Reciclagem Química de Materiais Plásticos Pós-Consumo por Pirólise - Avanços e Desafios

24º Congresso Brasileiro de Engenharia Química
Salvador 2023
24º COBEQ
01 a 04/outubro/2023

EngepolGrupo
Falandocomciencia
Falandocomciencia
Falando com Ciência
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UFRJ

Programa de Engenharia Química, COPPE/UFRJ
Programa de Engenharia de Processos Químicos e Bioquímicos, EQ/UFRJ

Grupo EngePol

Agradecimentos

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Elaine Albuquerque (DEQ/EP/UFBa)

Karen Pontes (Presidente do COBEQ)

Marcio Martins (Presidente do ENBEQ)

pelo convite e por todo carinho e atenção.

Muitos colegas, estudantes, empresas parceiras e agências de fomento.

Grupo EngePol

Outline

1. **EngePol Research Group**
2. **Chemical Recycling Overview**
3. **Pyrolysis Process and Challenges**
4. **EngePol Pyrolysis Capabilities & Studies**
5. **Concluding Remarks**

EngePol Research Group

EngePol Research Group

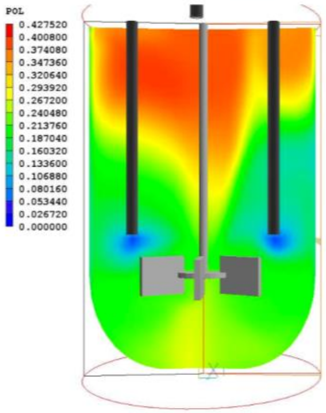
EngePol Research Group

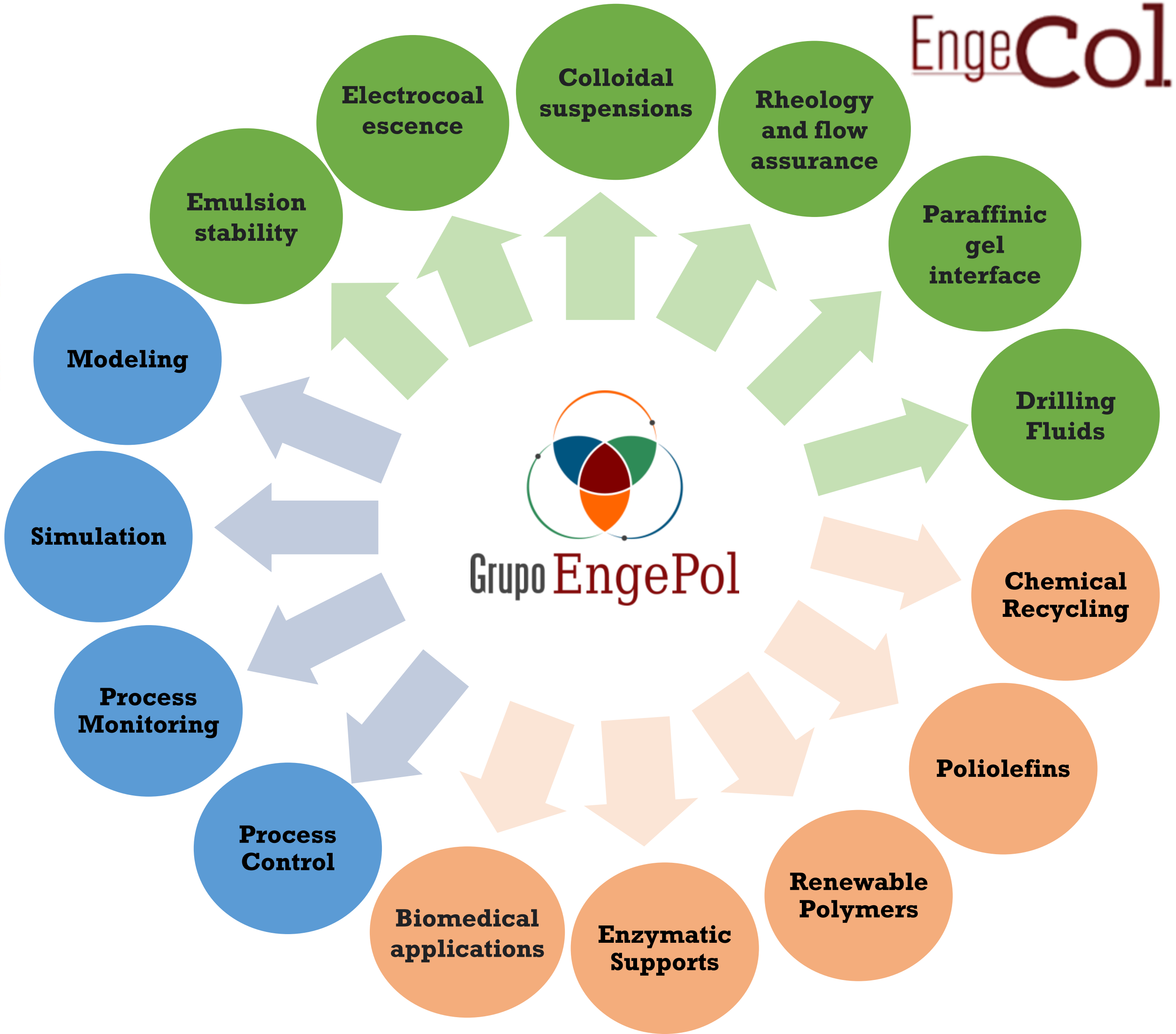
5 Professores
10 Pesquisadores
40 Pós-Graduandos
10 Graduandos

500 Papers – 20 por ano
40 Patentes
10 Capítulos de Livro
10 Livros
12000 Citações

EngePol Research Group

LMSCP
PEQ/COPPE/UFRJ





EngeCol

EngePol

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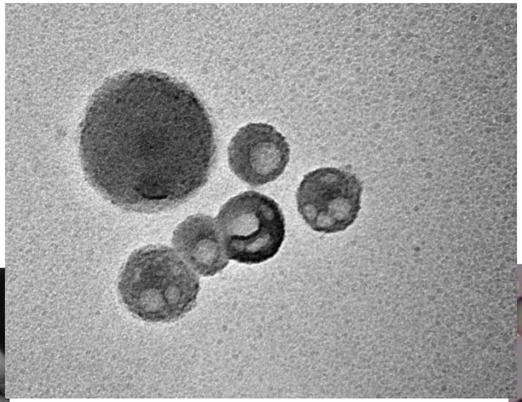
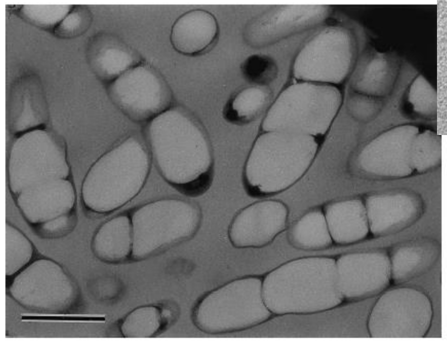
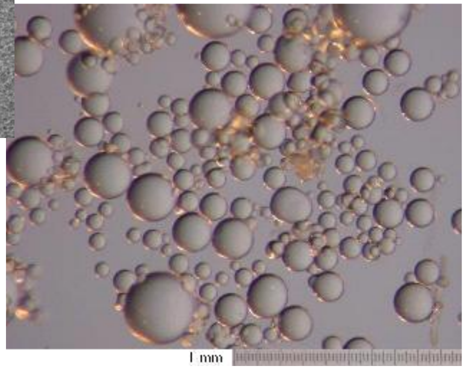
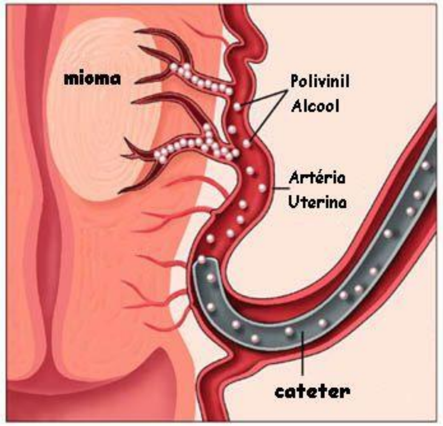
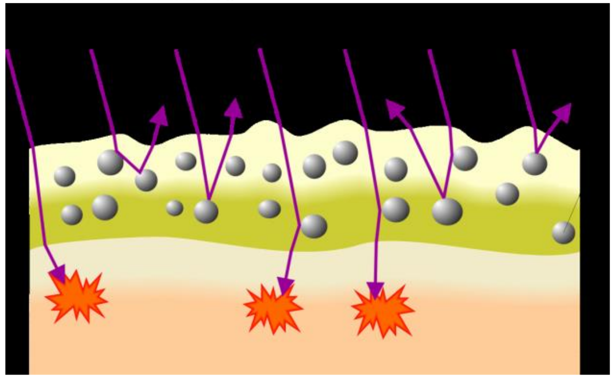
Biomedical Applications

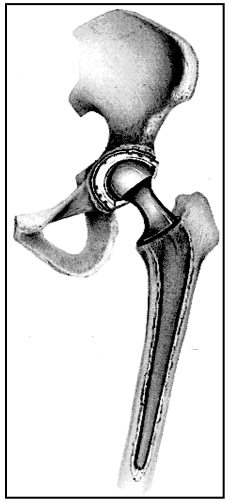












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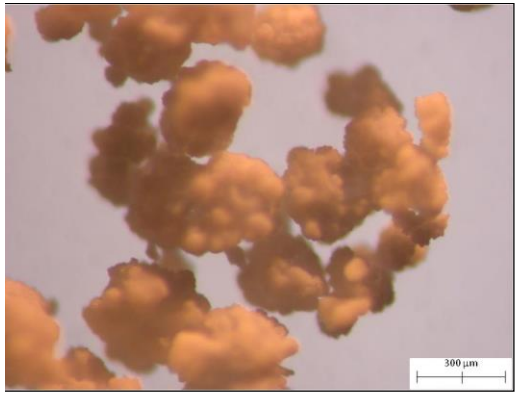
Sustainability



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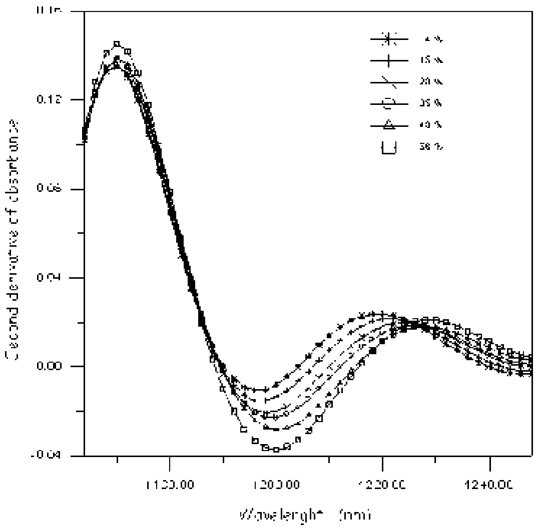
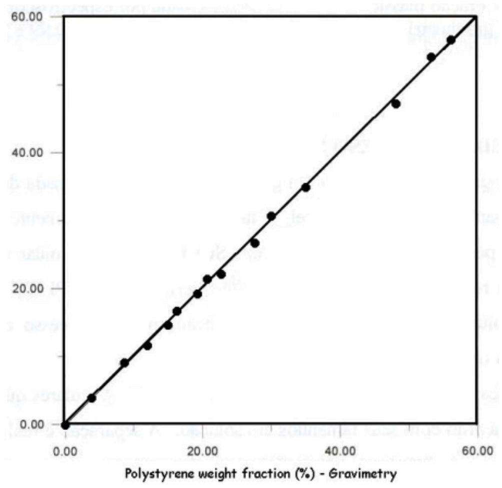
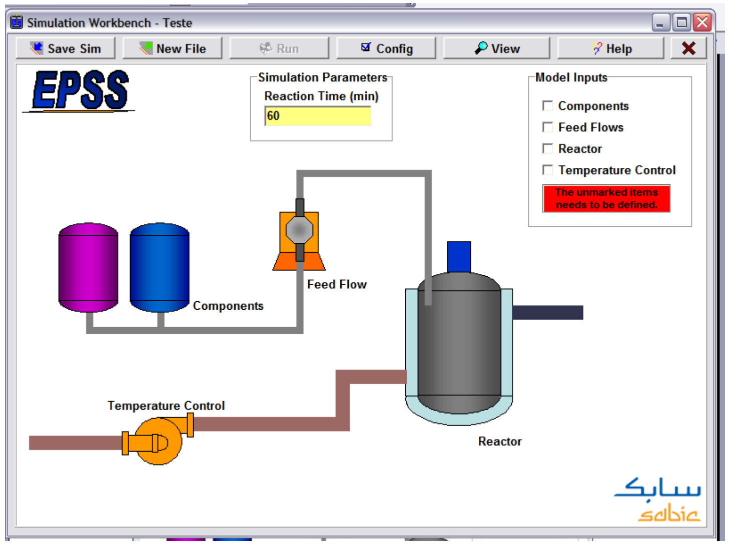
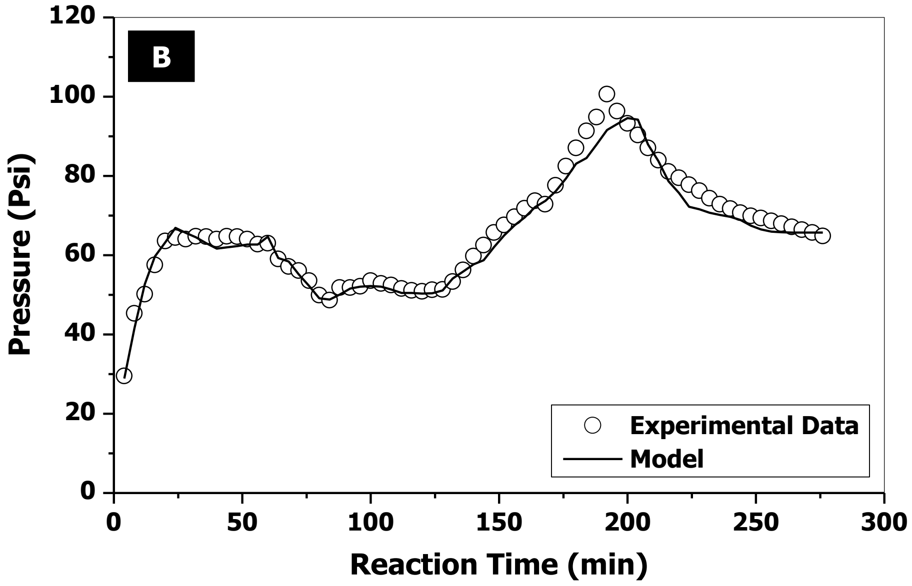


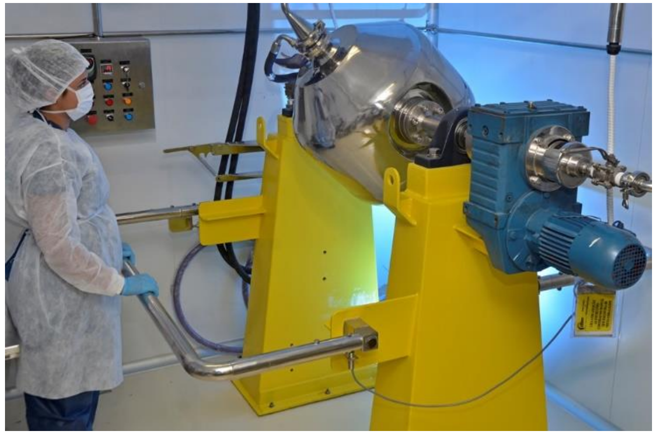




Industrial Applications



EngePol Research Group



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OPTIMATECH

BioSoul

BioBeads

MAGtech

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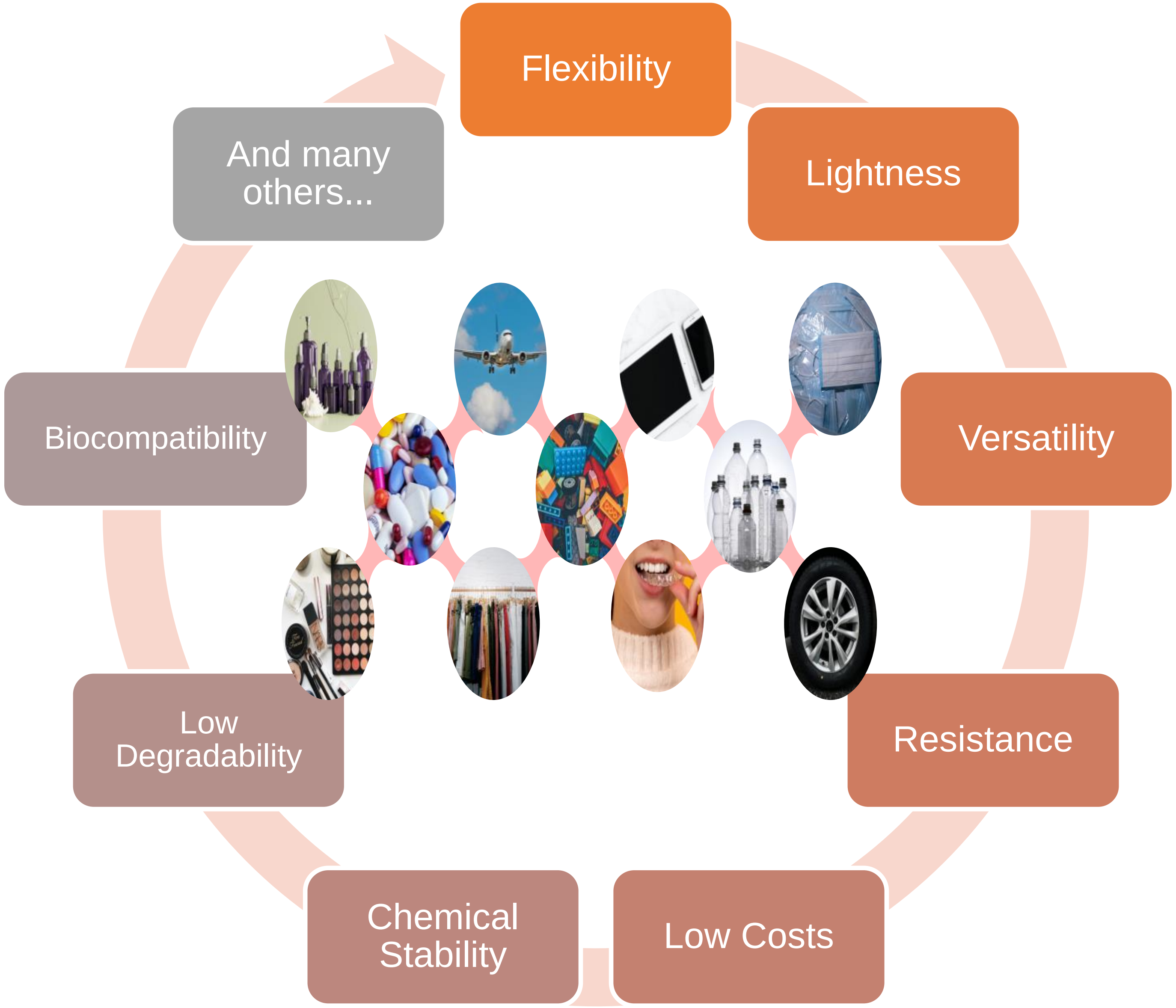
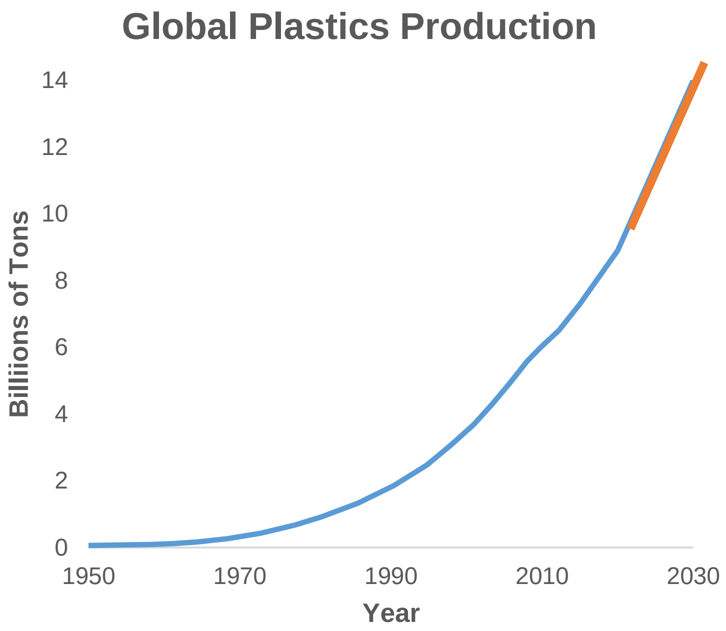
Chemical Recycling Overview

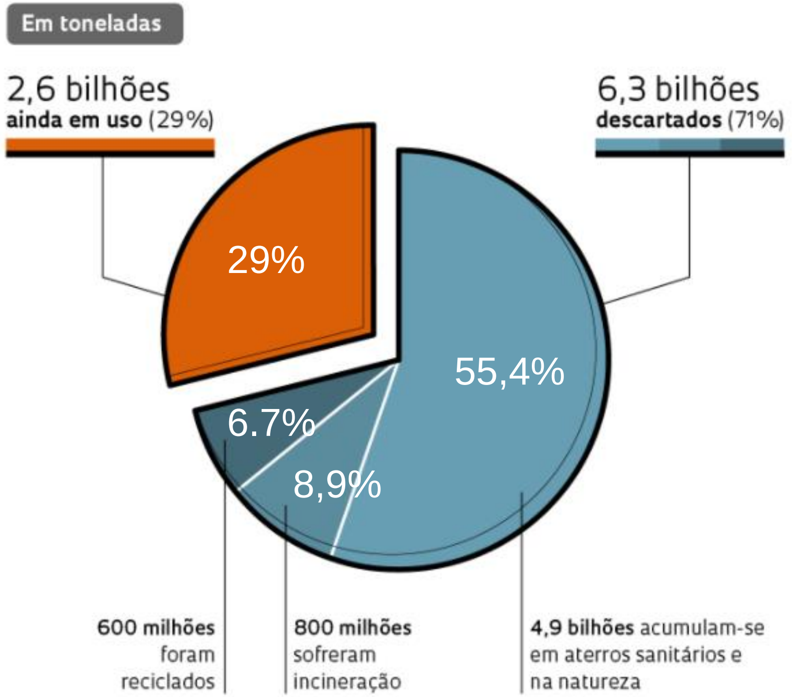
Competitive Advantages of Plastic Materials



Why Recycling?

