

Reciclagem Química de Polímeros

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

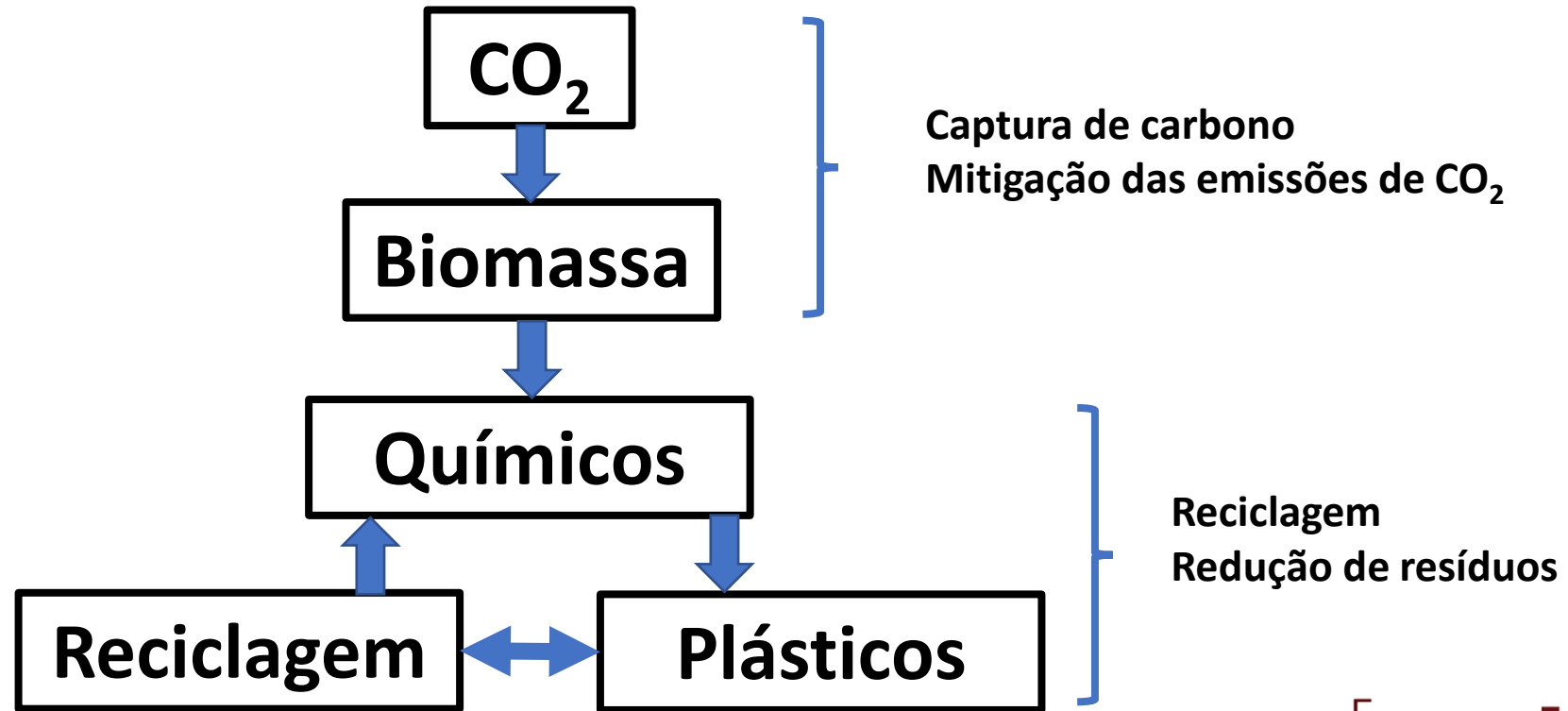
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Átomos de carbono podem circular na cadeia.

**Do berço ao berço !!!
Não é resíduo – é óleo sólido !!!**



Um paradigma sustentável e circular.



Uso de biomassa e de técnicas de reciclagem podem prover um novo paradigma circular e sustentável para a indústria de plásticos.

