m-Cyclohexane S (%)	Others
Ru/SNb <sub>2</sub> O <sub>5</sub>	<b>86.2</b>	<b>47.2</b>	<b>21.3</b>	<b>10.2 (MCH+CH)</b>	<b>21.3</b>
Pd/SNb <sub>2</sub> O <sub>5</sub>	70.1	8.9	9.7	18.1(MCH+CH)	63.3
Ru/ZSM-5	94.0	7.5	7.1	36.2 (MCH+CH)	49.2
Pd/ZSM-5	77.0	3.8	4.9	31.9 (MCH+CH)	59.4
Ru/ZrO	71.3	15.3	14.6	20.0 (MCH+CH)	50.1
Pd/ZrO	52.3	6.7	9.1	19.7 (MCH+CH)	64.5

Reaction conditions: 0.2 g CCB, 0.2 g catalyst, 20 g H<sub>2</sub>O, 240 °C, 10 h, 40 bar H<sub>2</sub>

## Water as a solvent

- Is a polar solvent that binds strongly with polar functionalities in PET thus, weakening the inter-chain interactions
- Does not react with hydrogen over metal-solid acid catalysts at the reaction temperature
- Poor performance of Pd catalysts was due to the fast hydrogenation of aromatic rings leading to ring opening and resulting in the formation of chemically more robust C–O linkages

# Reaction Results

Temperature	CCB conversion (%)	P-xylene S (%)	Toluene S (%)	m-Cyclohexane S (%)	Others
220	61.6	39.1	11.3	1.2 (MCH+CH)	48.4
<b>240</b>	<b>86.2</b>	<b>47.2</b>	<b>21.3</b>	<b>10.2 (MCH+CH)</b>	<b>21.3</b>
260	91.3	41.7	28.1	7.2 (MCH+CH)	23.0
280	97.1	36.0	29.3	9.1 (MCH+CH)	25.6

Reaction conditions: 0.2 g CCB, 0.2 g catalyst Ru/Nb<sub>2</sub>O<sub>5</sub>, 20 g H<sub>2</sub>O, Varying T, 8 h, 30 bar H<sub>2</sub>

Pressure	CCB conversion (%)	P-xylene S (%)	Toluene S (%)	m-Cyclohexane S (%)	Others
30	76.1	31.0	9.7	1.6 (MCH+CH)	57.7
<b>40</b>	<b>86.2</b>	<b>47.2</b>	<b>21.3</b>	<b>10.2 (MCH+CH)</b>	<b>21.3</b>
50	88.3	37.0	17.3	27.3 (MCH+CH)	18.4
60	90.1	24.6	12.0	35.6 (MCH+CH)	27.8

Reaction conditions: 0.2 g CCB, 0.2 g Ru/Nb<sub>2</sub>O<sub>5</sub>, 20 g H<sub>2</sub>O, 220 °C, 8 h, varying P.

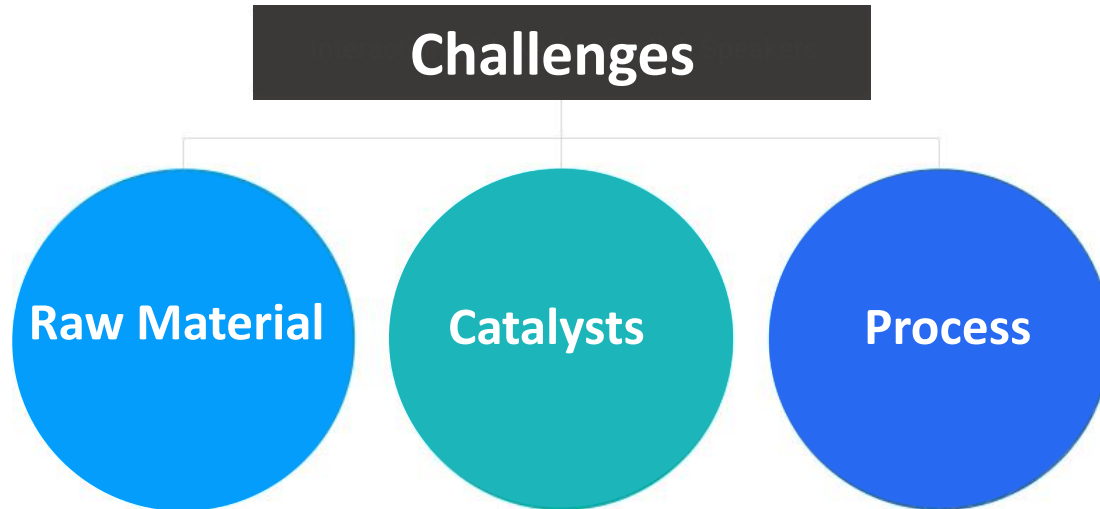
- The plastic conversion increased monotonically as a function of temperature
- Lower temperature led to low reaction rates, higher temperature favored the undesirable decarboxylation
- Higher pressure favored the hydrogenation of aromatic ring, lower pressure was not able to complete deoxygenation