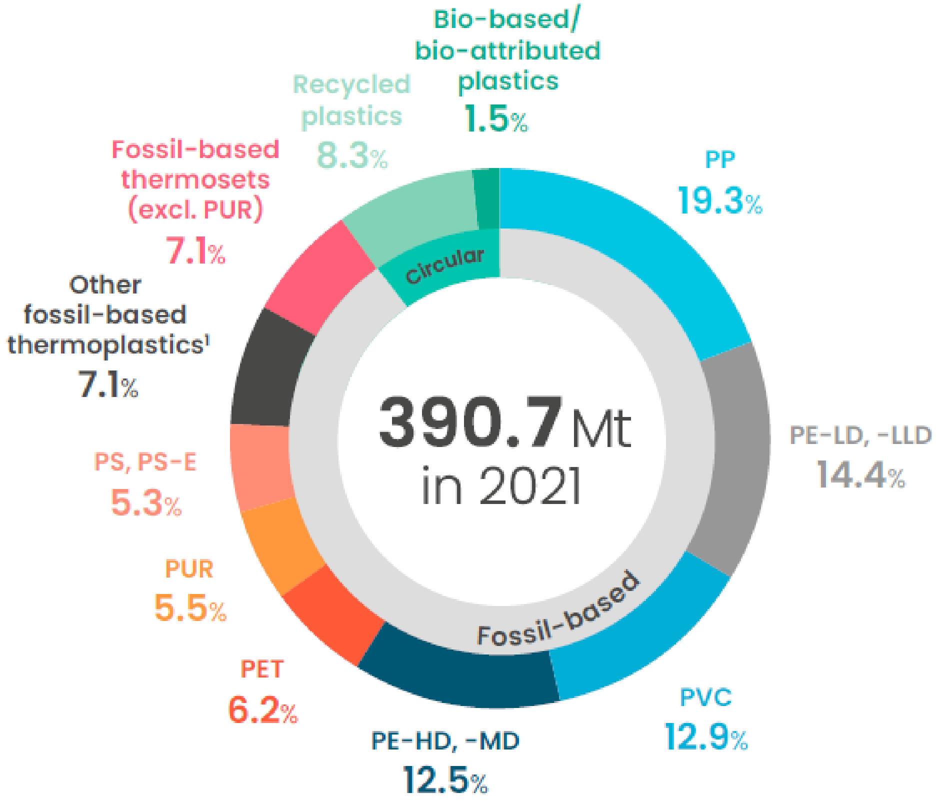
Worldwide Plastics Throughput



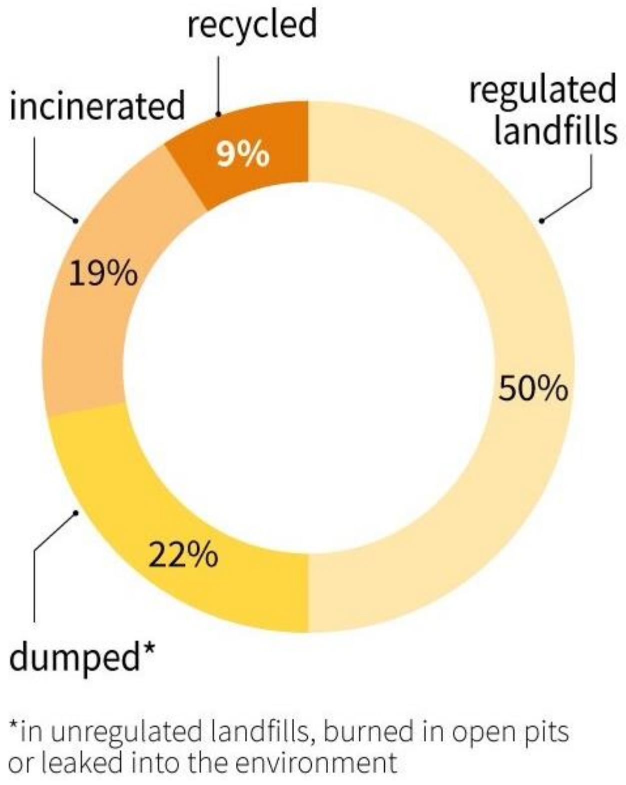


https://revistapesquisa.fapesp.br/planeta-plastico/

Why Recycling?



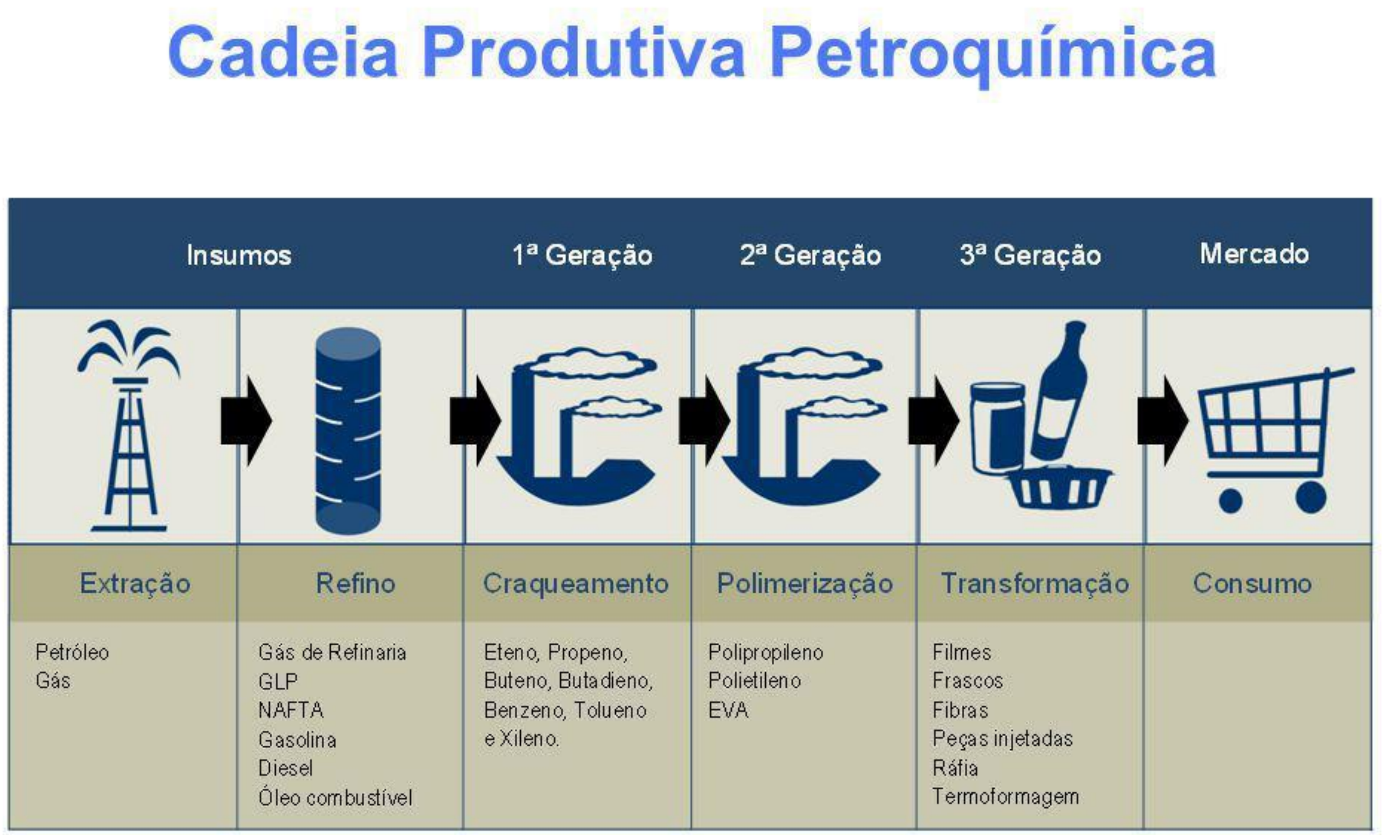
Source: PLASTICS EUROPE, 2022.



Source: https://phys.org/news/2022-02-percent-plastic-recycled-worldwide-oecd.html

Why Recycling?

Circular Economy



https://slideplayer.com.br/slide/1358319/

Projeto Aquapolo ambiental

Circular Economy

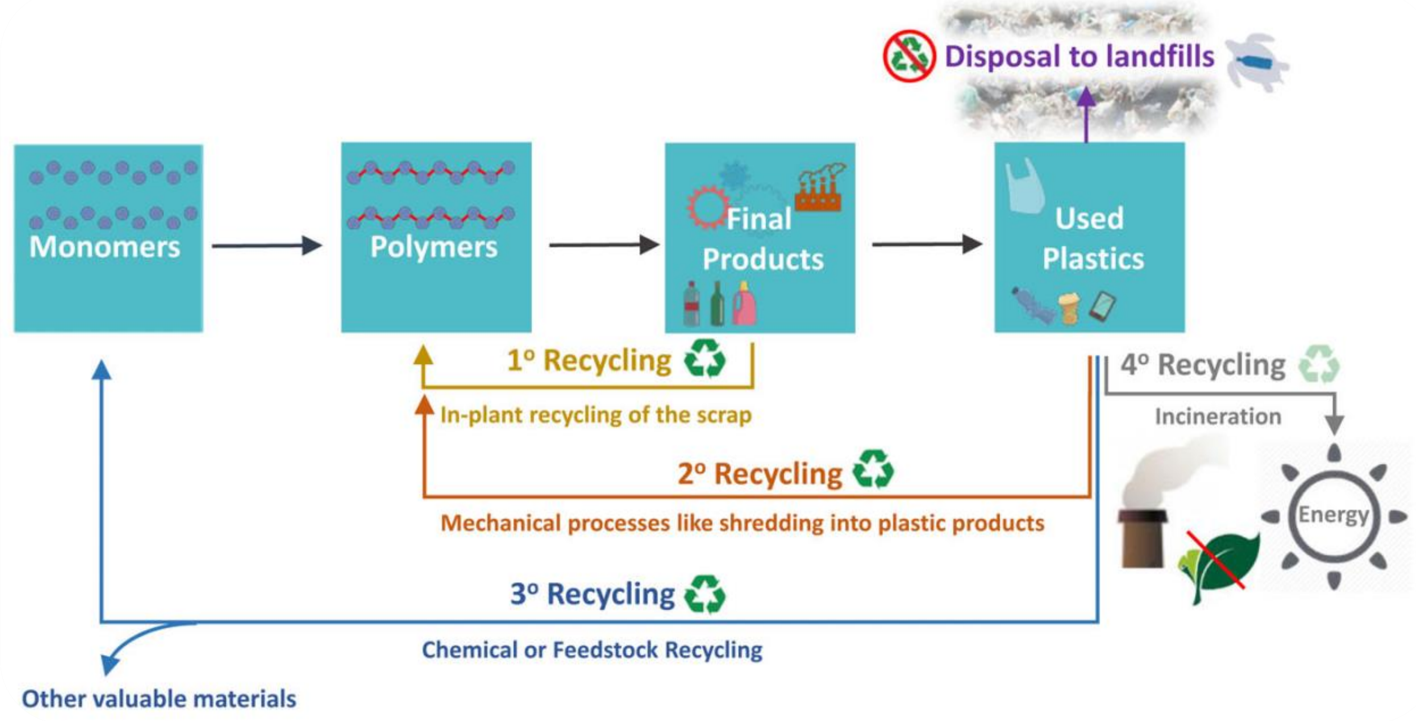
From cradle to cradle !!!!

https://slidemodel.com/circular-economy-to-save-the-planet/

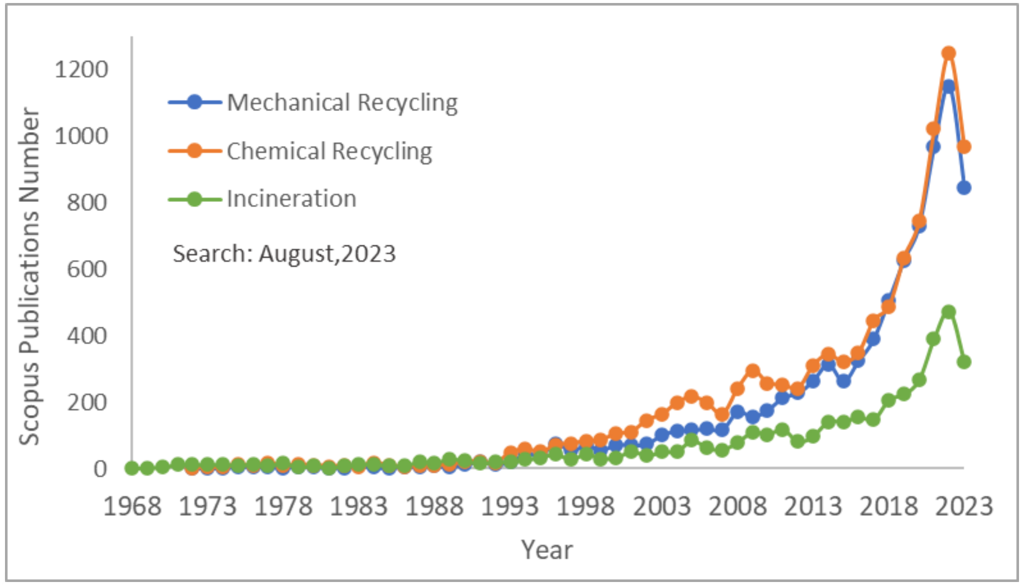
Circular Economy

Source: https://www.dsgc.nl/publications/DSGC-Transition-Time-A-Circular-Economy-for-Plastics-Publication-and-Summary.pdf

Recycling Methods



Source: OKAN; AYDIN; BARSBAY, 2019 (10.1002/jctb.5778)



Most plastic materials and wastes cannot be recycled mechanically !!!

Polym. Chem., 2019, 10, 172-186

Only 30%

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Chemical Recycling

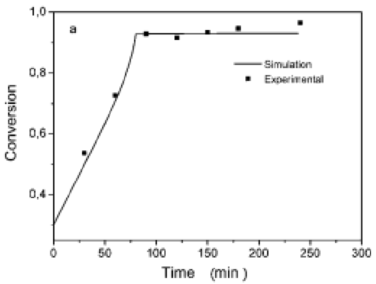
Chemical Recycling

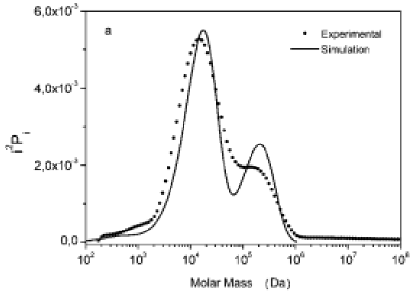
Incorporation | Solvolysis | Enzymatic | Thermolysis

Full Paper
Macromolecular Journals
Macromolecular Reaction Engineering

In Situ Incorporation of Recycled Polystyrene in Styrene Suspension Polymerizations

Caio K. Melo, Matheus Soares, Carlos A. Castor, Príamo A. Melo, José Carlos Pinto*





Journal of Polymers and the Environment (2022) 30:1893–1907
https://doi.org/10.1007/s10924-021-02313-0
ORIGINAL PAPER

Preparation of Polymer Microparticles Through Non-aqueous Suspension Polycondensations: Part VI—Analyses of Chemical and Enzymatic Degradation of Poly(Butylene Succinate) (PBS)

Luciana Dutra[1] · Martina C. C. Pinto[1,2] · Rafael C. Lima[3] · Mariana Franco[1] · Mariana Viana[1] · Eliane Pereira Cipolatti[4,5] · Evelin Andrade Manoel[2,4] · Denise Maria Guimarães Freire[2] · José Carlos Pinto[1,3]

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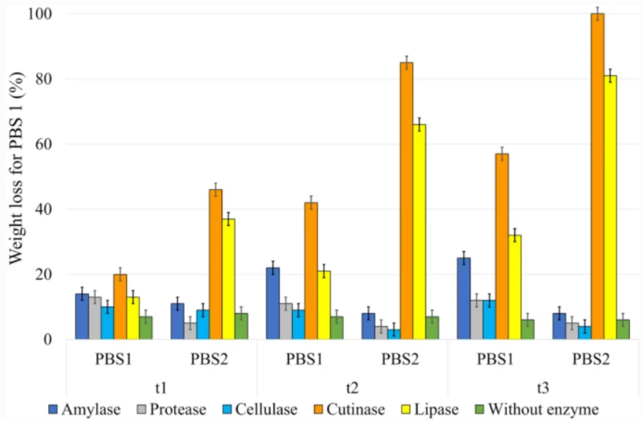
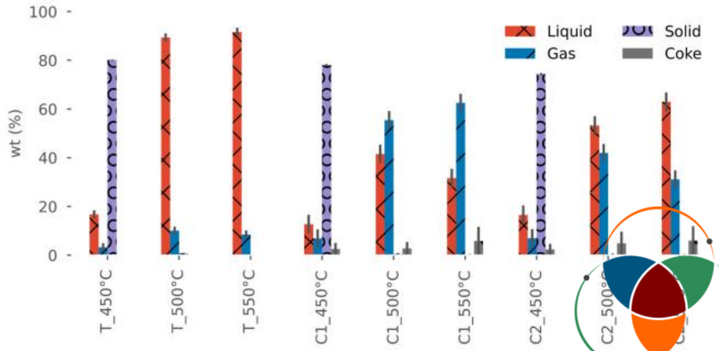


Journal of Analytical and Applied Pyrolysis 174 (2023) 106121
Contents lists available at ScienceDirect
Journal of Analytical and Applied Pyrolysis
journal homepage: www.elsevier.com/locate/jaap
ELSEVIER

A short-cut method for analysis of catalyst performances in pyrolytic reactor

Laura P. da M. Costa[a], Débora M. Vaz de Miranda[a], Cristiano Cardoso[b], José Carlos Pinto[a,*]
[a] Programa de Engenharia Química/COPPE, Centro de Tecnologia, Cidade Universitária da Universidade Federal do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro CP 68502, Brazil
[b] Braskem S.A., Rua Marumbi, 1400, Campos Elíseos, Duque de Caxias, Rio de Janeiro 25221-000, Brazil



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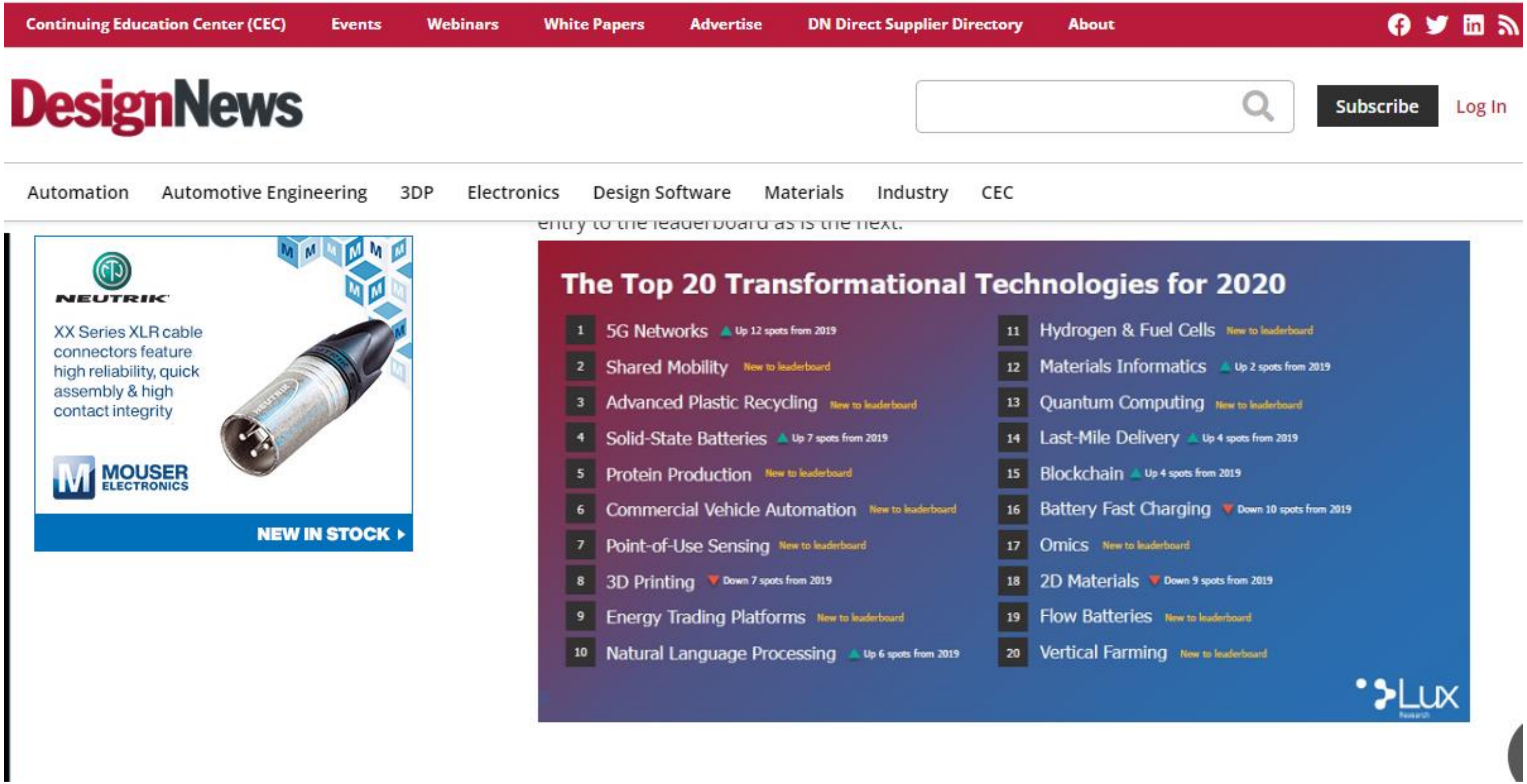
Pyrolysis Process and Challenges

Thermolysis



https://www.designnews.com/stub/transformational-technologies-can-change-world

Thermolysis

$$T_c = \frac{\Delta H_p}{\Delta S_p}$$

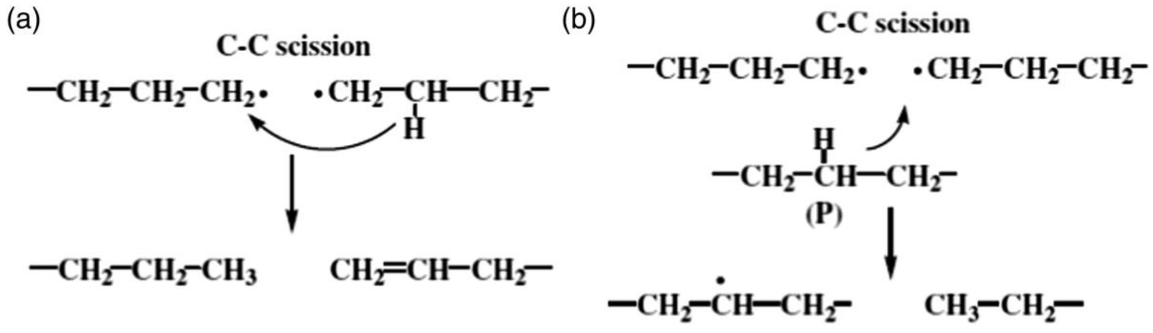
Ceiling temperatures of common monomers [edit]