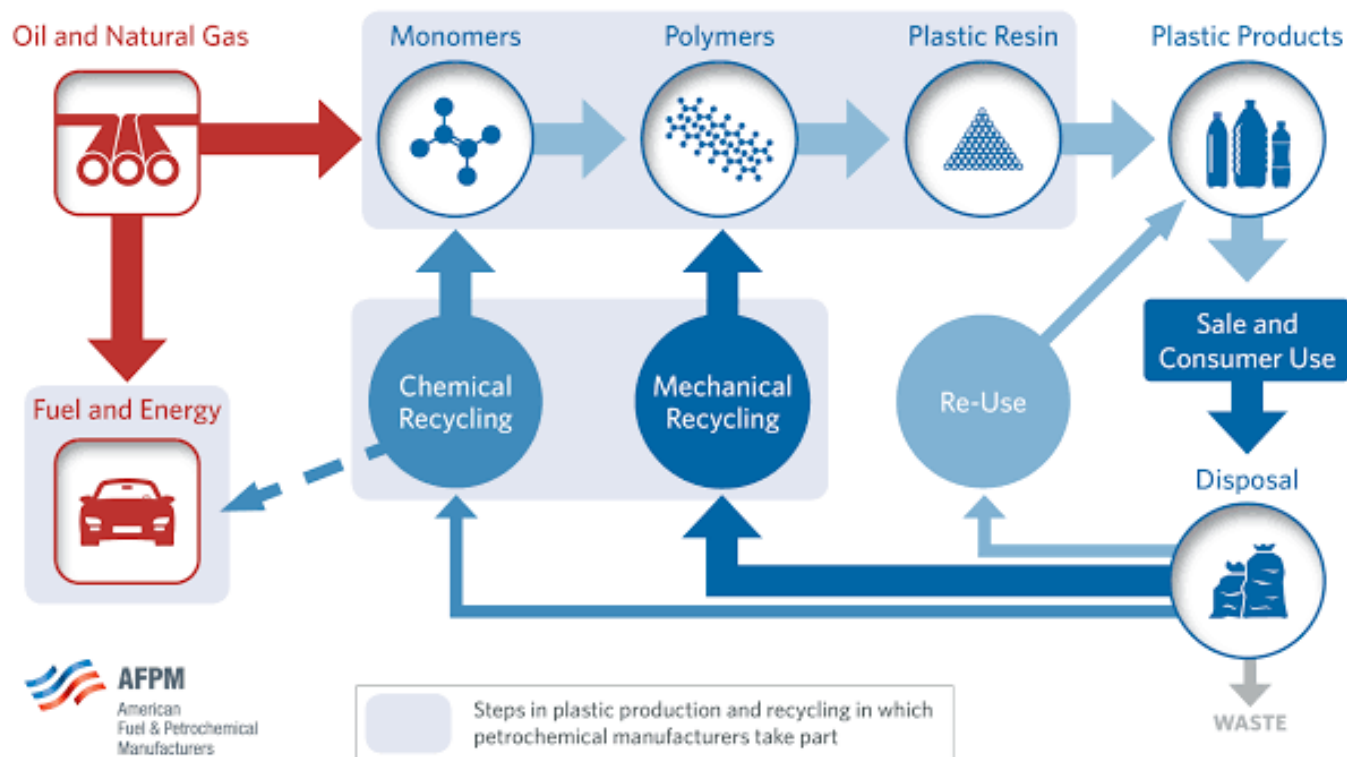
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Plásticos são quase 100% recicláveis !