# Hydrogenolysis Summary

Substrate	Catalyst	Reaction conditions	Products	Yield [%]	Solvent
PE, PP	silica-supported Zr-H Ni and NiMo sulfides/HZSM-5 + Si-Al support	150–190 °C, 1 bar H <sub>2</sub> , 5–15 h	short-chain alkanes	40–84	none
HDPE		375 °C, ≈ 70 bar H <sub>2</sub> , 1 h	gasoline-range fuels	42–65	none
PE	Pt/HZSM-5; Pt/HY; Pt/HMCM-41	120–340 °C, H <sub>2</sub> flow	paraffins, olefins, and alkyl aromatics	N.A.	none
PS, LDPE, PEP	PtRe/SiO <sub>2</sub>	170 °C, ≈ 35 bar D <sub>2</sub> , 17 h	poly (cyclohexylethylene); low-M <sub>w</sub> oligomers	> 90	isooctane
squalane	Ru/CeO <sub>2</sub>	240 °C, 35 bar H <sub>2</sub> , 3–48 h	branched, short- chain alkanes	≈ 70	none
squalane	Ru–V/SiO <sub>2</sub>	240 °C, 35 bar H <sub>2</sub> , 96 h	branched short-chain alkanes	> 70	none
PEs, PP	Ru/CeO <sub>2</sub>	200–240 °C, 20–35 bar H <sub>2</sub> , 8–144 h	liquid fuels and waxes	83–92	none
PEs	Pt/SrTiO <sub>3</sub>	300 °C, ≈ 12 bar H <sub>2</sub> , 96 h	narrow-range lubric- ant-like products	42–99	none
PET	hydrogenation: Pt/C; HDO: RuCu/SiO <sub>2</sub>	methanolysis: 140–200 °C, 3.5–14 h hydrogenation: 80–160 °C, 50 bar H <sub>2</sub> , 1– 10 h HDO: 350–400 °C, 40 bar H <sub>2</sub> , 8–22 h	C <sub>7</sub> /C <sub>8</sub> cycloalkanes and aromatics	overall ≈ 94	methanol
PC	HDO: Pt/C + H-β	methanolysis: 140–200 °C, 3 h; HDO: 100 °C, 30 bar H <sub>2</sub> , 1 h	polycycloalkanes	overall ≈ 72	methanol
PC	Raney Ni + USY	1st step: 190 °C, Raney Ni, 1 h 2nd step: 190 °C, USY added, 1–5 h (H <sub>2</sub> -free for the two steps)	C <sub>6</sub> –C <sub>15</sub> cyclic hydro- carbons	≈ 75	isopropanol
PC	Rh/C + H-USY	200 °C, 35 bar H <sub>2</sub> , 12 h	propane-2,2-diyldicy- clohexane	≈ 95	water
PEs	Ru/C	200–225 °C, 20–30 bar H <sub>2</sub> , 2–16 h	gaseous and liquid alkanes, CH <sub>4</sub>	alkanes: ≈ 82 CH <sub>4</sub> : ≈ 100	none
PE	SnPt/γ-Al <sub>2</sub> O <sub>3</sub> + Re <sub>2</sub> O <sub>7</sub> /γ-Al <sub>2</sub> O <sub>3</sub> Ru/Nb <sub>2</sub> O <sub>5</sub>	200 °C, 20–40 bar He, 15 h	low-M <sub>w</sub> oligomers	N.A.	n-pentane
PET, PS, PC, PPO, and mixtures		280–320 °C, 3 bar H <sub>2</sub> , 8–16 h	arenes	75–85	H <sub>2</sub> O/octane
PET	Ru/Nb <sub>2</sub> O <sub>5</sub>	220 °C, 20 bar N <sub>2</sub> , 12 h	BTX	≈ 91	water
LDPE/HDPE	Pt/γ-Al <sub>2</sub> O <sub>3</sub>	280 °C, H <sub>2</sub> -free, 24 h	alkylaromatics and alkylnaphthenes	55–80	none
PET	single-site MoO <sub>3</sub> /C	260 °C, 1 bar H <sub>2</sub> , 24–96 h	TPA and ethylene	85–90	none
PS	Ru/SNb <sub>2</sub> O <sub>5</sub>	320 °C, 40 bar H <sub>2</sub> , 20h	Arenes and cyclic-alkanes	~ 72	water
PET	Ru/SNb <sub>2</sub> O <sub>5</sub>	240 °C, 40 bar H <sub>2</sub> , 12h		~ 76	
CCB	Ru/SNb <sub>2</sub> O <sub>5</sub>	240 °C, 40 bar H <sub>2</sub> , 8h		~ 86	