Monomer	Ceiling temperature (°C)[6]	Structure
1,3-butadiene	585	$CH_2{=}CHCH{=}CH_2$
ethylene	610	$CH_2{=}CH_2$
isobutylene	175	$CH_2{=}CMe_2$
isoprene	466	$CH_2{=}C(Me)CH{=}CH_2$
methyl methacrylate	198	$CH_2{=}C(Me)CO_2Me$
α-methylstyrene	66	$PhC(Me){=}CH_2$
styrene	395	$PhCH{=}CH_2$
tetrafluoroethylene	1100	$CF_2{=}CF_2$

https://en.wikipedia.org/wiki/Ceiling_temperature

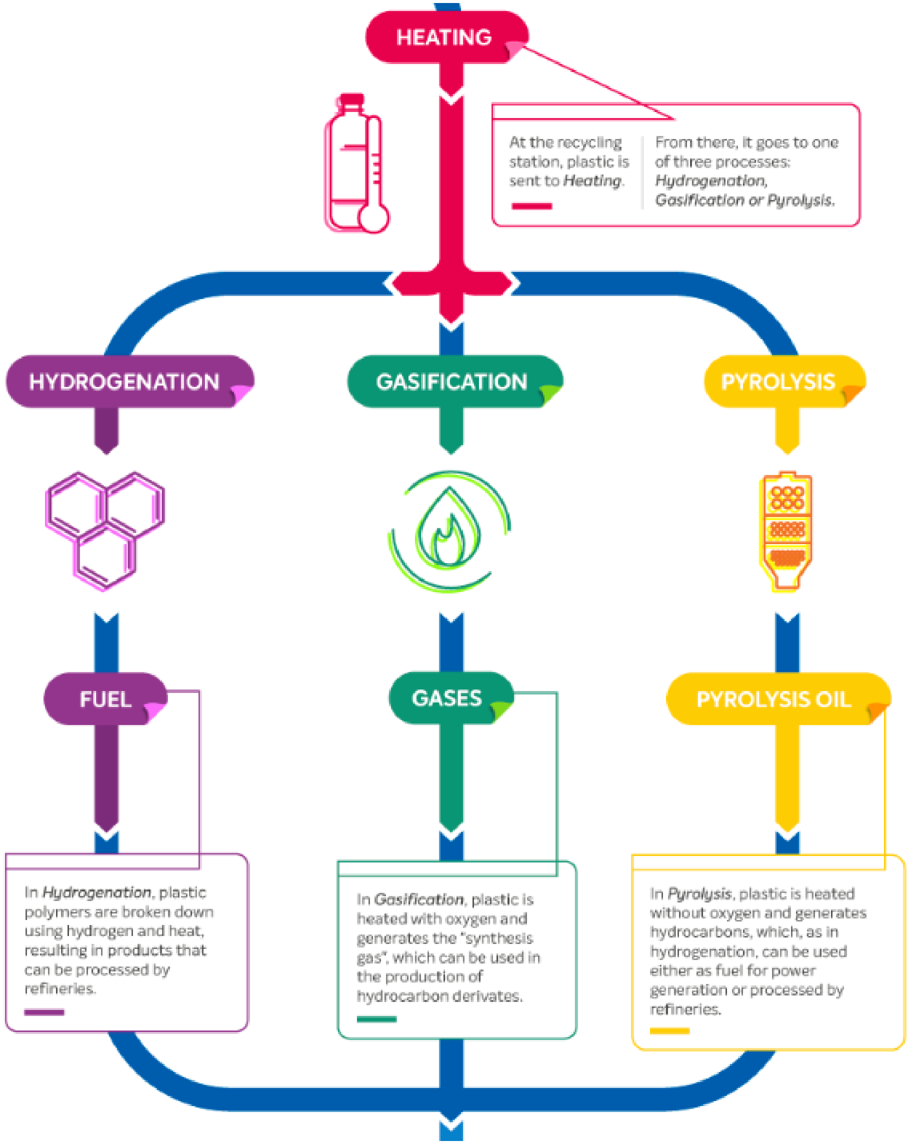
$$T_c <???> T_d$$

T_d (bond cleavage temperature)



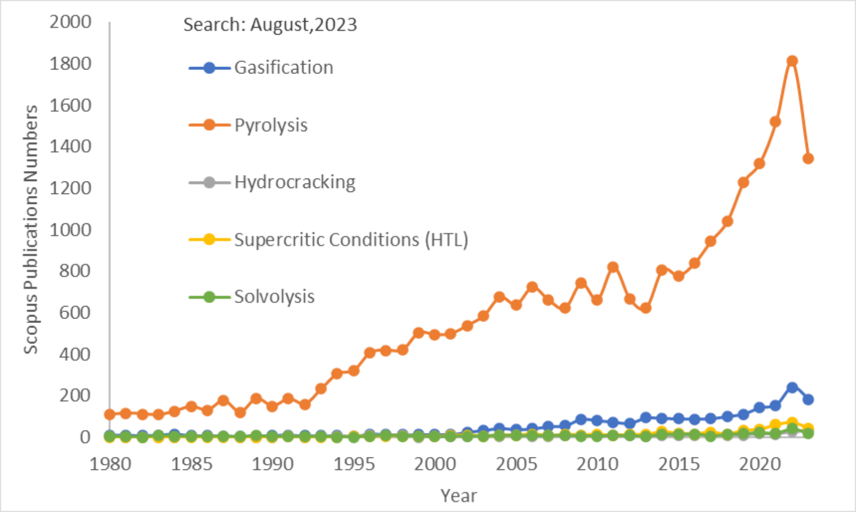
https://journals.sagepub.com/doi/10.1177/00952443221140473

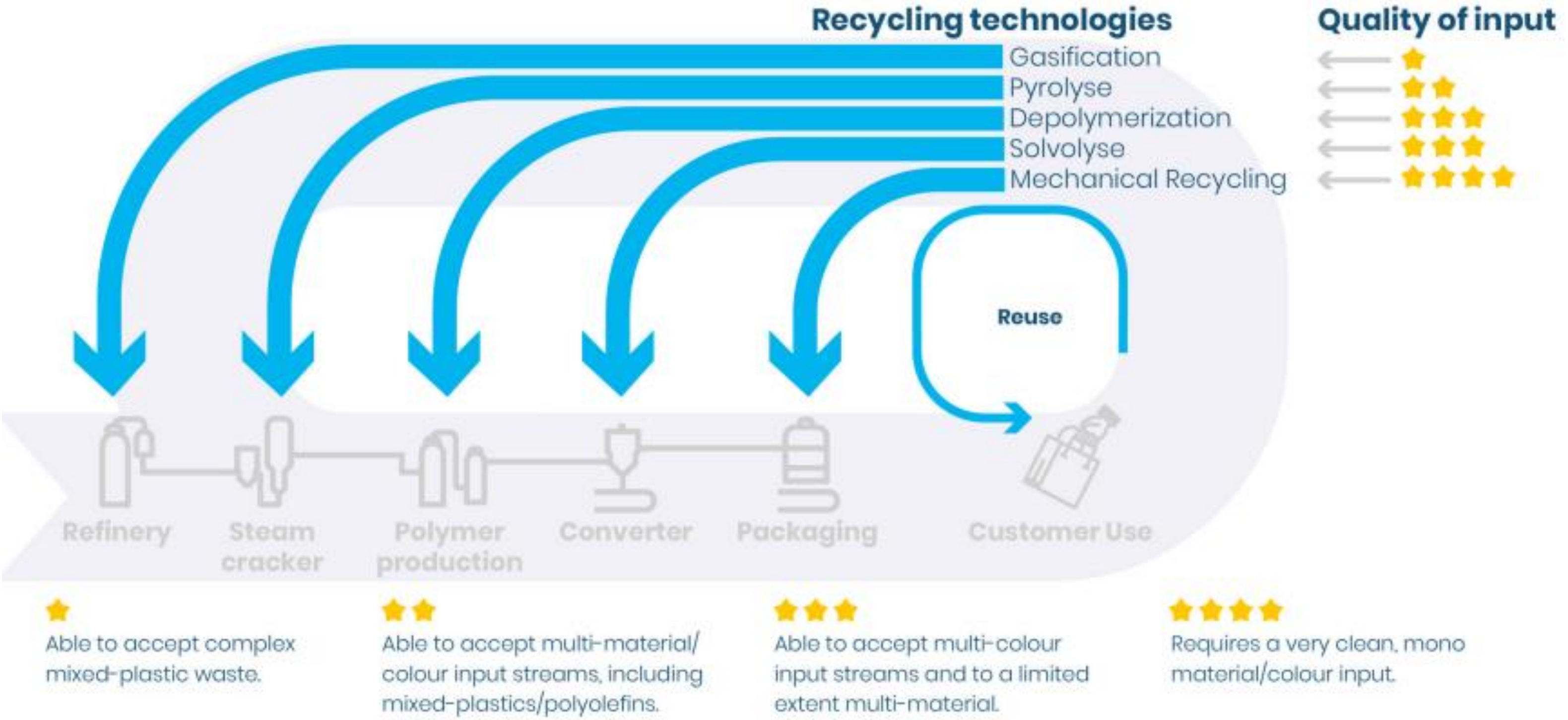
Thermolysis



Source: https://www.circulareconomyasia.org/chemical-recycling/

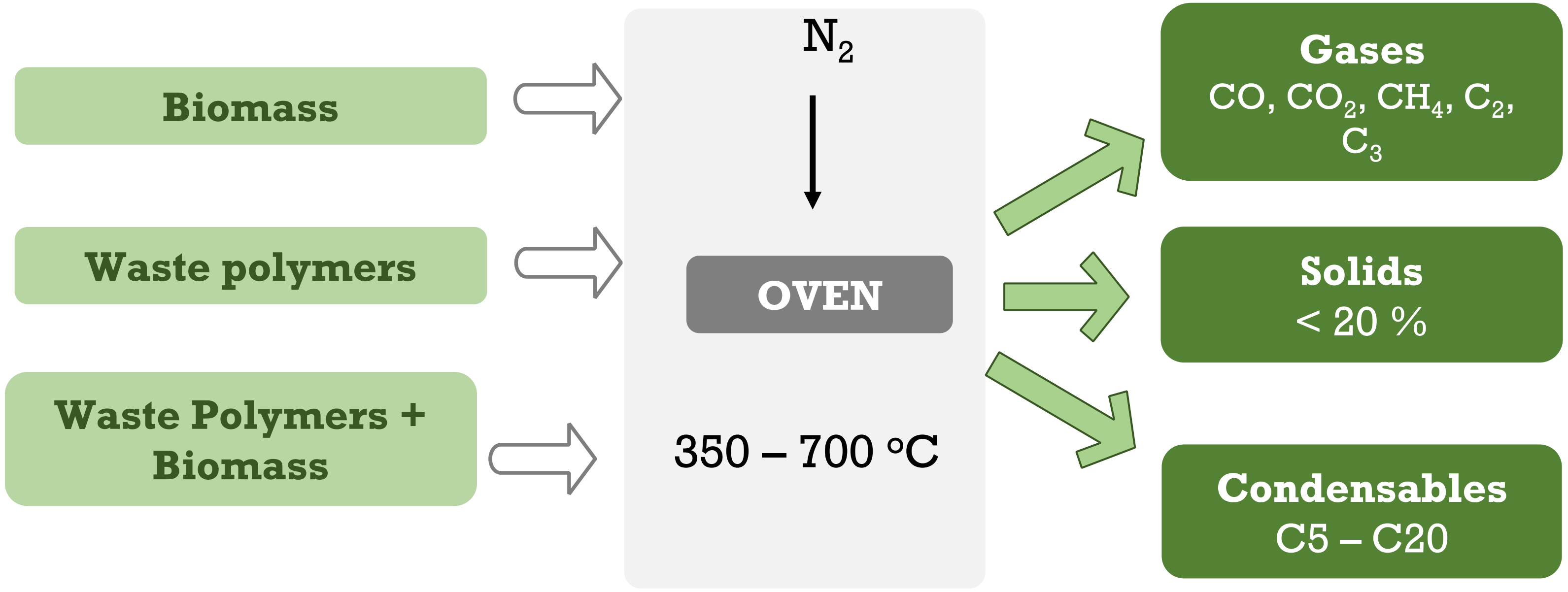
Thermolysis





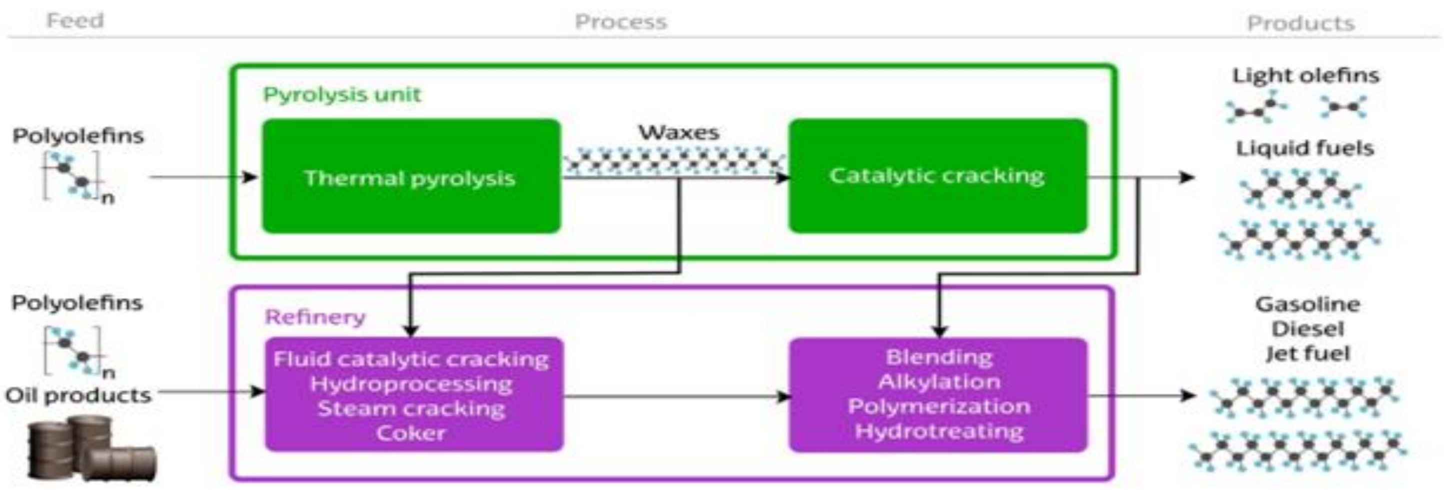
Source: https://www.dsgc.nl/publications/DSGC-Transition-Time-A-Circular-Economy-for-Plastics-Publication-and-Summary.pdf

Pyrolysis



Important Variables

- Heating Rate
- Catalyst
- Residence Time
- Pressure
- Feedstock Composition
- Temperature
- Gas Recycle
- Pre or Post Treatments



Source: Lopez et al. (2017) – Themochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals.

Pyrolysis



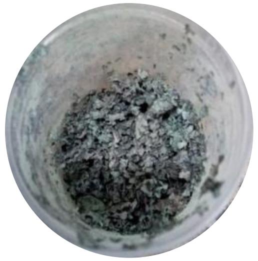



OVEN

350 – 700 °C

N_2

Gases
CO, CO_2, CH_4, C_2, C_3

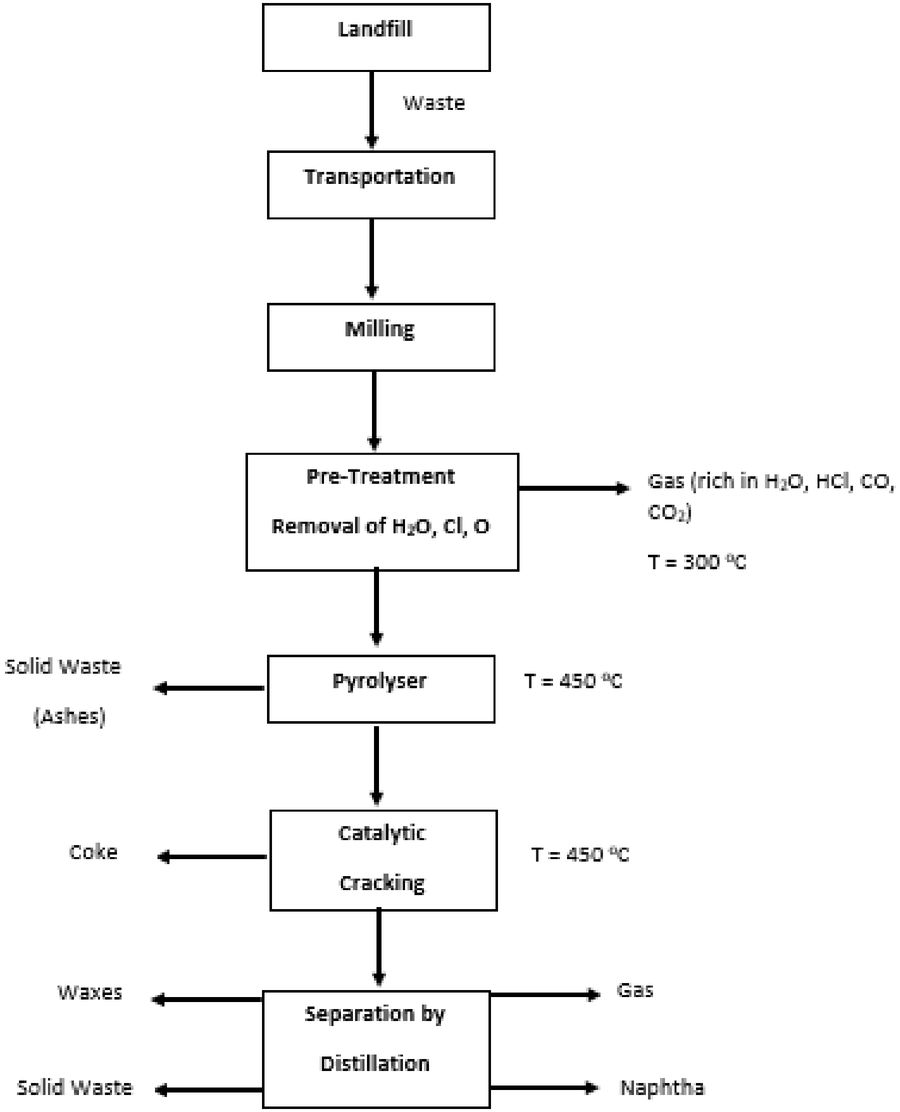



Solids
< 20 %




Condensables
C5 – C20

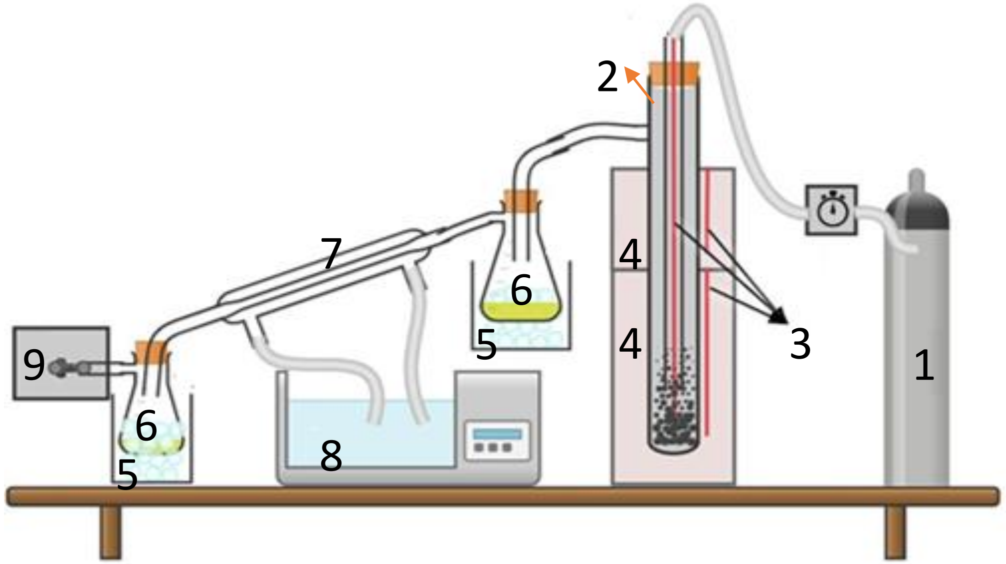
Thermolysis

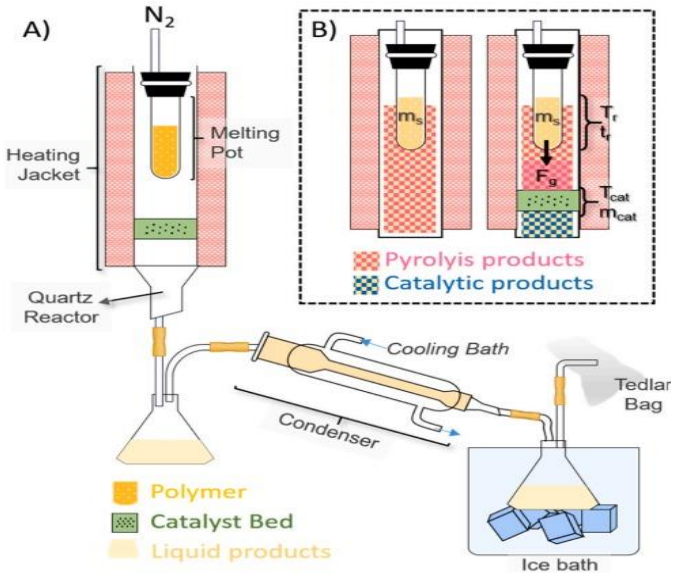


More complex flowsheet.
Challenges everywhere.