MCREL

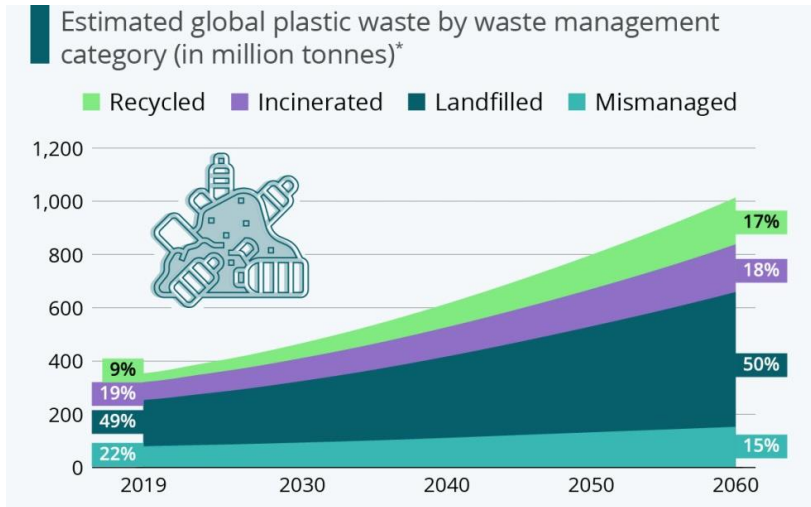




1. The solid-solid contact problem between plastic and solid catalyst remains a challenge
2. Designing an advanced solvent system to increase plastic swelling and solubility is highly desirable
3. Establish hydrogen transfer systems using renewable alcohols and acids as hydrogen sources
4. Economical and advanced catalysts with higher activity need to be explored
5. Improving plastic waste conversion efficiency and selectivity to SAF for mixed plastic
6. Systematic experimental process development and condition optimization