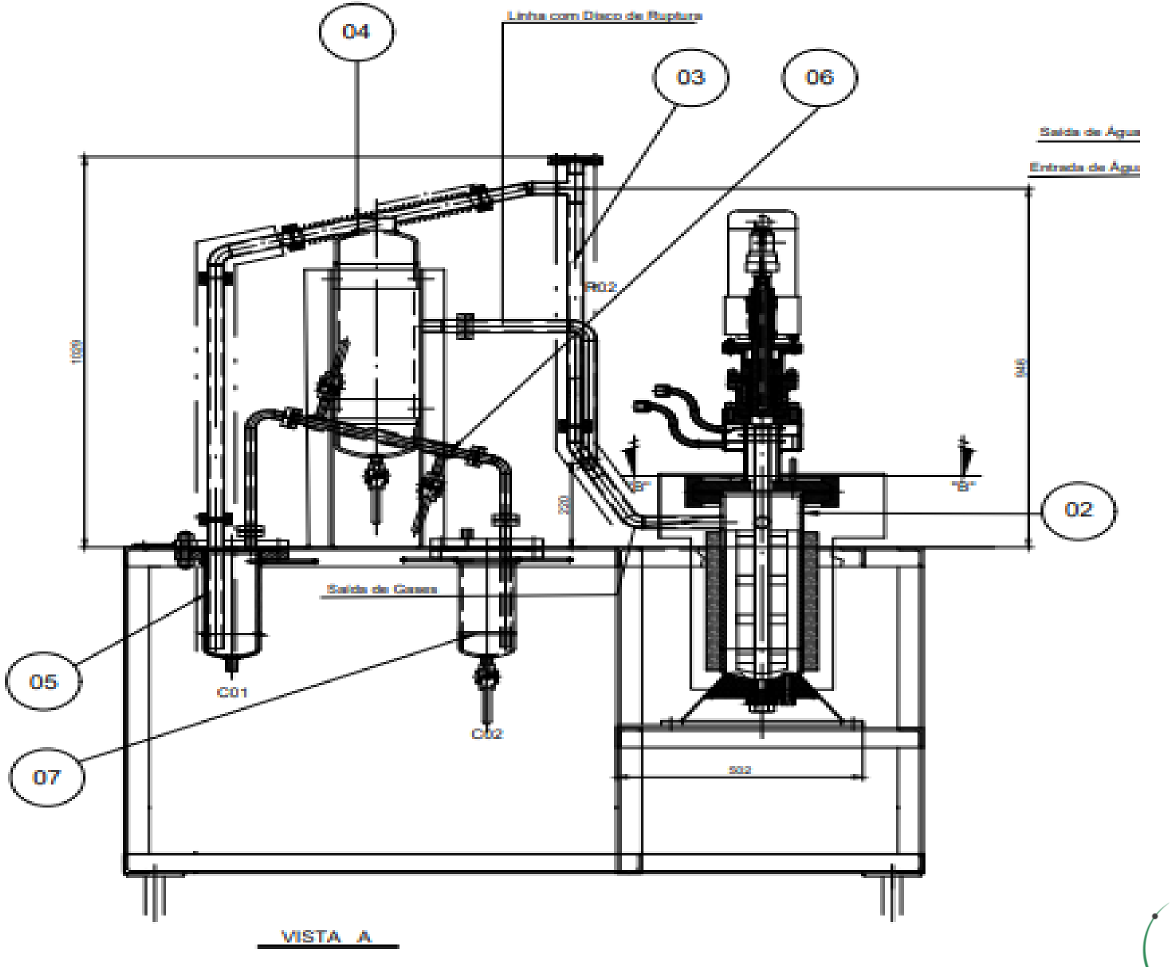
EngePol Pyrolysis Capabilities & Studies

Bench-Scale Reactors





Semi-Pilot Reactor



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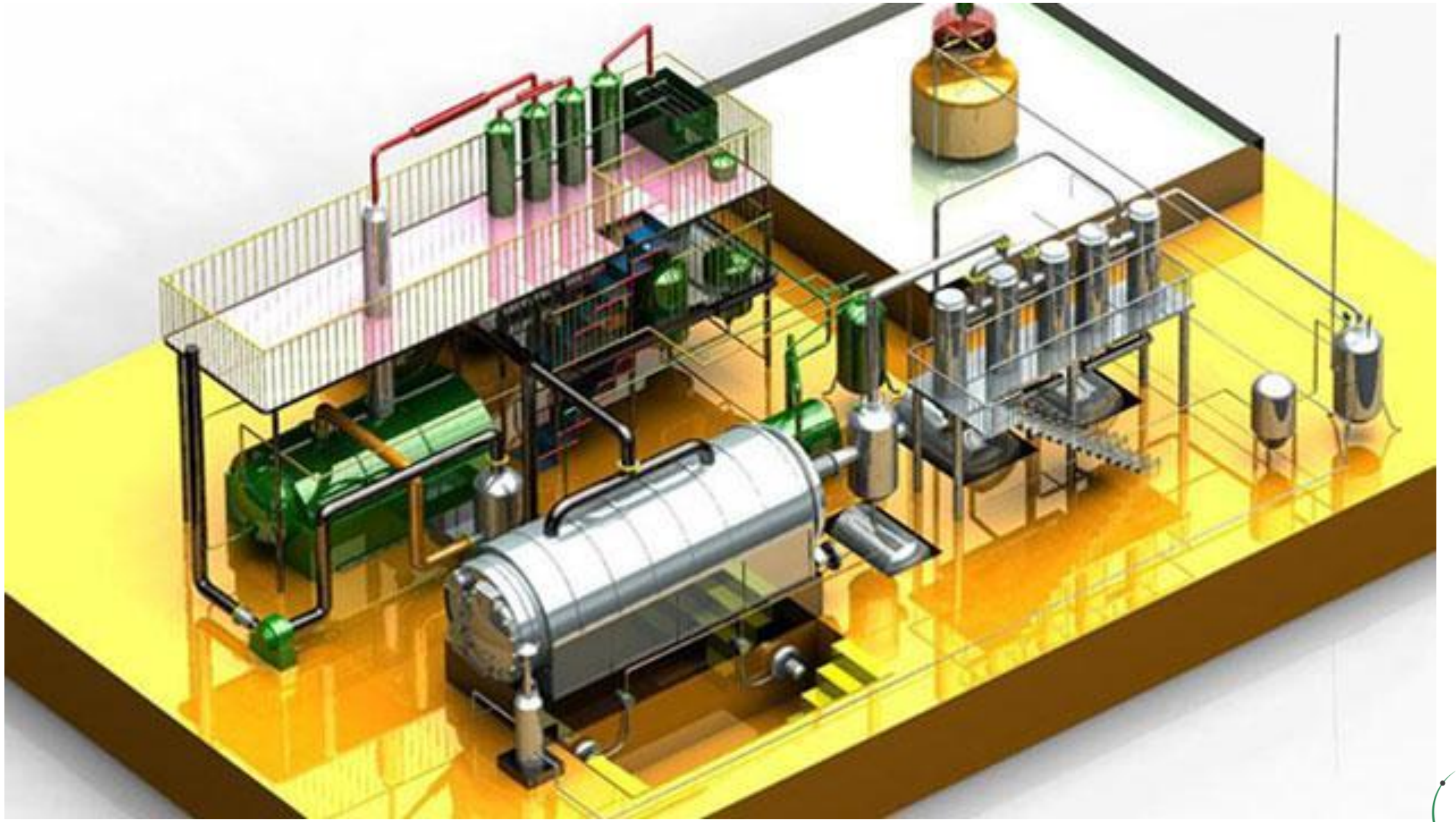
Soon…

PETROBRAS

1 ton / day



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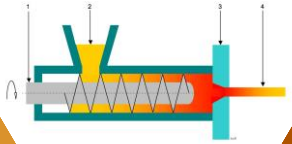
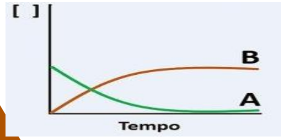
EngePol Initiatives

Effects of Extrusion Pretreatment



Catalysts



Kinetic Studies

Effects of Contaminants

Wastes from the Beverage Industry

Unit Design

Pretreatment for Contaminant Removal

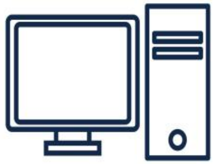
Effects of Reflux

Life Cycle Analyses

Effect of Mixing Plastics and MSW

Lignocellulosic Biomass

Modeling and Simulation



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EngePol Initiatives

Economia circular

PESQUISAS CIENTÍFICAS APOIAM AVANÇOS EM SUSTENTABILIDADE

Texto de Antonio Carlos Santomauro, Fotos Divulgação

Assim como outros países, também o Brasil estruturou um aparato de pesquisas empenhadas em adequar os plásticos às propostas da economia circular. Integrando recursos e *know how* públicos e privados provenientes de governo, empresas e instituições acadêmicas, ela explora as mais diversas possibilidades: reciclagens química e mecânica; reciclagem de resíduos ainda pouco aproveitados; processos mais eficazes de produção das resinas e de suas aplicações; utilização de materiais provenientes de fontes renováveis, entre outras.

Questões como essa são abordadas em instituições como o Coppe (Instituto Alberto Luiz Coimbra de Pós-Graduação e Pesquisa de Engenharia), da Universidade Federal do Rio de Janeiro (UFRJ), onde os estudos sobre reciclagem química receberão o impulso de um projeto recentemente acordado com a Petrobras para construção de uma planta que reciclará quimicamente uma tonelada diária de resíduos plásticos gerados na Ilha do Fundão (onde fica a UFRJ), cuja operação deve ter início em 2024. Além de zerar a emissão de resíduos plásticos no campus da UFRJ, "a planta e o óleo ali produzidos serão utilizados para o desenvolvimento de pesquisas para o escalonamento dos processos", ressalta José Carlos Pinto, professor do Programa de Engenharia Química da Coppe.

O Coppe também mantém estudos sobre catalisadores, cuja função principal é permitir ou direcionar reações químicas que transformem correntes de produção com características particulares em um desejado produto final. "Tecnologias desenvolvidas em parceria com a Braskem que fazem uso de nafta proveniente da reciclagem química de plástico pós-consumo de natureza poliolefínica já estão sendo utilizadas no Polo Petroquímico de Triunfo", afirma Pinto.

No campo dos materiais obtidos de fontes renováveis, um dos focos dessa instituição recai nos polímeros derivados do ácido succínico, componente importante para a produção de poliésteres e poliamidas. Por enquanto, ele ressalta, o ácido succínico de origem fóssil representa a maior parte desse ingrediente utilizado na produção de PBS (poli-succinato de butileno) e PES (poli-succinato de etileno), dois poliésteres utilizados em filmes e fibras, entre outras aplicações.

Mas algumas unidades de produção dessas resinas já utilizam ácido succínico derivado da fermentação anaeróbica de açúcares naturais ou derivados da degradação enzimática da celulose, havendo nesse caso uma outra vantagem ambiental, além da fonte renovável: o processo de fermentação anaeróbico fixa o CO_2, levando a emissões negativas desse gás. "É tanto o butanodiol quanto o etilenoglicol necessários para produzir o PBS e o PES podem ser obtidos de forma renovável a partir do próprio ácido succínico e do etanol, de maneira que os polímeros obtidos podem ser 100% renováveis e circulares", explica o pesquisador.

Já se sabe que poliamidas e poliésteres que contêm esses poli-succinatos têm características muito apropriadas para a produção de filmes, sendo alguns já utilizados para a fabricação de embalagens de

Pinto: Coppe e Petrobras somam forças na reciclagem química

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PLÁSTICO MODERNO - agosto, 2023

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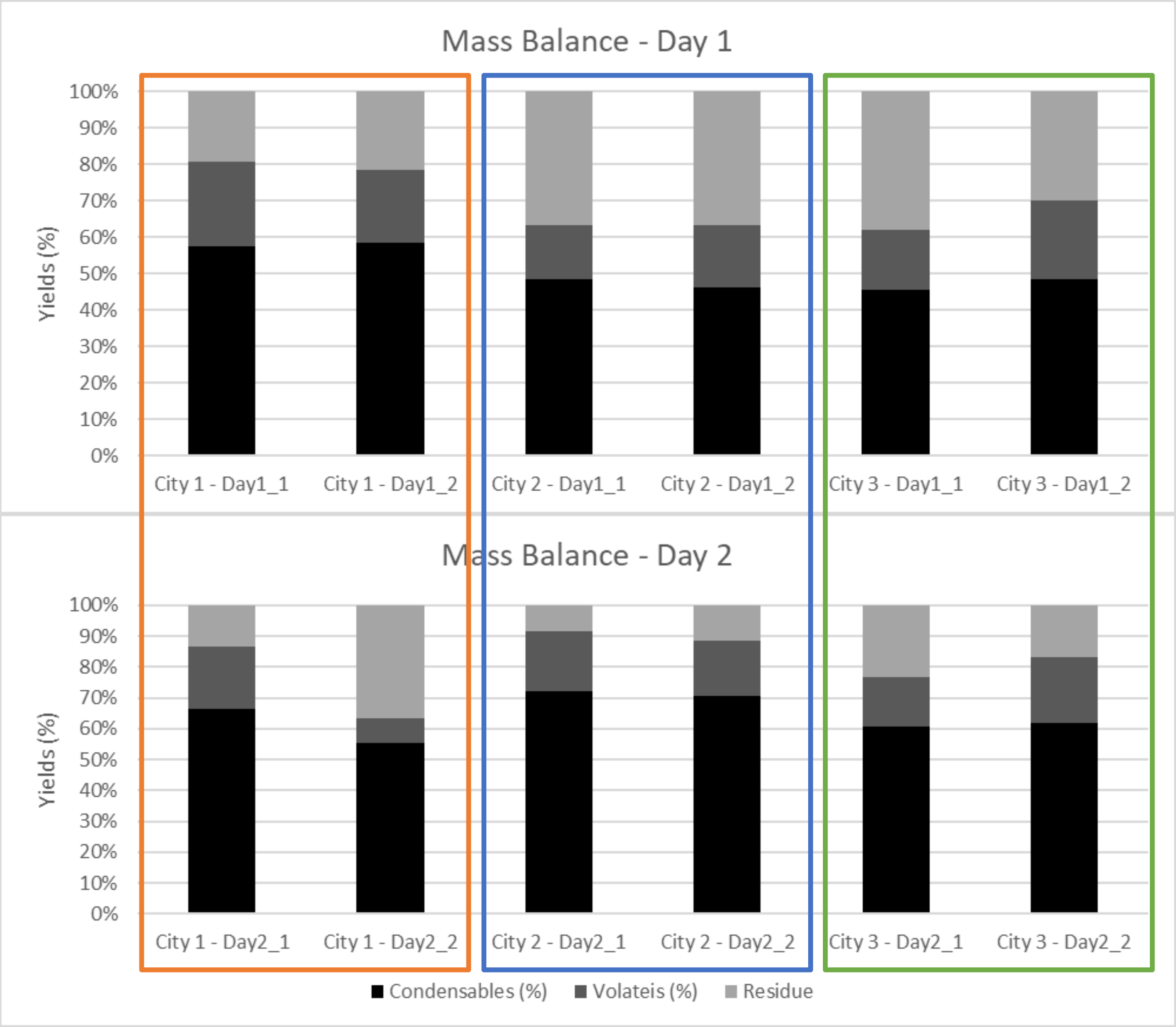
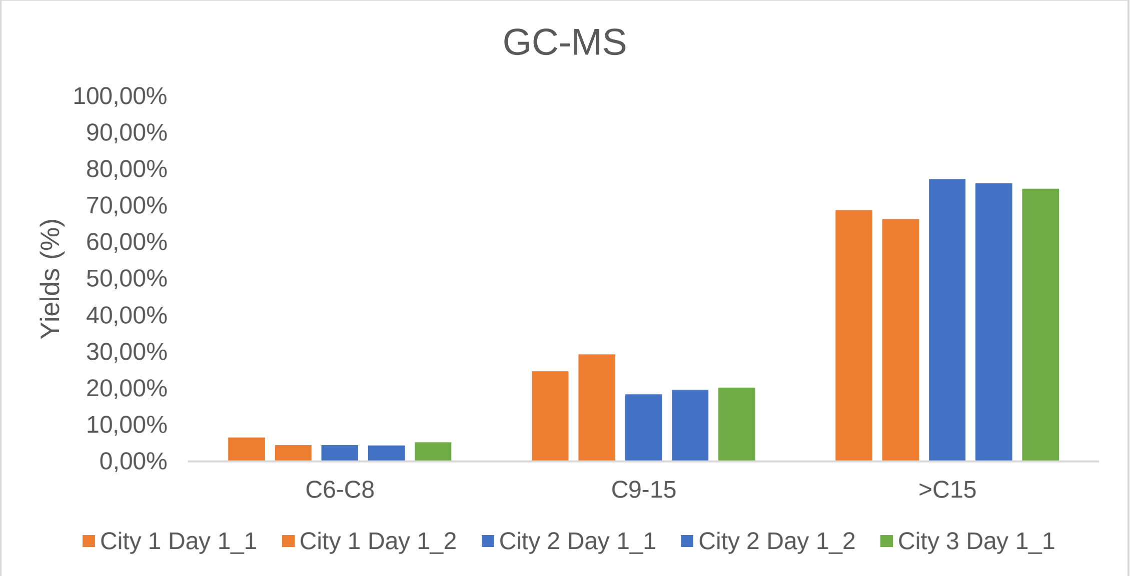
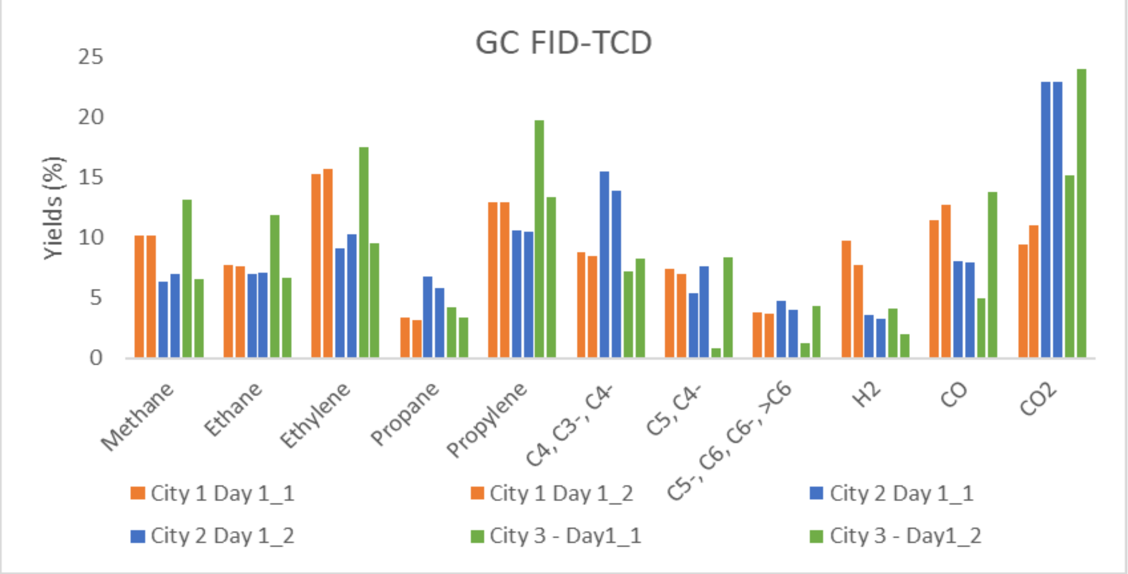
Feedstock Variability







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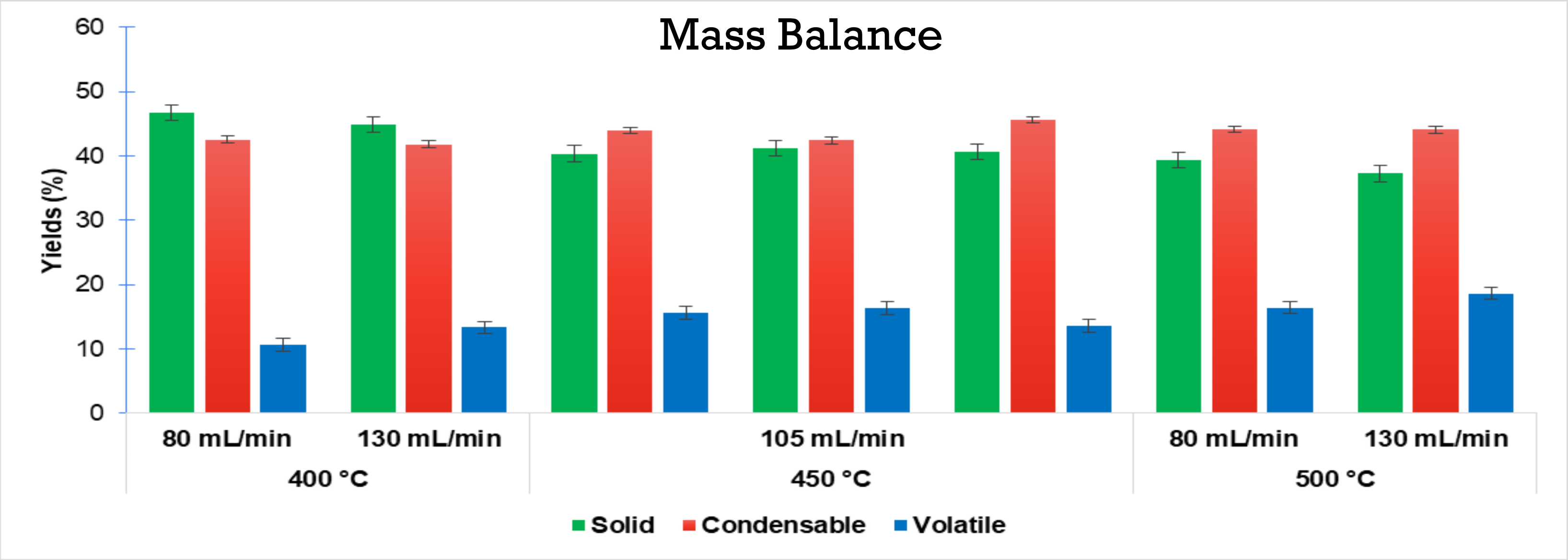
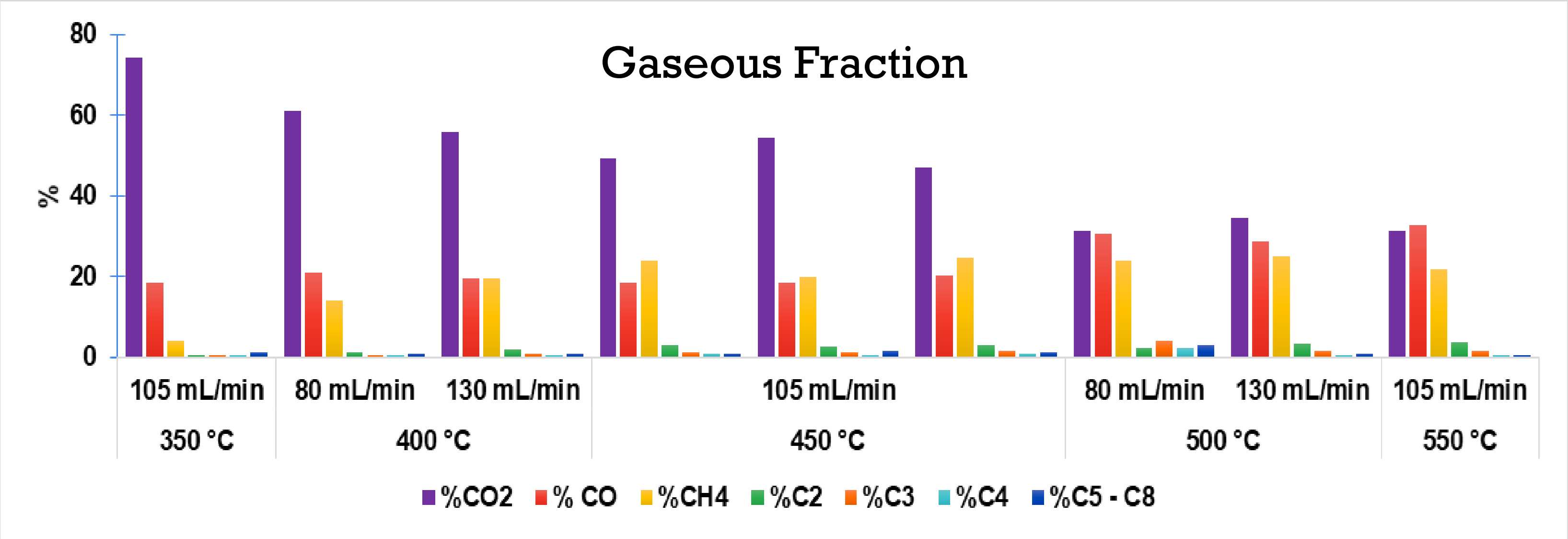
Biomass – Lignin Cake

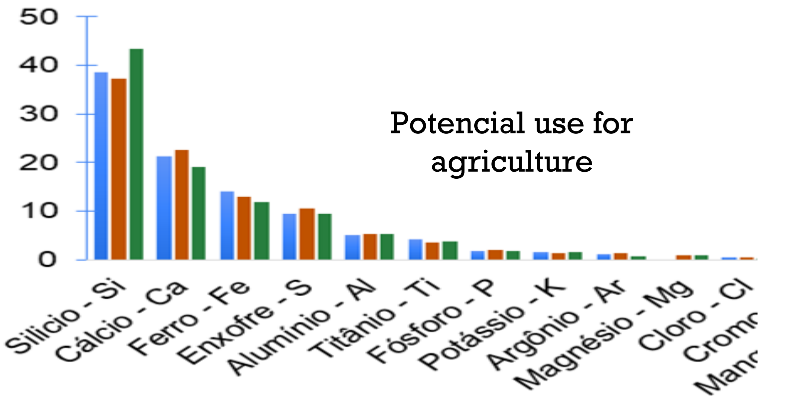


Condensable Fraction

Class	400 °C	500 °C
	Area (%)	
Phenols	34,72	37,92
Aldehydes	17,88	16,78
Ketones	12,82	9,46
Alcohols	9,34	12,56
Hydrocarbons	9,06	10,42
Acids	8,14	6,36
Esters	4,89	5,94
Amides	1,68	0,26
Amines	0,29	0,00
Derived from sugar	0,17	0,30
Nitrates	0,16	0,00
Others	0,84	0,00
Total	100	100