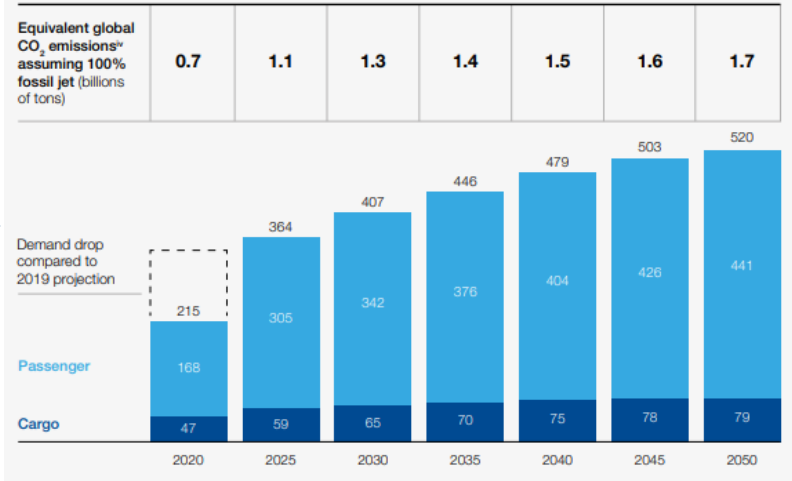
# Outlooks

## Plastic waste



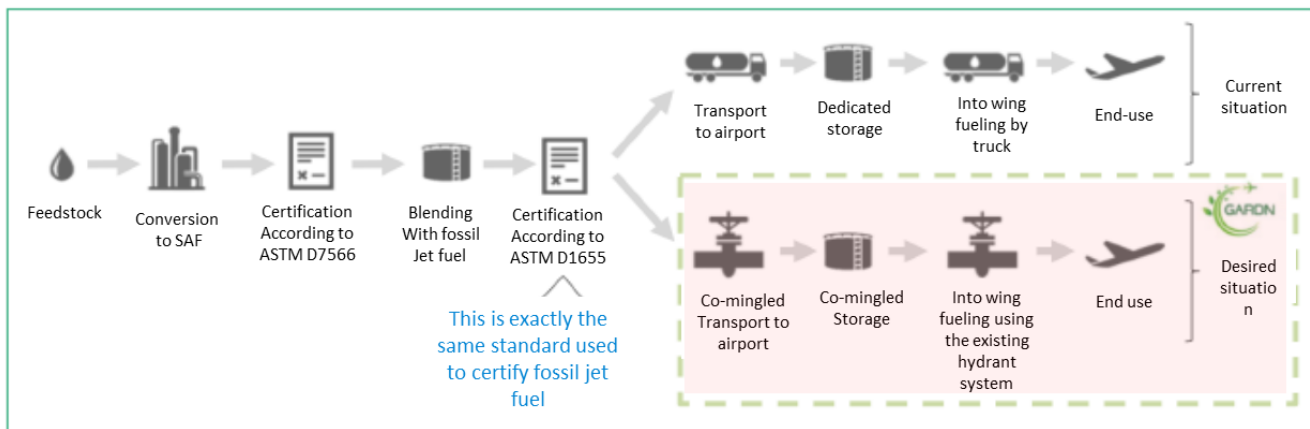
## SAF

Global aviation energy demand projection (million of tons of jet fuel per year)



Given a policy framework, SAF is perhaps on the cusp of rapid expansion and replication

- Many members of entire supply chains are working towards SAF development (academia, national labs, entrepreneurs, big oil, fuel suppliers, pipeline companies, aviation partners)



Clean Skies for Tomorrow Sustainable Aviation Fuels as a Pathway to Net-Zero Aviation, INSIGHT REPORT NOVEMBER 2020

# Conclusion

- Various chemical methods including hydrogenolysis, pyrolysis, solvolysis, and others have been employed to convert a single or mixture of plastic wastes into valuable chemicals.
- The hydrogenolysis reaction of waste plastic can be combined with other reactions such as solvolysis and thermal degradation to increase the selectivity to SAF.
- Ru has shown significant results for most plastic to SAF hydrogenolysis reactions.
- $\text{Nb}_2\text{O}_5$  catalyst support plays two roles in the selective cleavage of C–O/C–C bonds in aromatic plastic waste into arenes.
- Ru/ $\text{Nb}_2\text{O}_5$  does not only catalyze the selective conversion of single-component plastic waste into bulk chemicals (PET to p-xylene and PPO to m-xylene), but also enables the conversion of mixed aromatic plastics into arenes.
- Innovative transformation routes are anticipated in the future to generate more diversified and high-value products from plastic wastes.