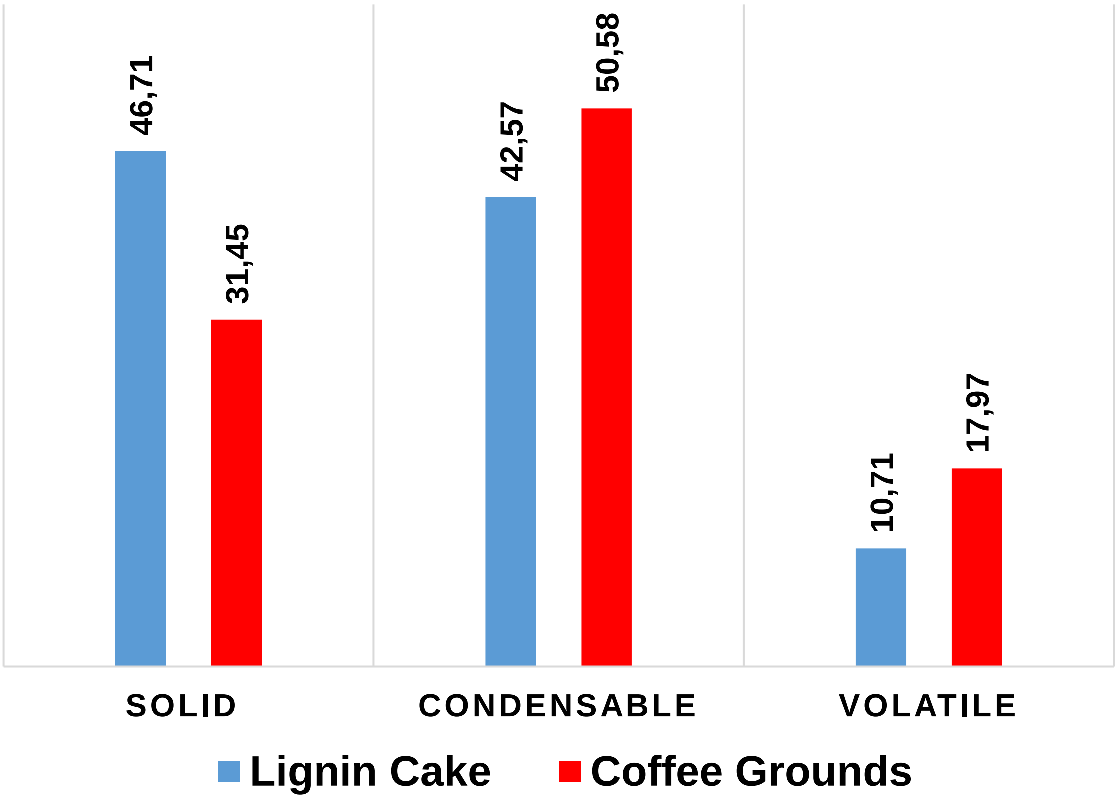


Residue Fraction



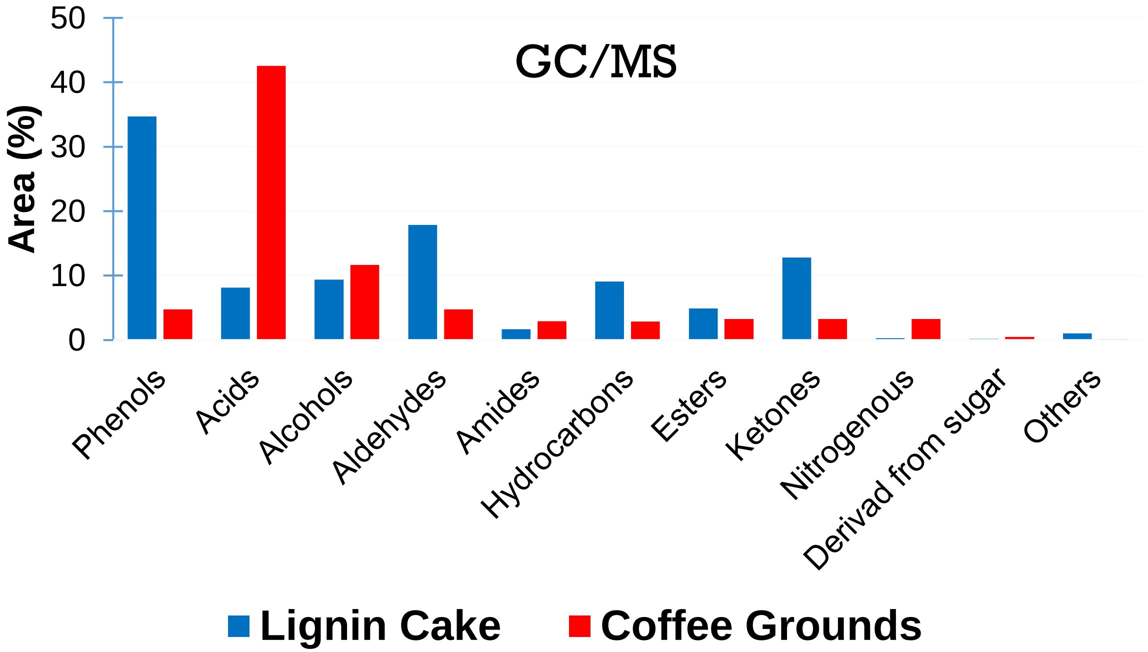
Biomass

Mass Balance



Lignin Cake

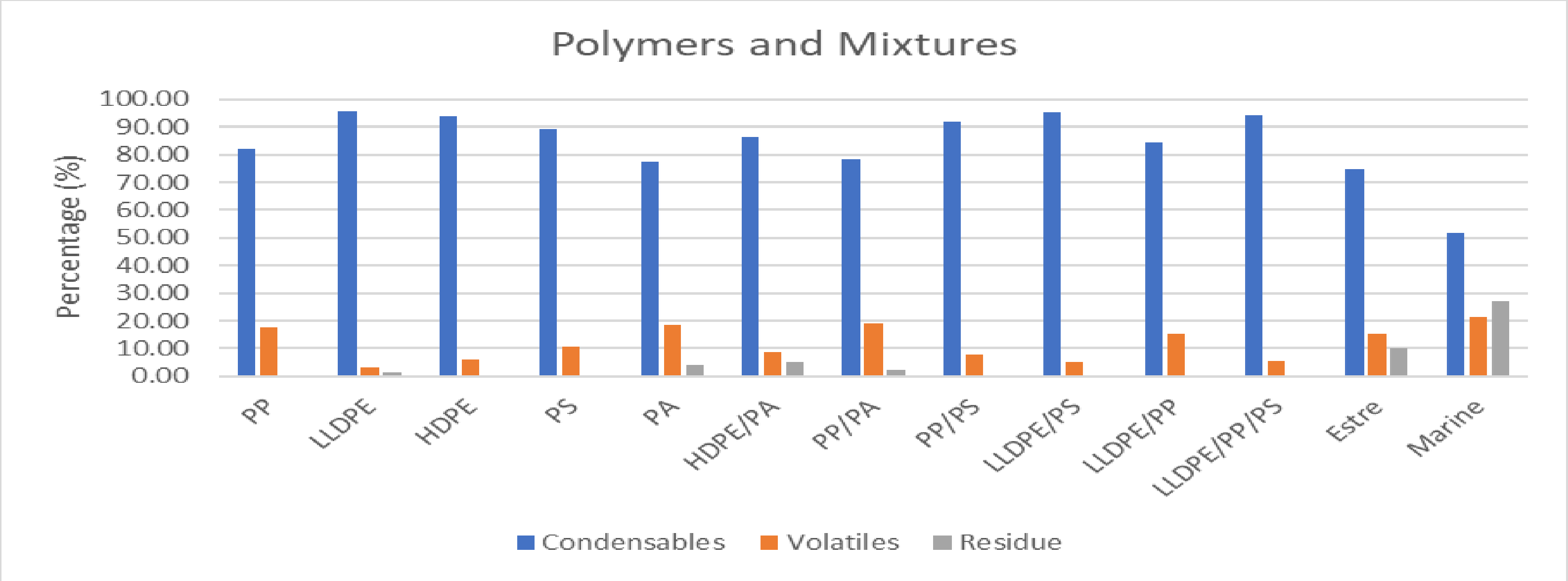
Coffee Grounds



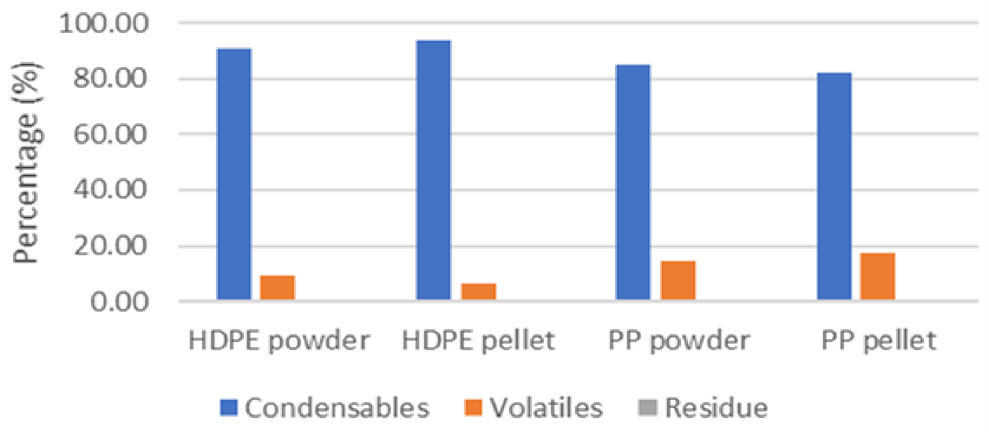
Pyrolysis conditions: 400 °C; 80 mL/min and 30 min.

Grupo EngePol

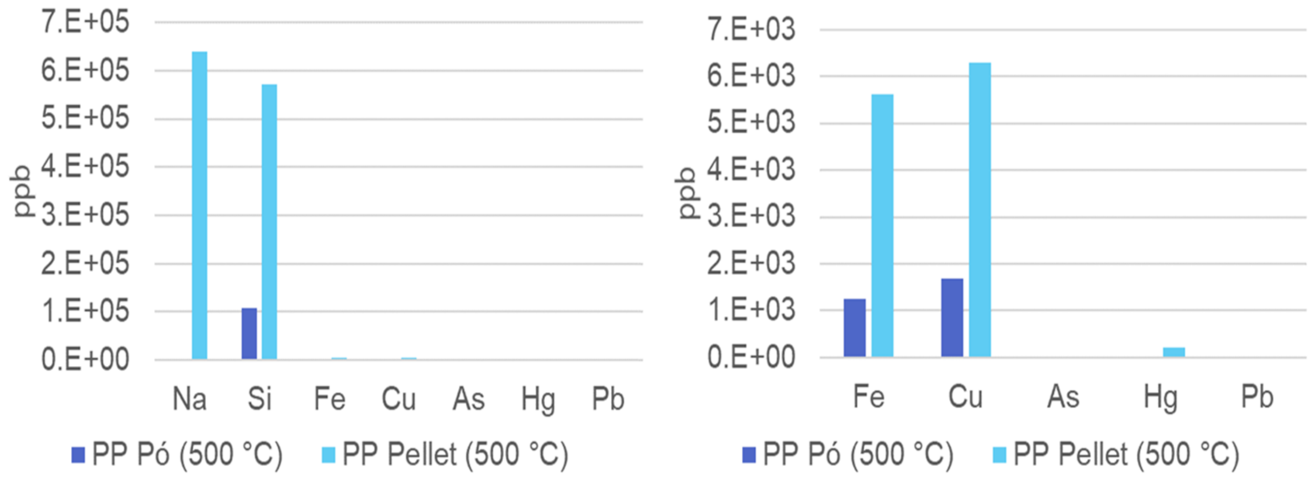
Virgin Polymers and Blends (Sorting)



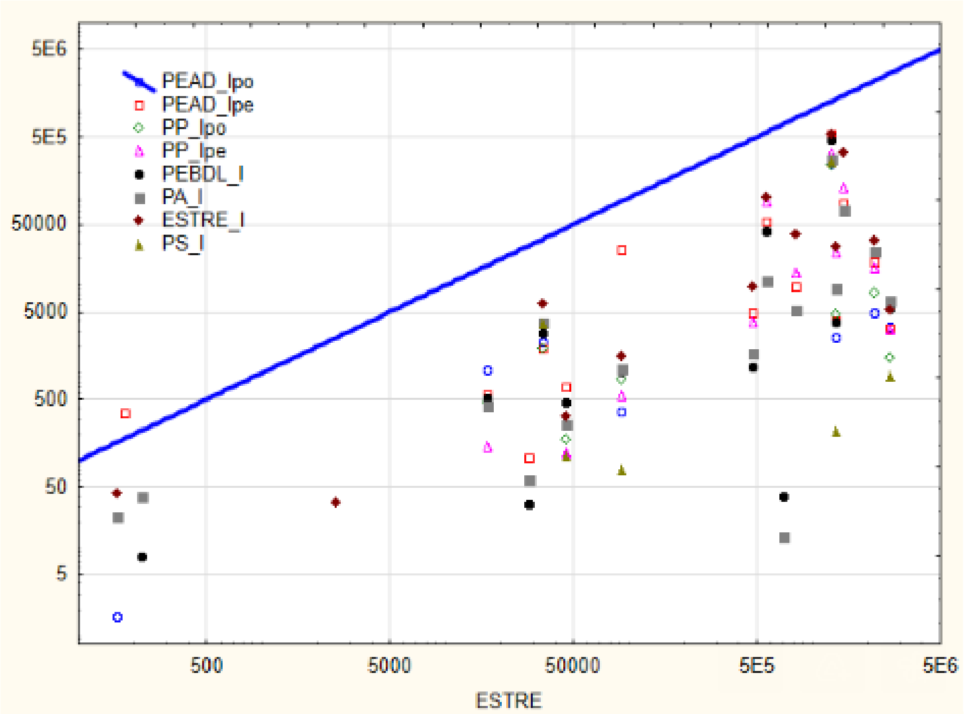
Mass Balance



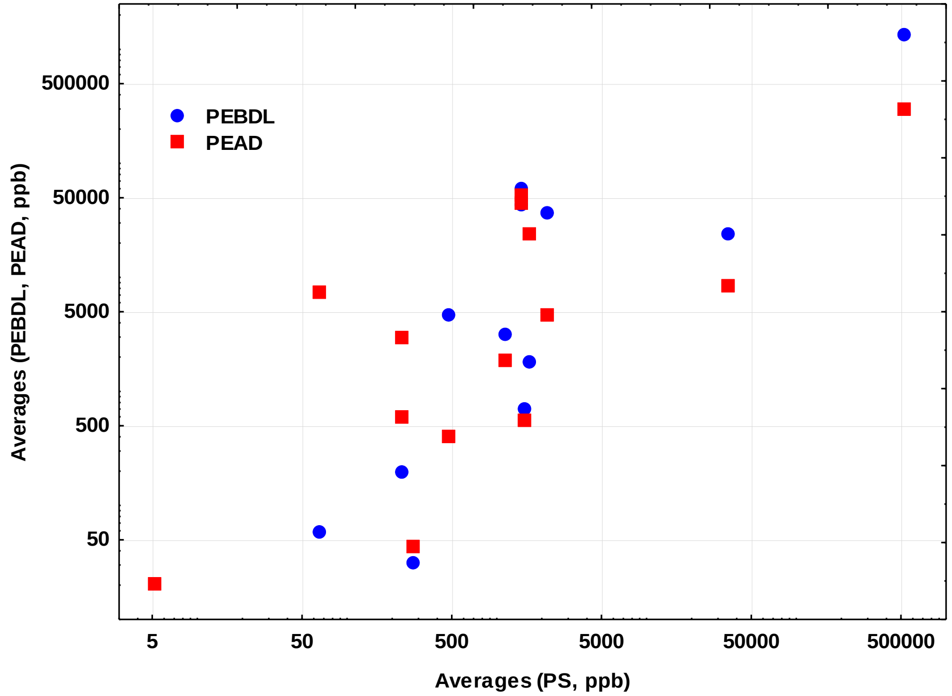
ICP Analyses



Effect of Contaminants



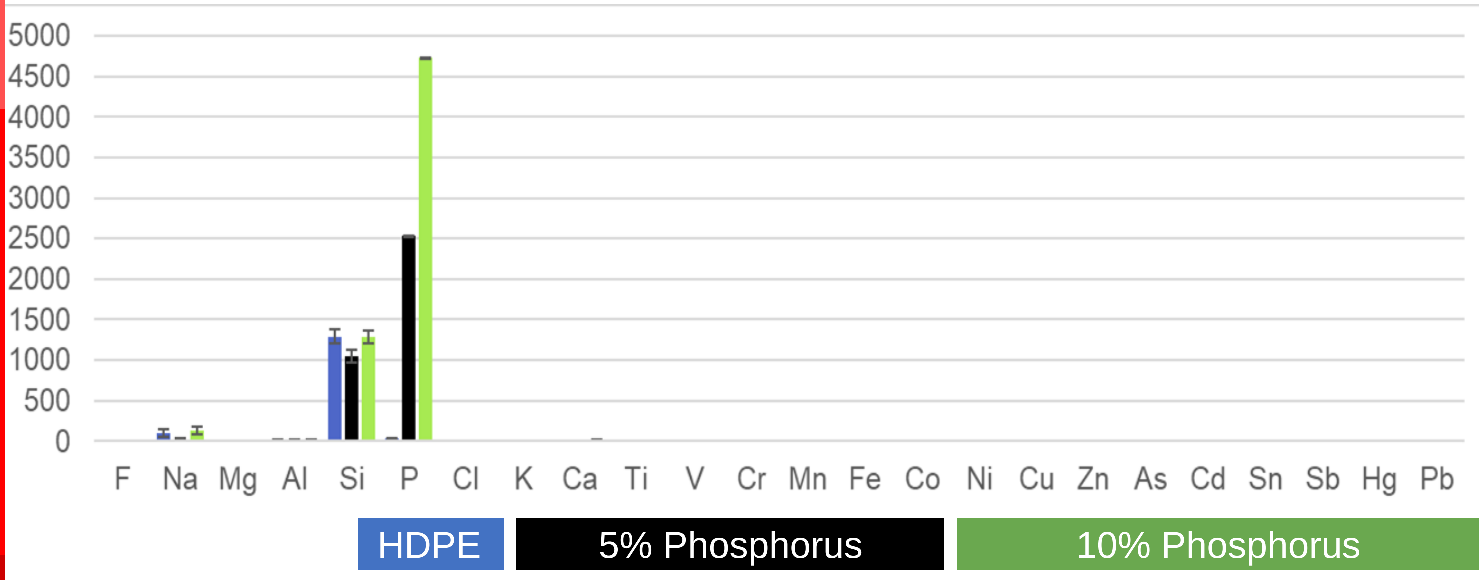
All tested pyrolysis oils were cleaner than the original PCRs

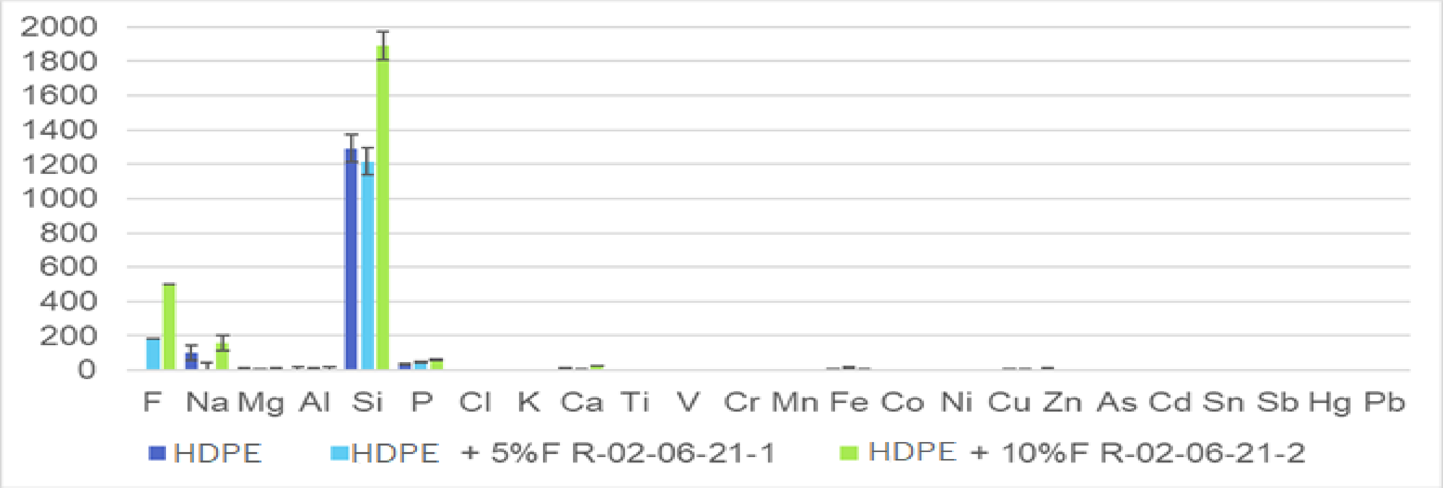


Contamination levels were different, but correlated

Effect of Contaminants (Phosphorus and Fluorine)

ICP Analyses of condensables





Mass Balance

	CONDENSABLES (%)	VOLATILES (%)	SOLIDS (%)
HDPE	83.33	16.19	0.47
5 % Phosphorus	78.97	20.89	0.14
10% Phosphorus	71.14	27.14	1.71

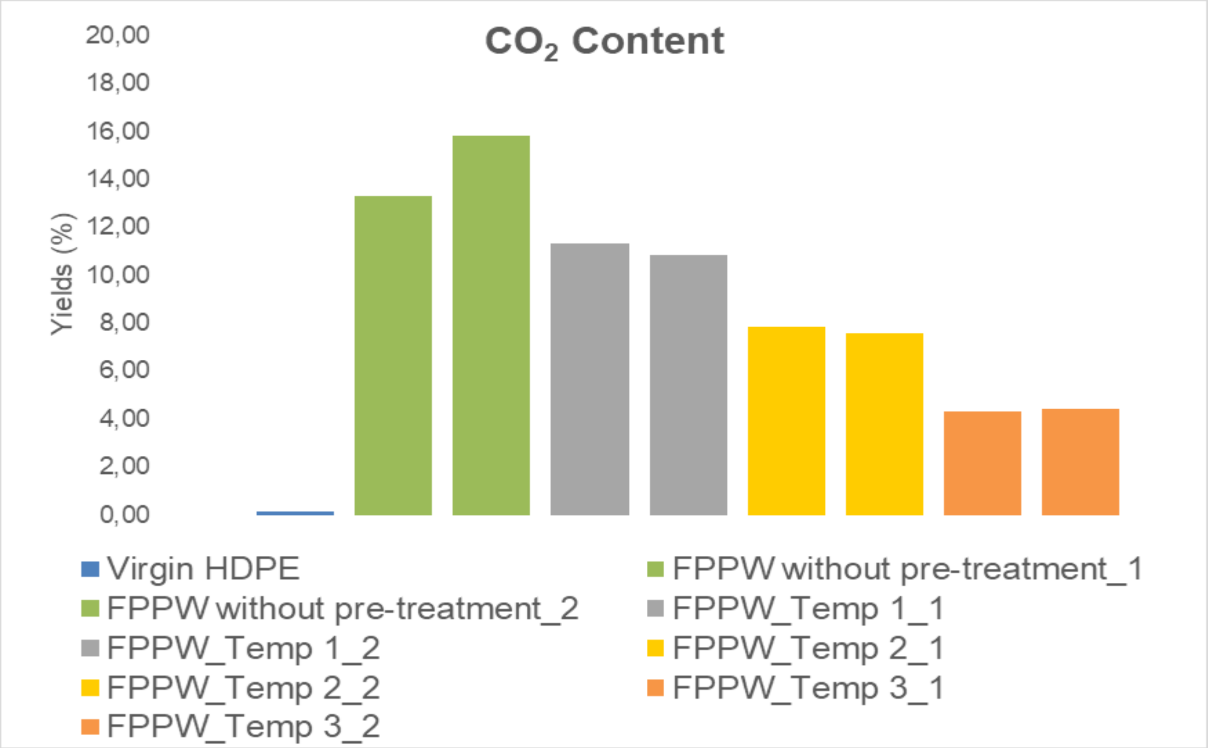
- Phosphorus contaminants became distributed between the gas and liquid;

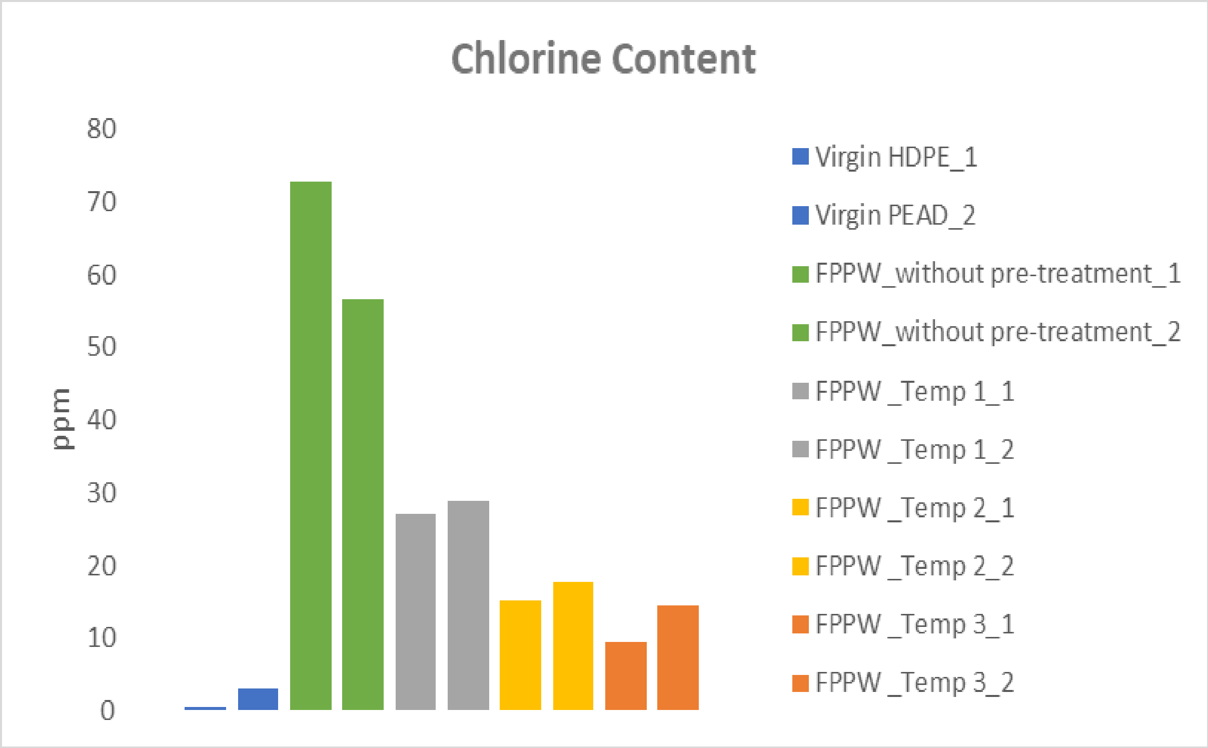
	CONDENSABLES (%)	VOLATILES (%)	SOLID WASTE (%)
HDPE	83.33	16.19	0.47
5 % FLUORINE	82.91	16.81	0.28
10% FLUORINE	89.08	9.79	1.13

- Most of the fluorine contaminants remained in the gas phase;

Pre-Treatment for Removal of Contaminants

FPPW – Flexible Packaging Plastic Waste

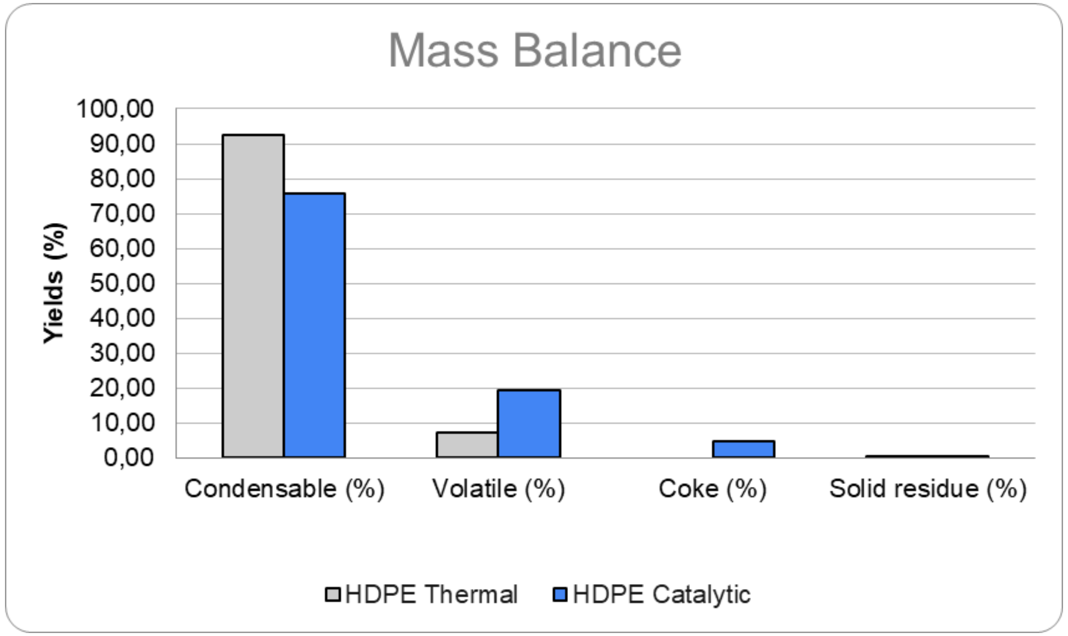


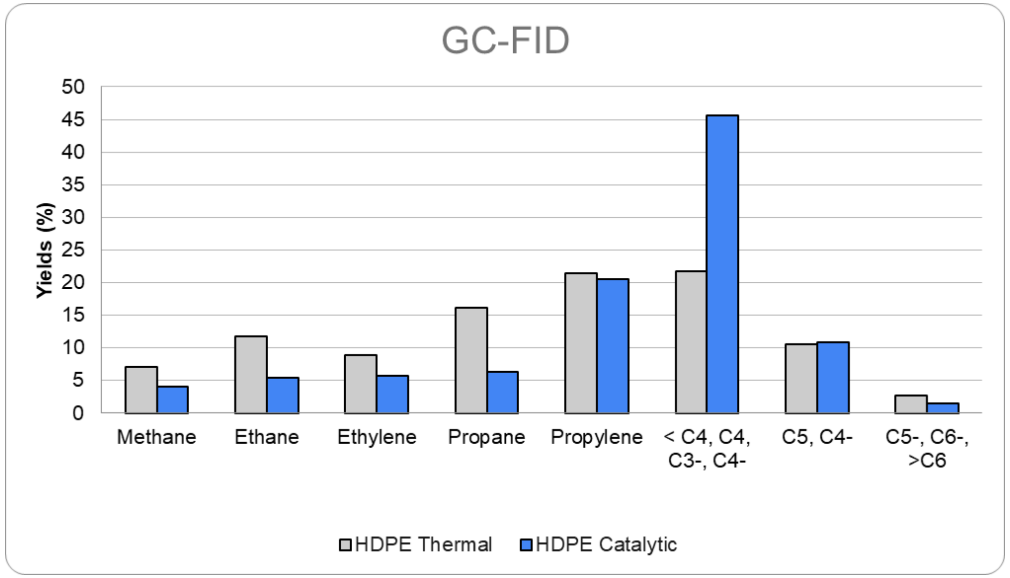


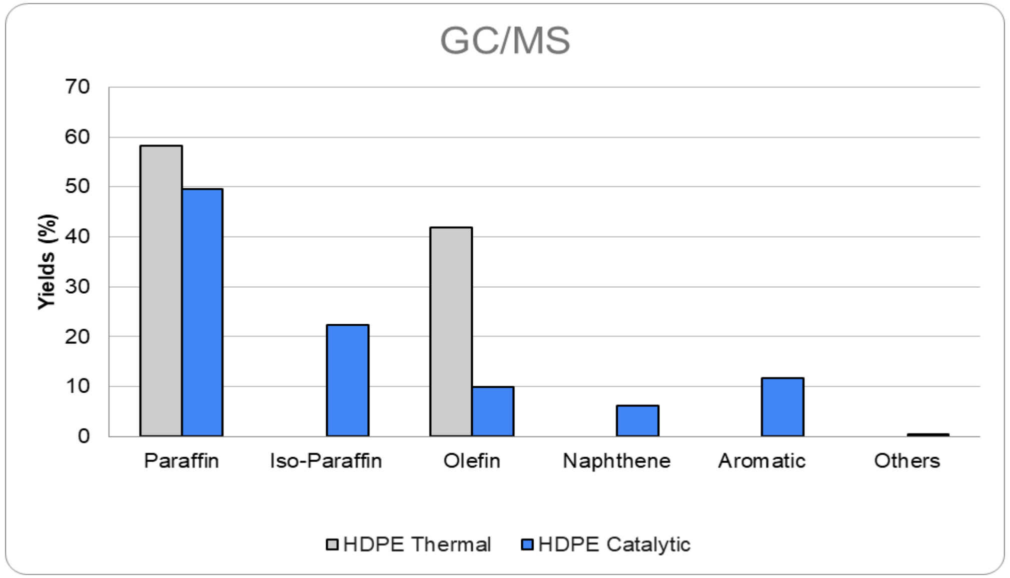
Higher pre-treatment temperatures lead to lower CO_2 levels in the gas phase .

Higher pre-treatment temperatures lead to lower clhorine levels in the condensable phase .

Catalyst Effect



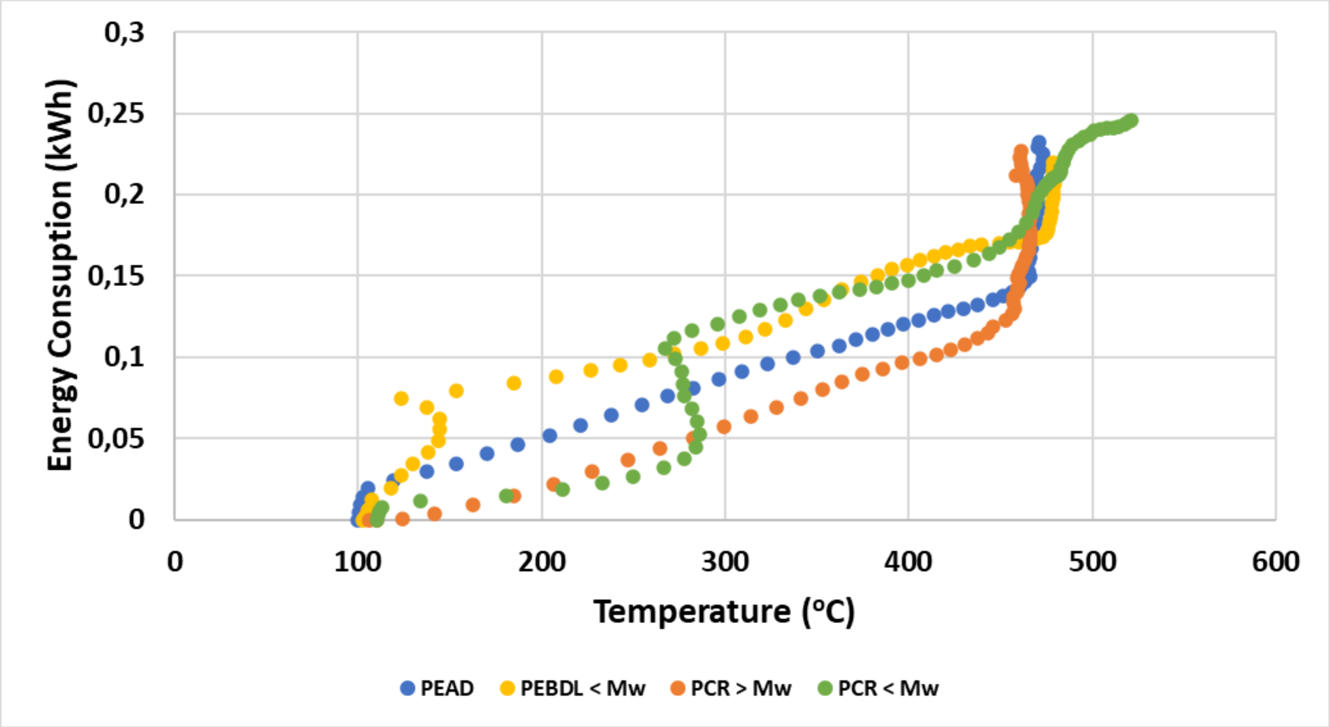


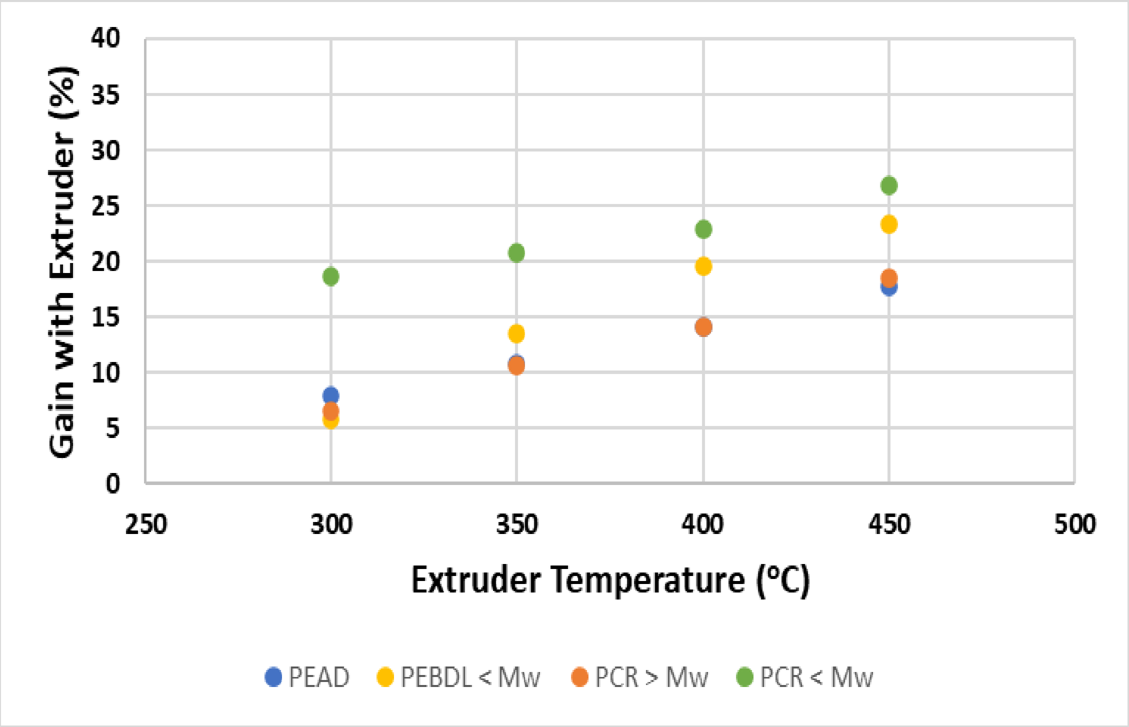


Thermal

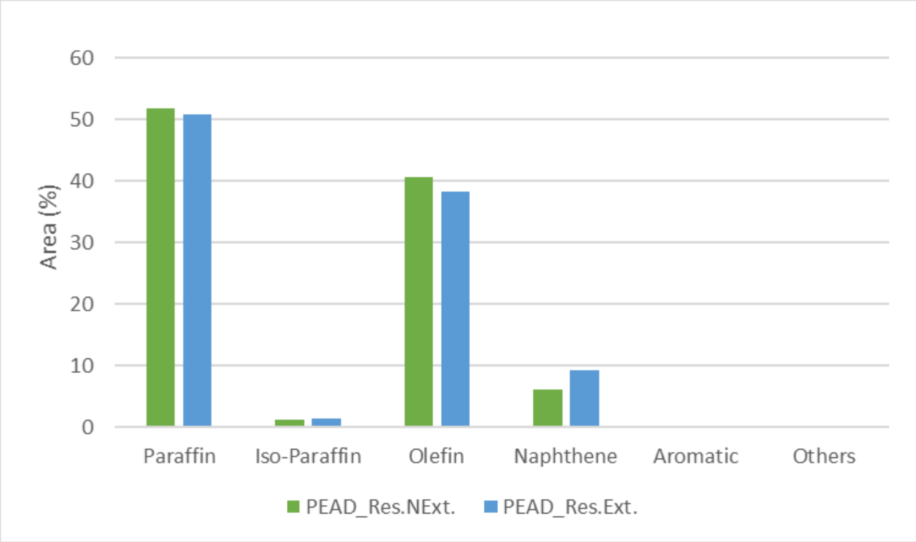
Catalytic

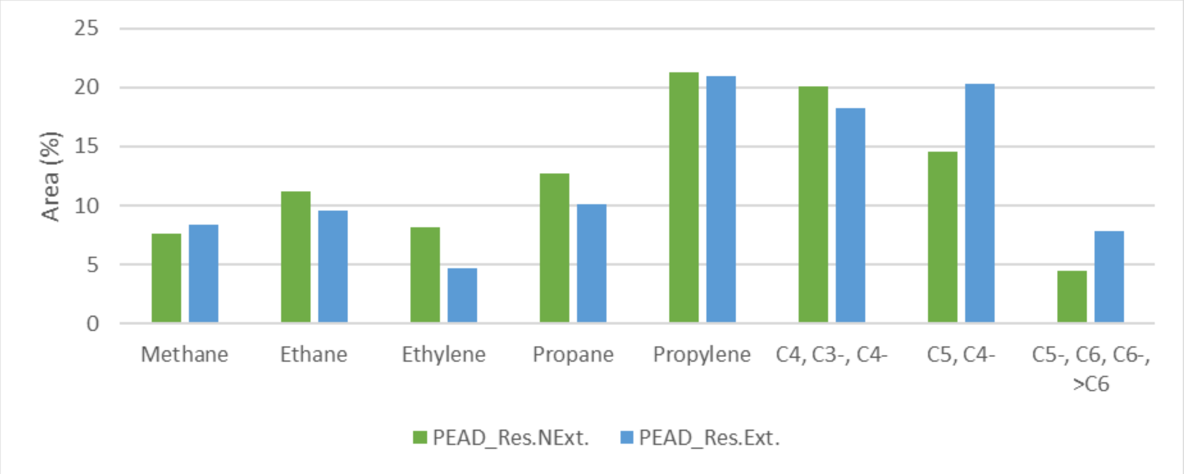
Extrusion Pre-treatment

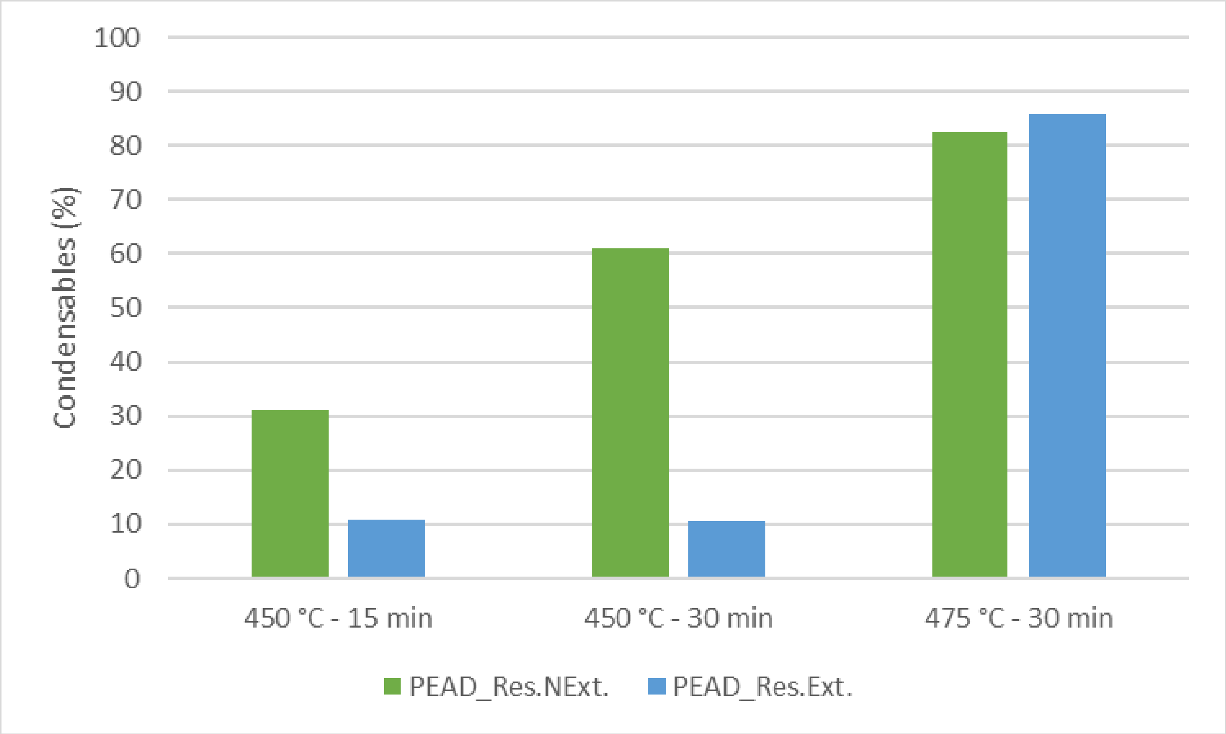




Extrusion Pre-treatment

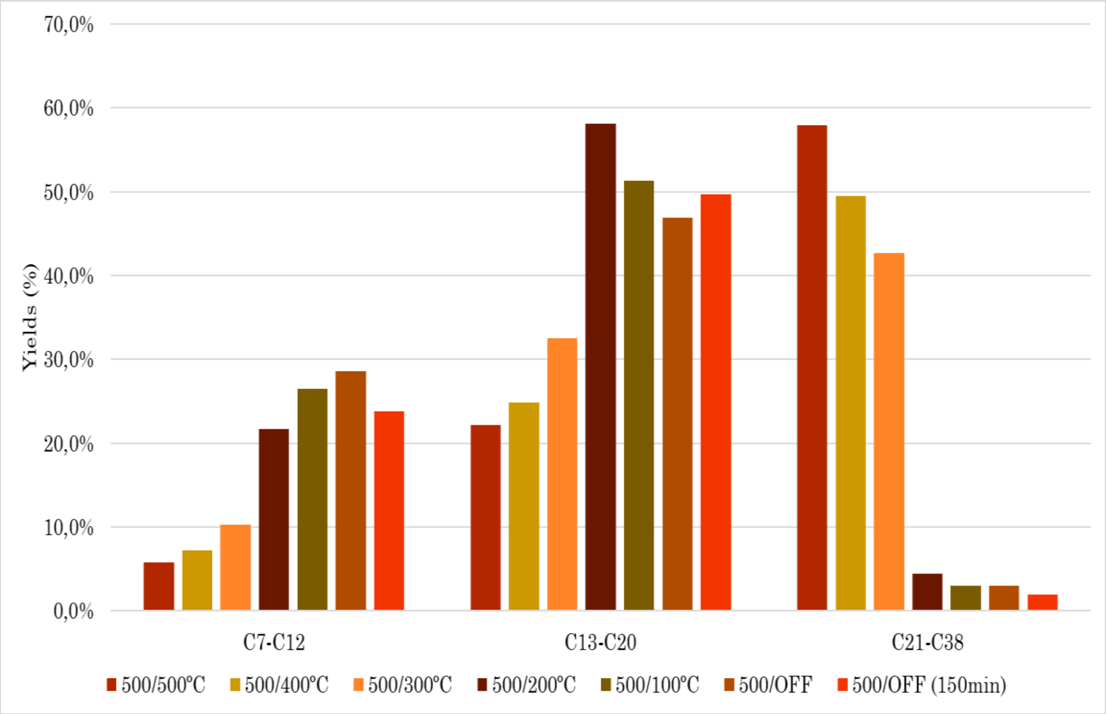




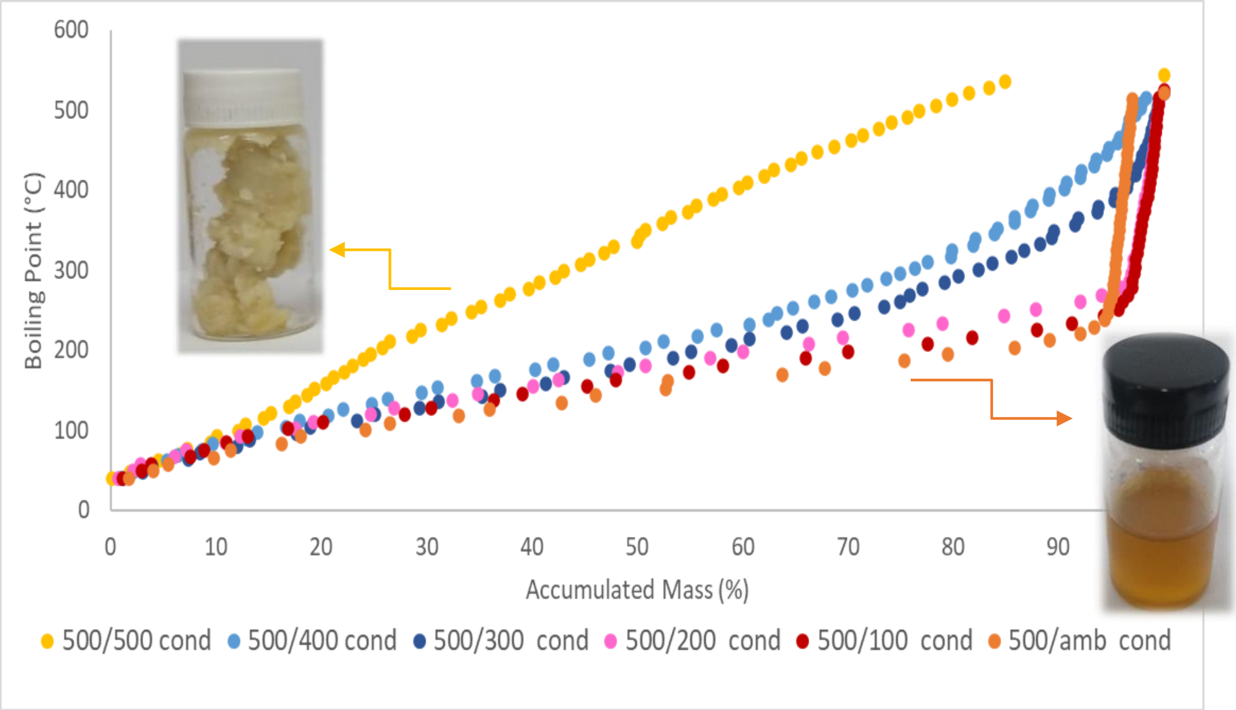


Effect of Reflux

GC MS



Simulated Distillation

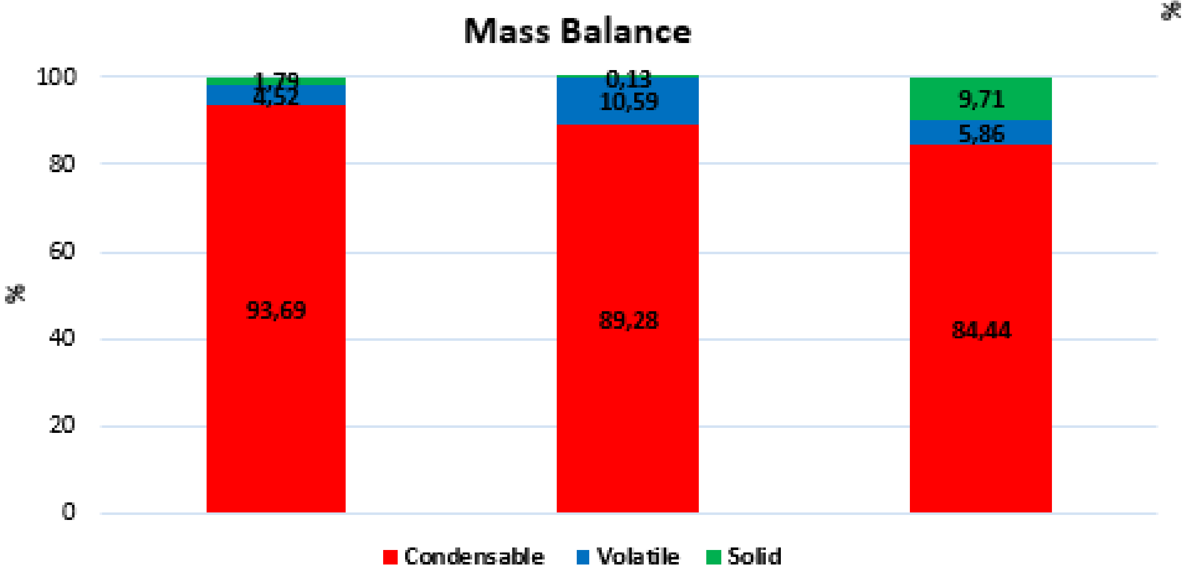


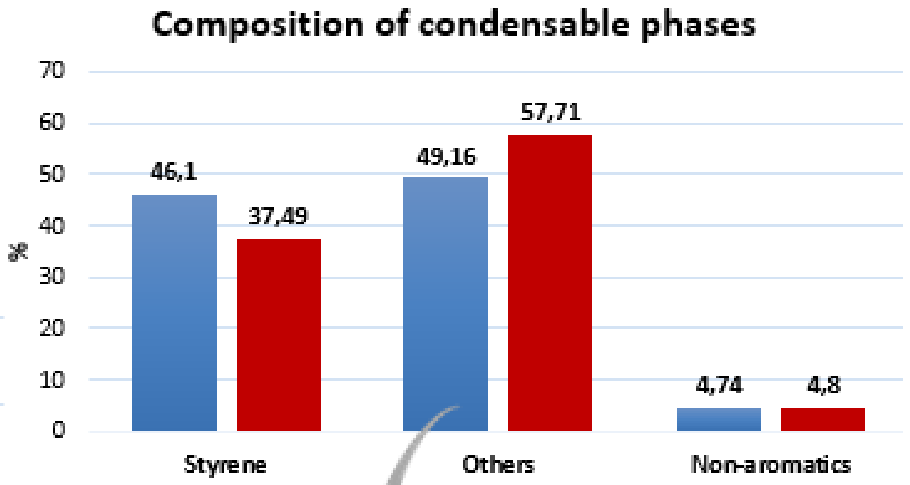
Solids

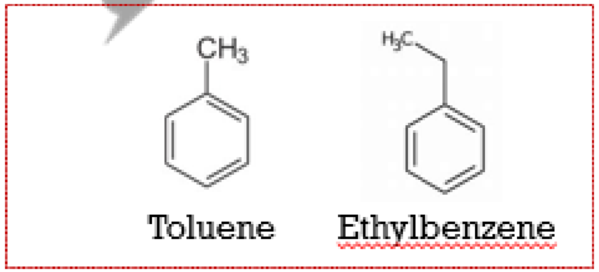
Adsorbents

Fillers

Scaling-Up







UFPE

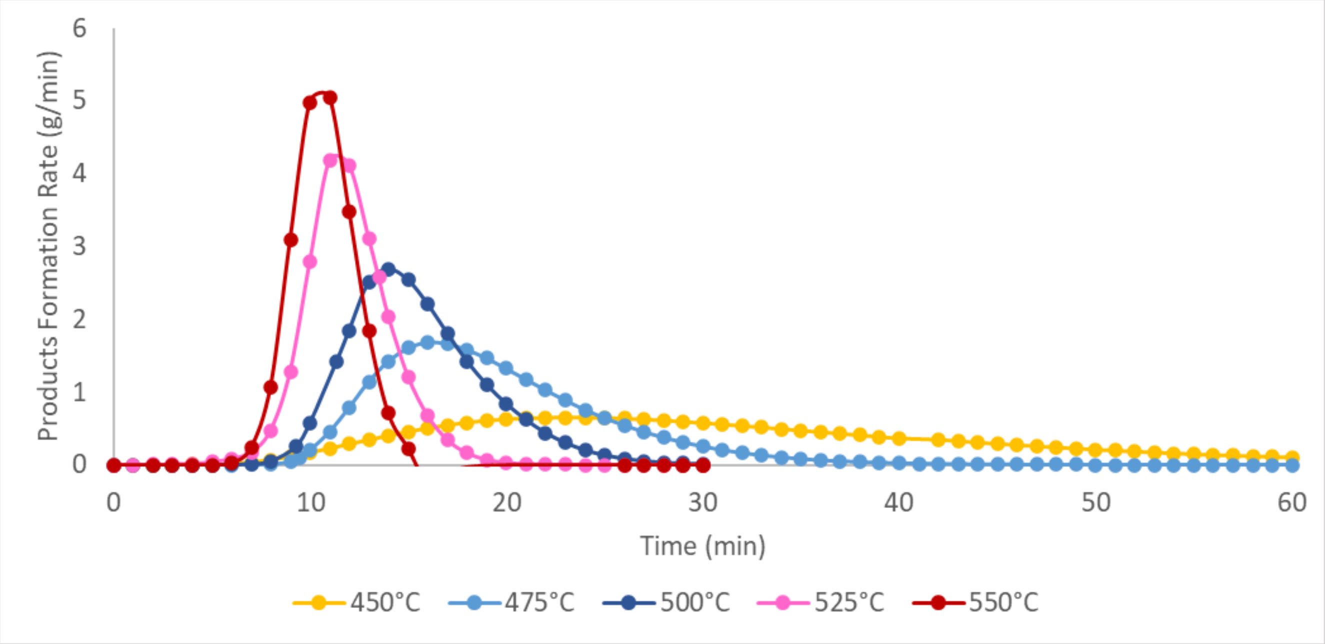
Kinetic Modeling

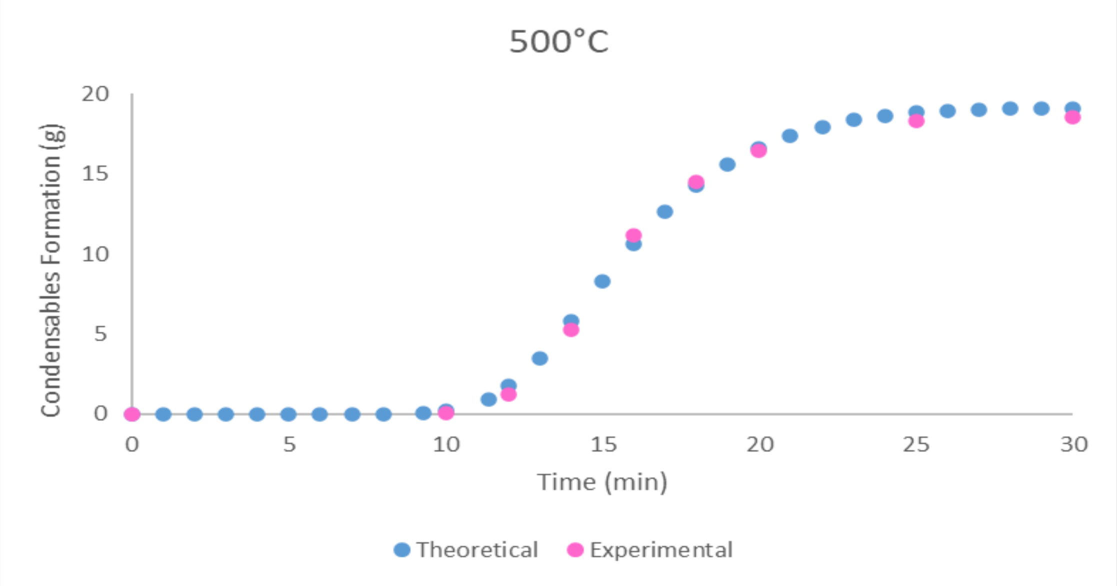
$$k = e^{A+B\left(\frac{T-T_{ref}}{T}\right)}$$

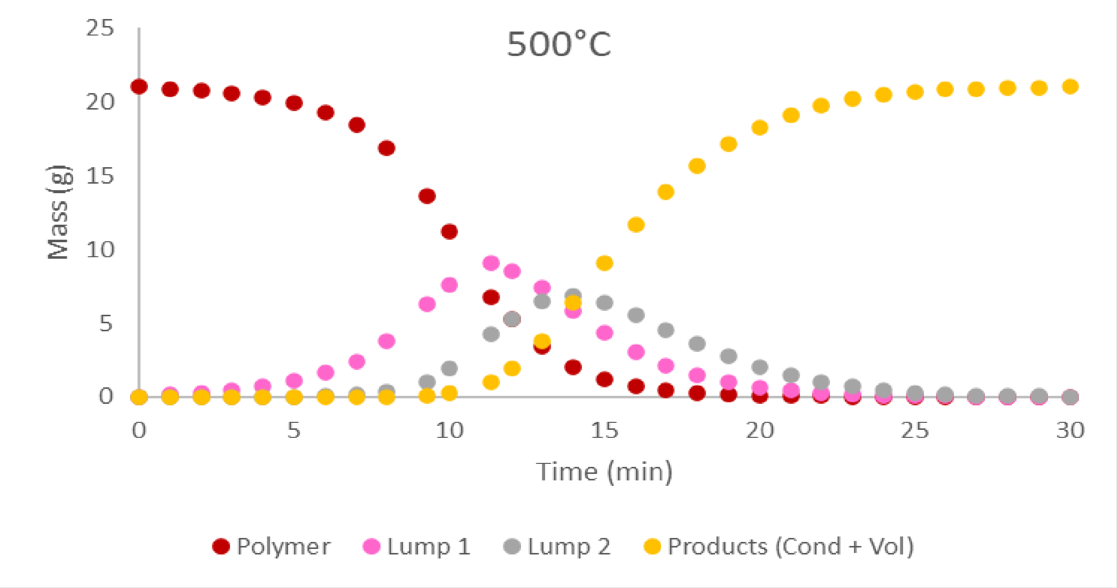
$$Ea = B\,R\,T_{ref}$$

$$k_0 = \exp(A+B)$$

$$A \xrightarrow{k} B \xrightarrow{k} C \begin{cases} \xrightarrow{k} L \\ \xrightarrow{k} G \\ \xrightarrow{k} S \end{cases}$$







Modeling

1 Without Catalyst

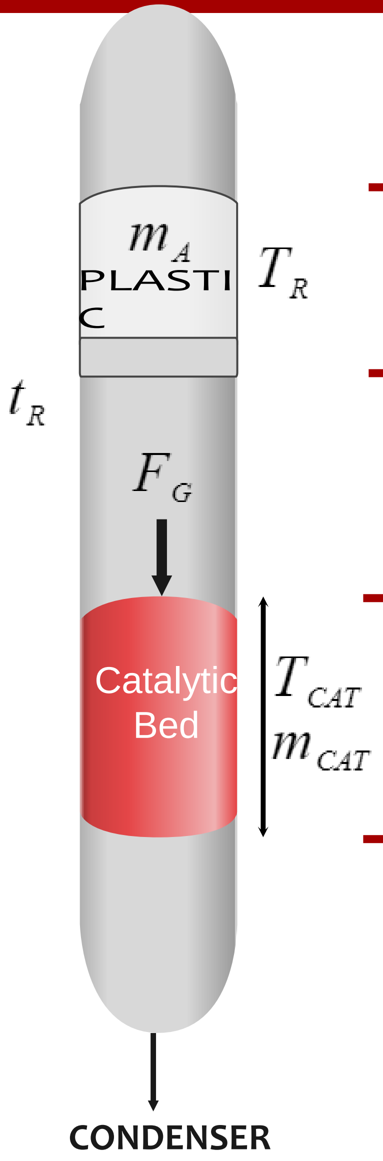
$$\frac{dM_i}{dt} \cong R_i = \frac{M_A\, \varphi_L\, x_{iL}}{\Delta t}$$

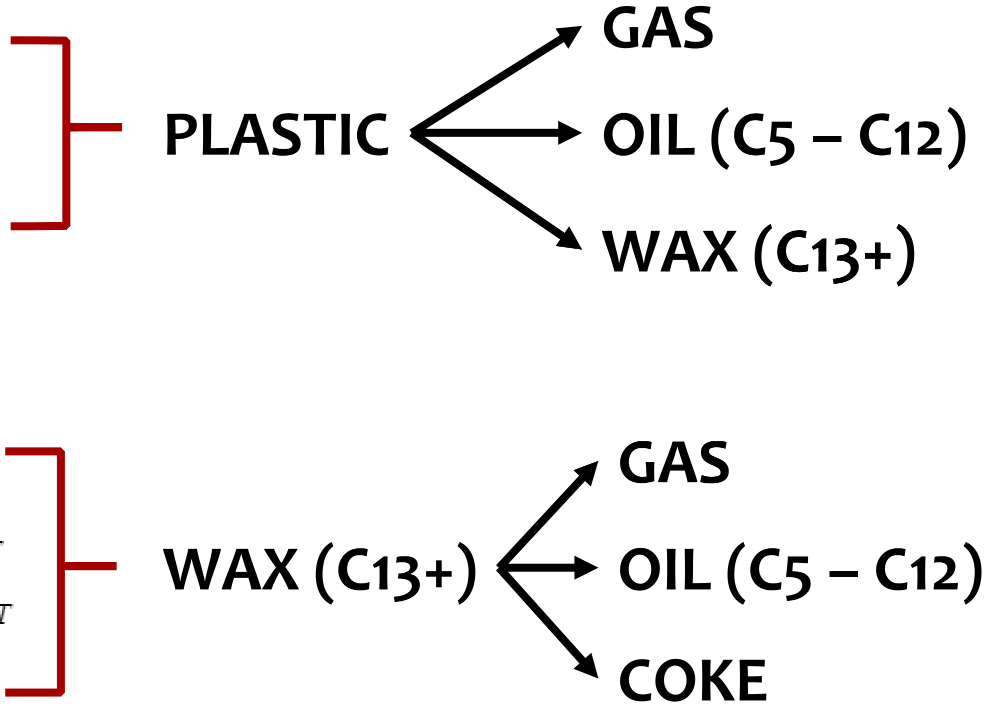
2 With Catalyst

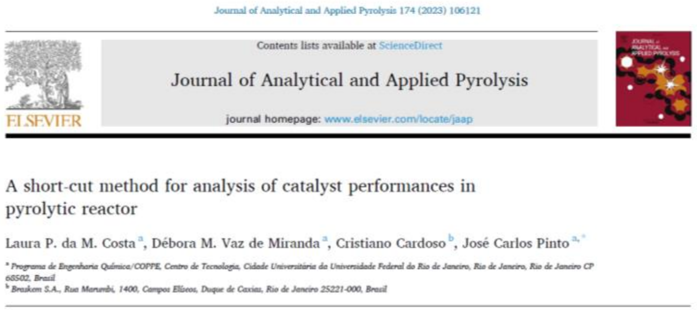
$$\frac{dM_i^{cat}}{dt} \cong R_i^{cat} = \frac{M_A\, \varphi_L\, x_{iL}}{\Delta t}$$

3 Due to catalyst transformation

$$\frac{d\left(M_i^{cat} - M_i\right)}{dt} \cong R_i^{int} = \frac{M_i^{cat} - M_i}{\left[\left(\frac{\varepsilon\, M_{cat}}{(1-\varepsilon)\rho_{cat}}\right) \Big/ F_G\right]}$$







Journal of Analytical and Applied Pyrolysis 174 (2023) 106121

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

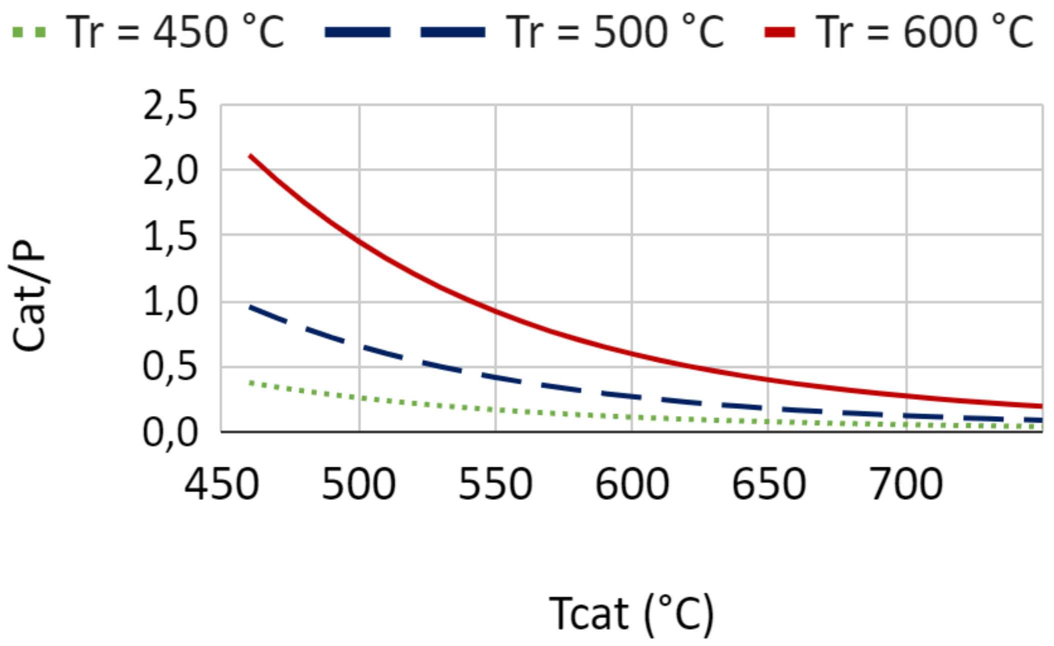
journal homepage: www.elsevier.com/locate/jaap

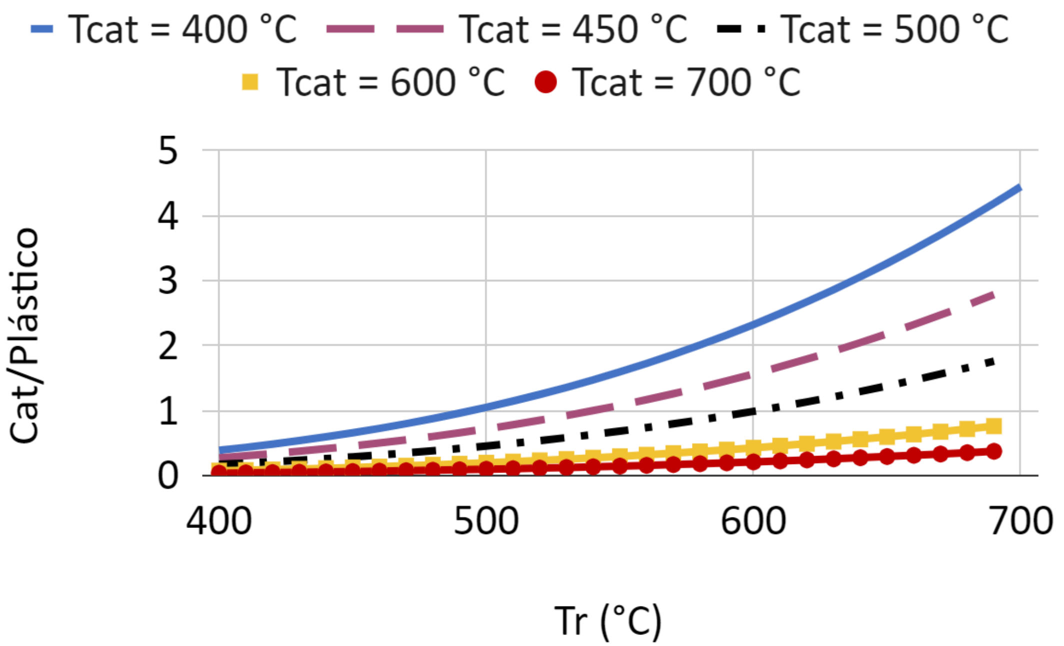
A short-cut method for analysis of catalyst performances in pyrolytic reactor

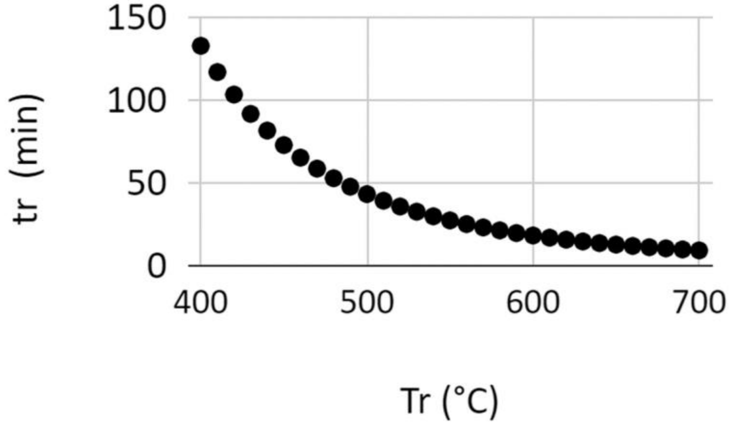
Laura P. da M. Costa [a], Débora M. Vaz de Miranda [a], Cristiano Cardoso [b], José Carlos Pinto [a,*]

[a] Programa de Engenharia Química/COPPE, Centro de Tecnologia, Cidade Universitária da Universidade Federal do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro CP 68502, Brasil
[b] Braskem S.A., Rua Marumbi, 1400, Campos Elíseos, Duque de Caxias, Rio de Janeiro 25221-000, Brasil

Modeling

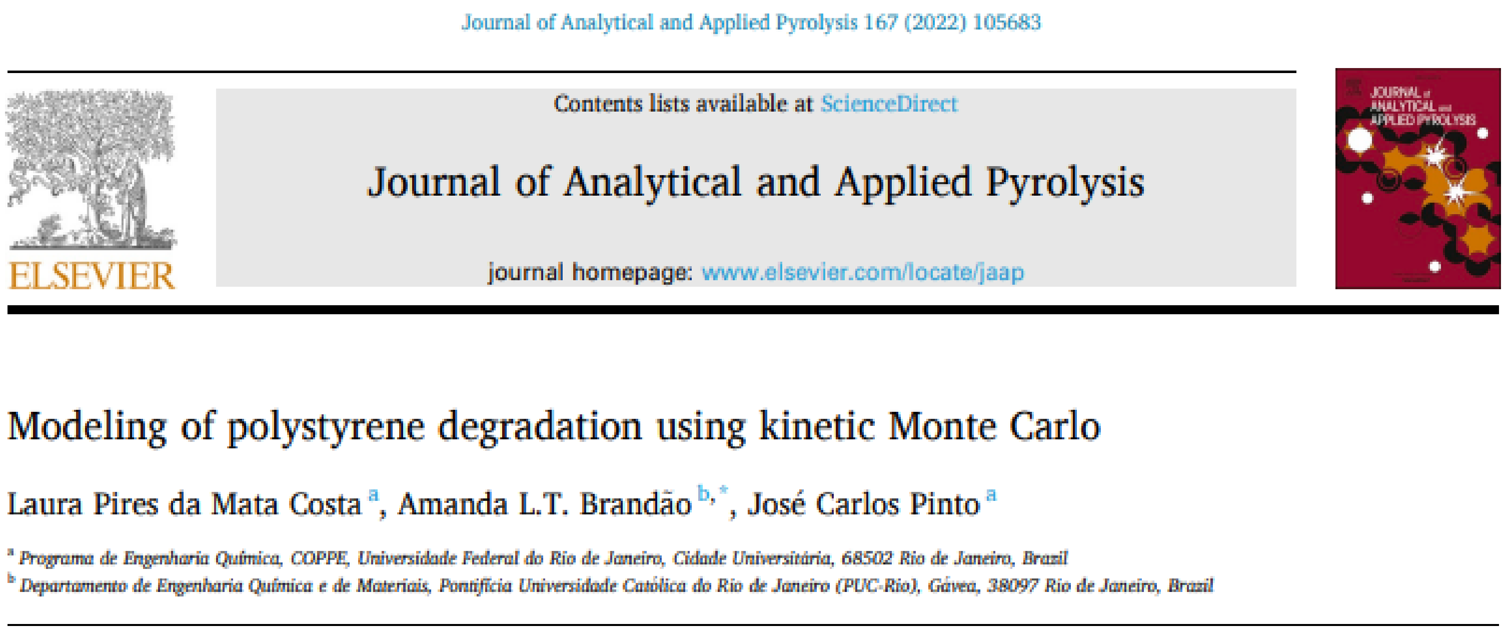






With the mass balances, it is possible to obtain the catalyst mass needed to convert the wax into lighter products according to the pyrolysis temperature or to the catalytic bed temperature.

Modeling


Journal of Analytical and Applied Pyrolysis 167 (2022) 105683

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Modeling of polystyrene degradation using kinetic Monte Carlo

Laura Pires da Mata Costa [a], Amanda L.T. Brandão [b,*], José Carlos Pinto [a]

[a] Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, 68502 Rio de Janeiro, Brazil
[b] Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Gávea, 38097 Rio de Janeiro, Brazil

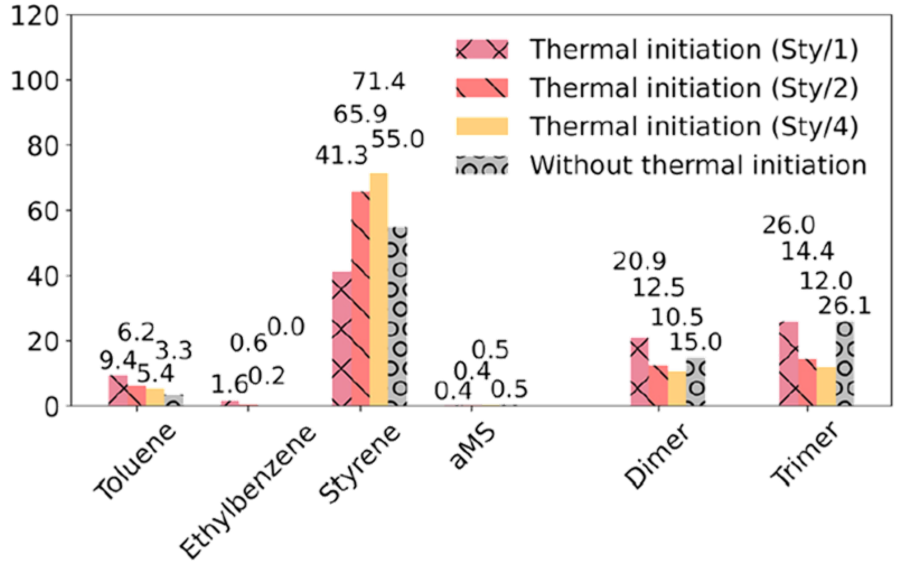
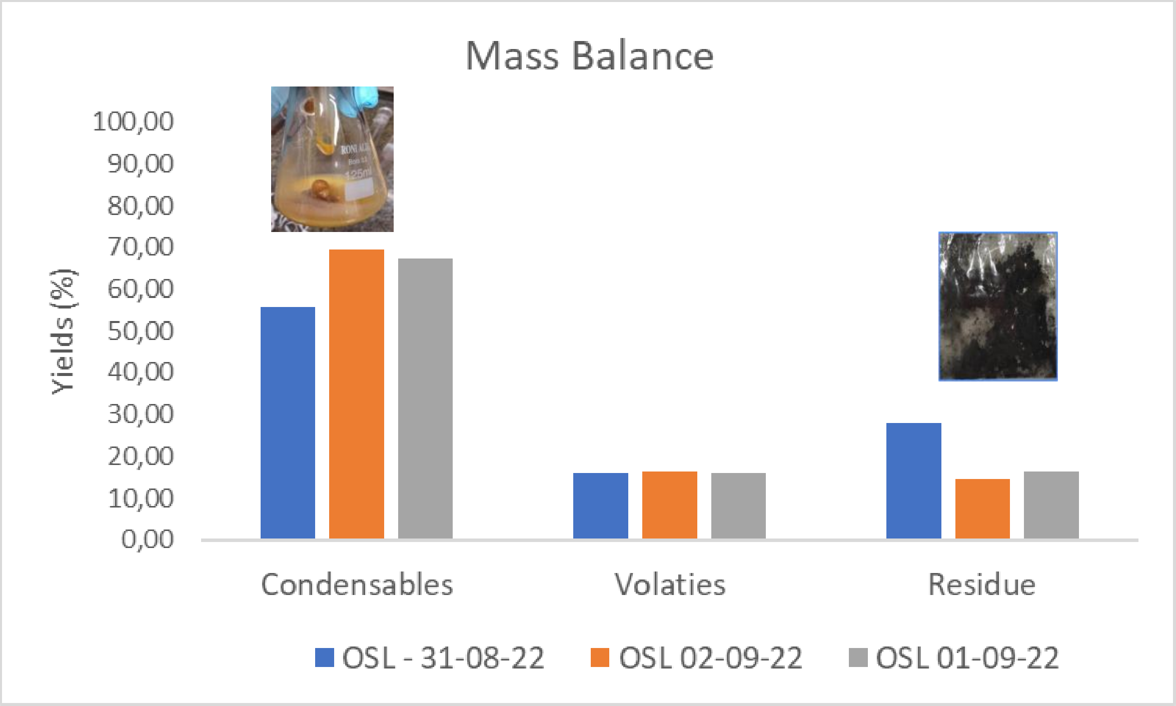


Fig. 11. Product distribution for PS thermal degradation performed at 500 °C considering thermal initiation of styrene.

- Polystyrene chemical recycling via pyrolysis constitutes an appropriate route for disposal of post-consumption material;
- High styrene amounts can be obtained and used for production of recycled styrene-based materials, avoiding the use of virgin fossil feedstocks.

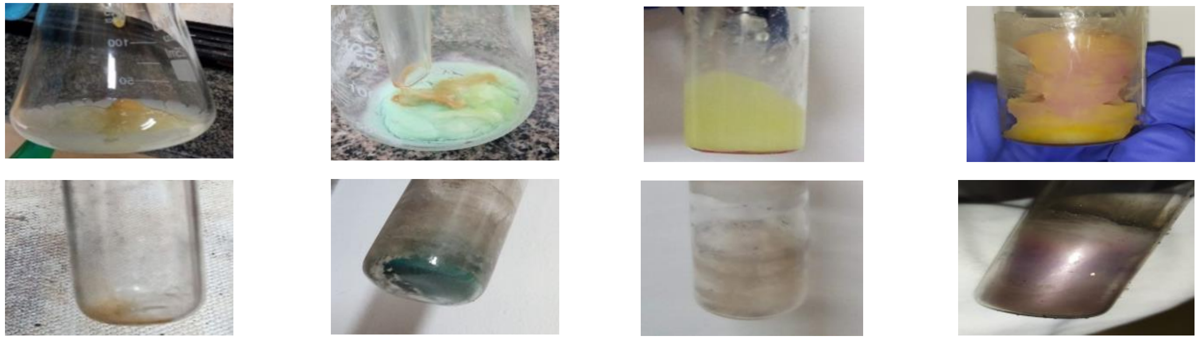
OSL

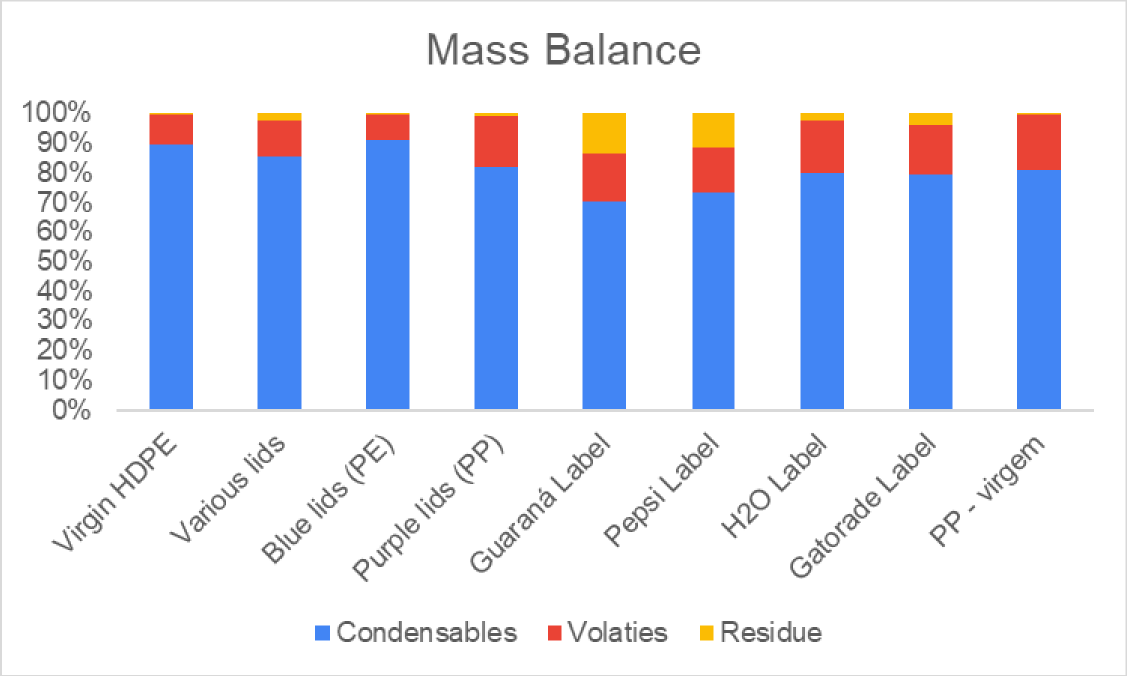
ORLA SEM LIXO

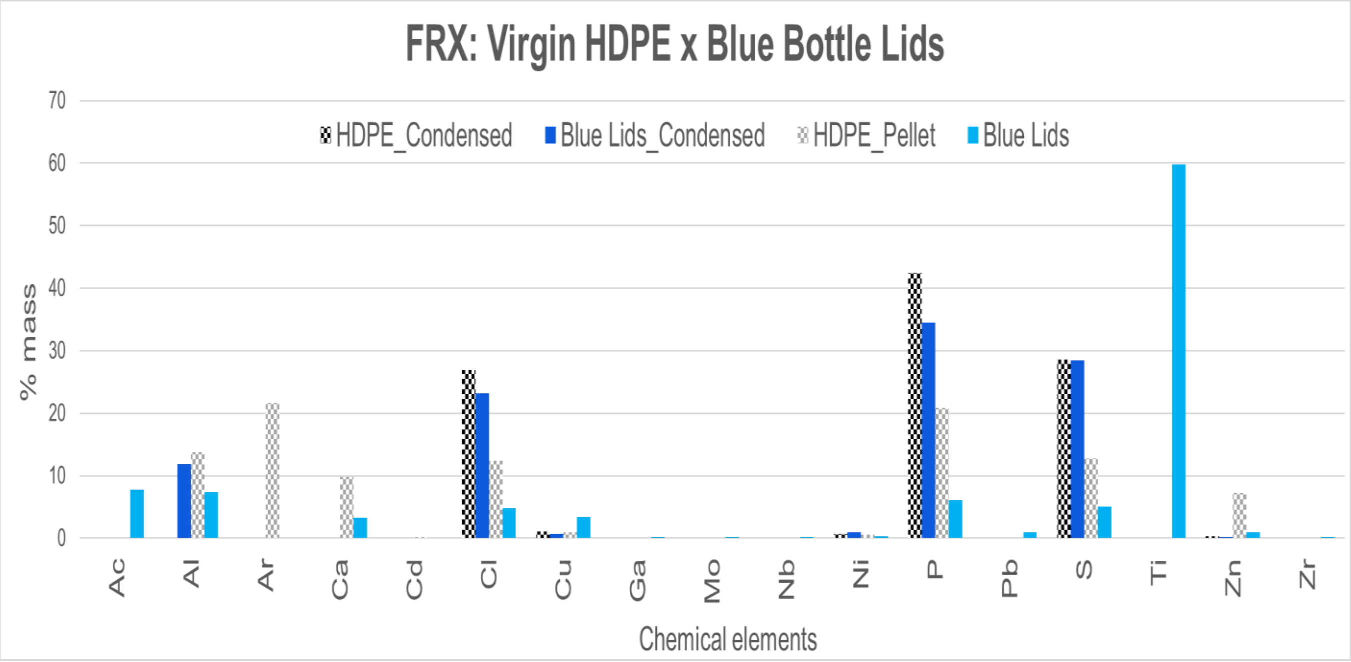


Lids and labels

Virgin HDPE | Blue lids | Virgin PP | Purple lids







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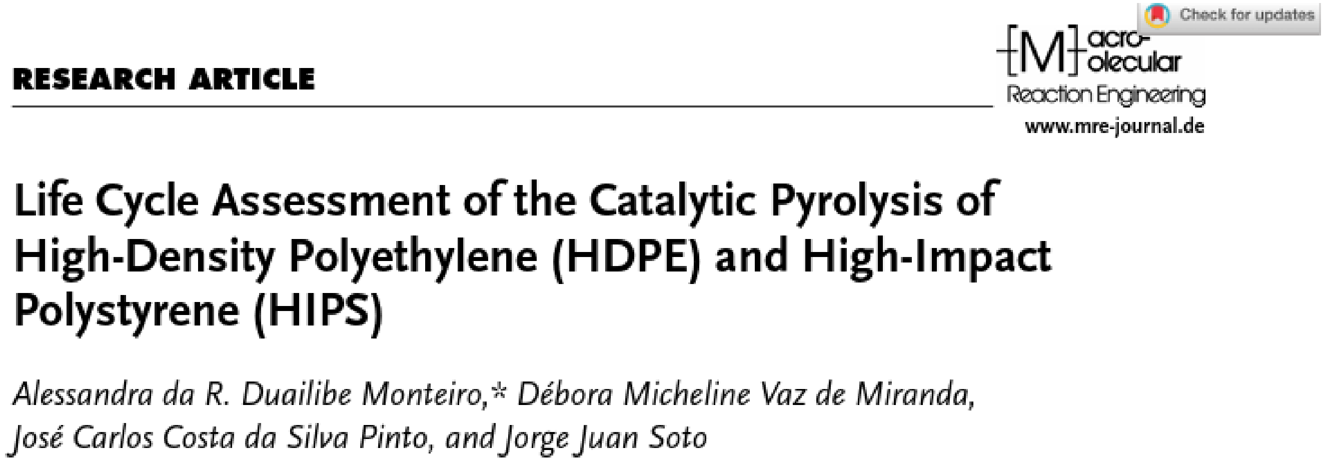
Life Cycle Analyses



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RESEARCH ARTICLE

Macromolecular Reaction Engineering
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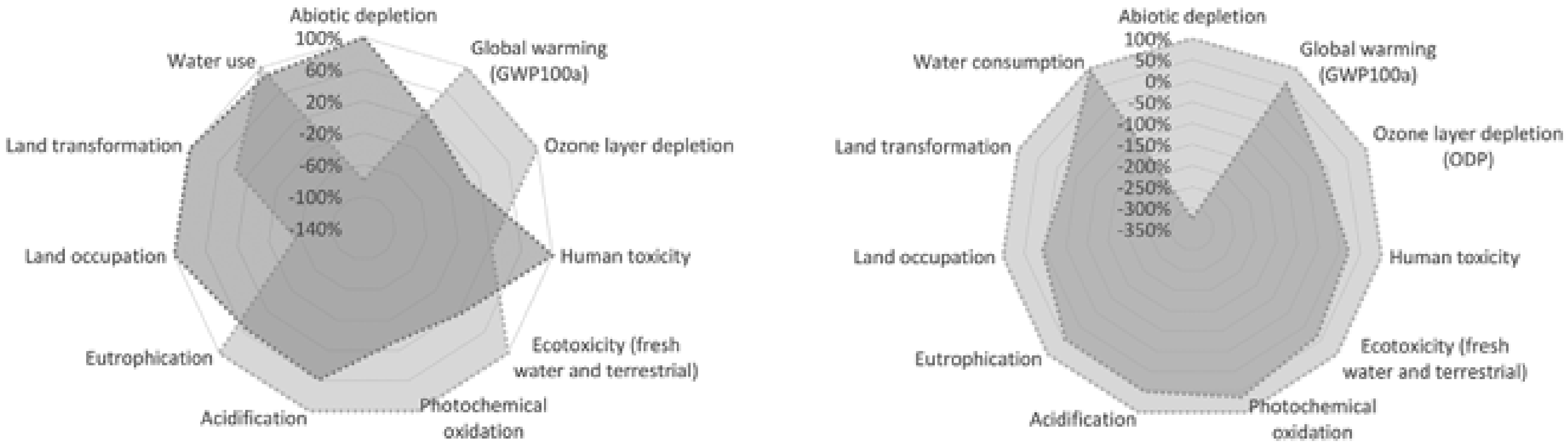
Life Cycle Assessment of the Catalytic Pyrolysis of High-Density Polyethylene (HDPE) and High-Impact Polystyrene (HIPS)

Alessandra da R. Duailibe Monteiro, Débora Micheline Vaz de Miranda, José Carlos Costa da Silva Pinto, and Jorge Juan Soto*



- Pollution by plastics constitutes an urgent problem that demands immediate actions, including development of efficient polymer recycling technologies;
- Chemical recycling through pyrolysis is competitive and leads to lower environmental impacts than plastic disposal in landfills.
- Environmental impacts depend on the selected process operation conditions.

Fig7. Radar chart of the LCA for non-catalytic and catalytic pyrolysis of HIPS and HDPE.

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Life Cycle Analyses

ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg

Letter

Critical Evaluation of Life Cycle Assessment Analyses of Plastic Waste Pyrolysis

Laura Pires Costa, Débora Micheline Vaz de Miranda, and José Carlos Pinto*

Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 3799–3807

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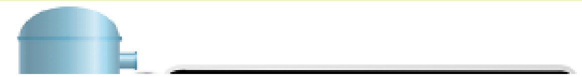
ABSTRACT: Pyrolysis is a chemical recycling technology that is experiencing fast development, is complementary to mechanical recycling, and is used to



Concluding Remarks

Concluding Remarks

1. **Plastic business is at risk, despite the many competitive advantages of these materials;**
2. **Principles of circular economy are changing paradigms in the chemical chain.**
3. **Plastic materials are extremely well-suited for recycling and circular strategies;**
4. **Chemical recycling constitutes an important technological challenge for the 21st century;**
5. **Chemical recycling is still in its infancy and demands fundamental research in many areas;**
6. **Research must be supported by fundamental LCA investigations.**

Grupo EngePol

Thank you!

pinto@peq.coppe.ufrj.br

- EngepolGrupo
- Falandocomciencia
- Falandocomciencia
- Falando com Ciência
- José Carlos Pinto

Grupo EngePol