Evolving the Plastic Recycling Supply Chain

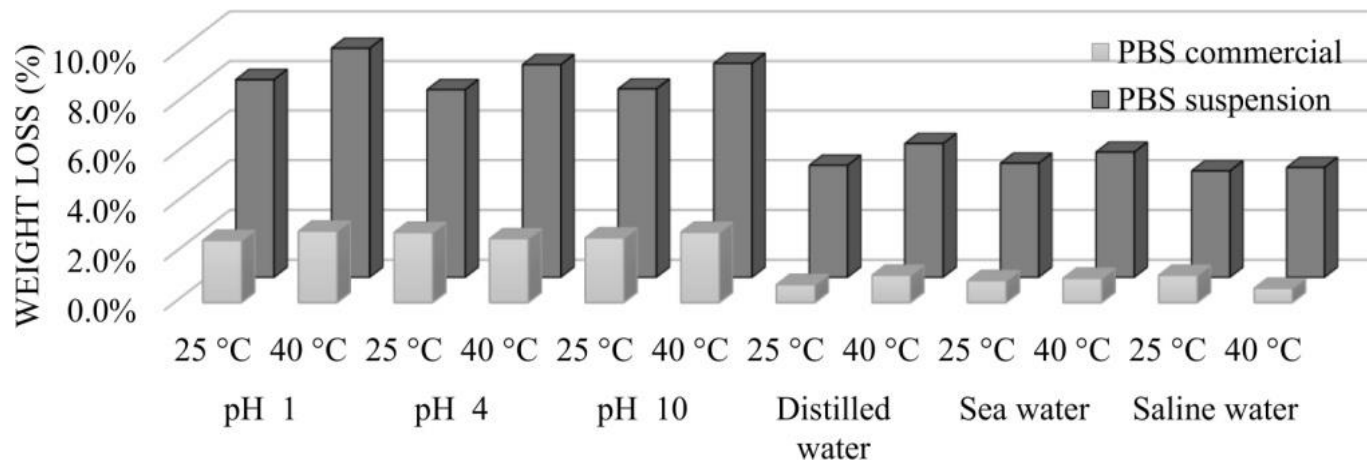


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Solvólise



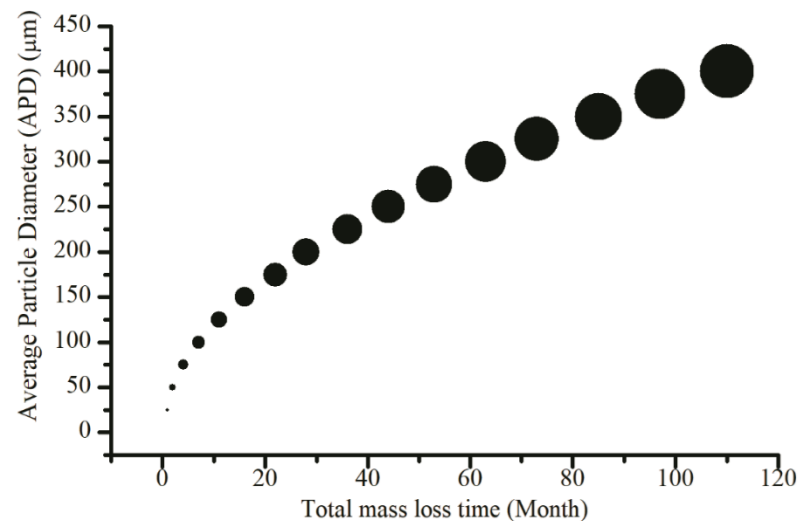
Journal of Polymers and the Environment (2019) 27:176–188
<https://doi.org/10.1007/s10924-018-1329-x>

ORIGINAL PAPER



Preparation of Polymer Microparticles Through Non-aqueous Suspension Polycondensations: Part III—Degradation of PBS Microparticles in Different Aqueous Environments

Luciana da Silva Dutra¹ · Thiago de Souza Belan Costa¹ · Victor Tozatto Verissimo Lobo¹ · Thamiris Franckini Paiva² · Marcio de Souza Nele¹ · Jose Carlos Pinto²



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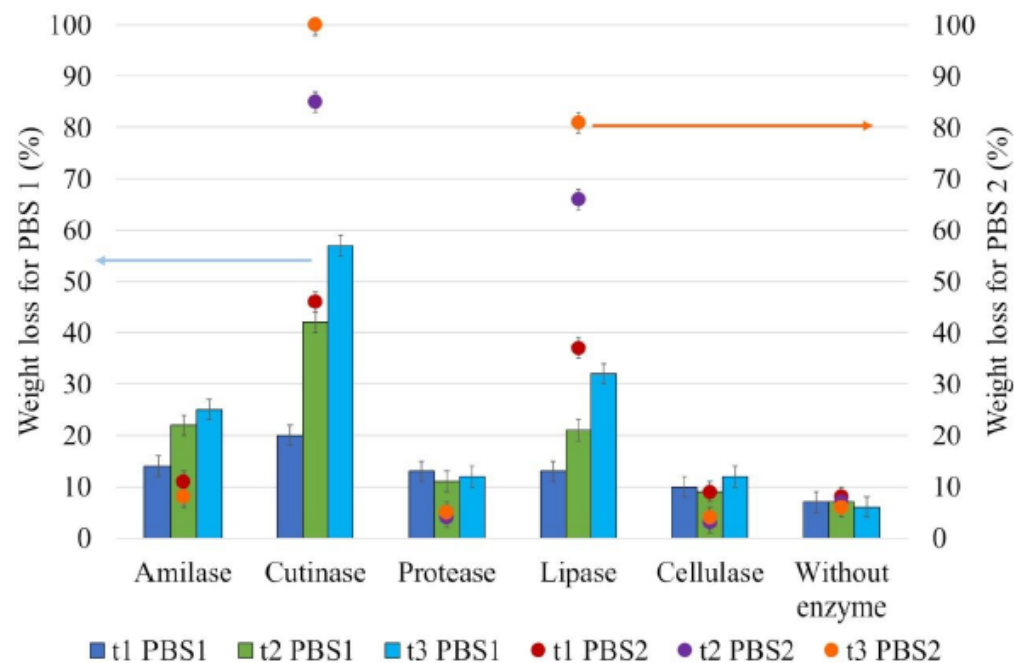


Fig. 9 Weight loss for PBS1 and PBS2 in different enzymatic media (t1 - 1 day of experiment; t2 - 2 weeks after the beginning of the assay; t3 - 4 weeks of experiment).

Journal of Polymers and the Environment

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

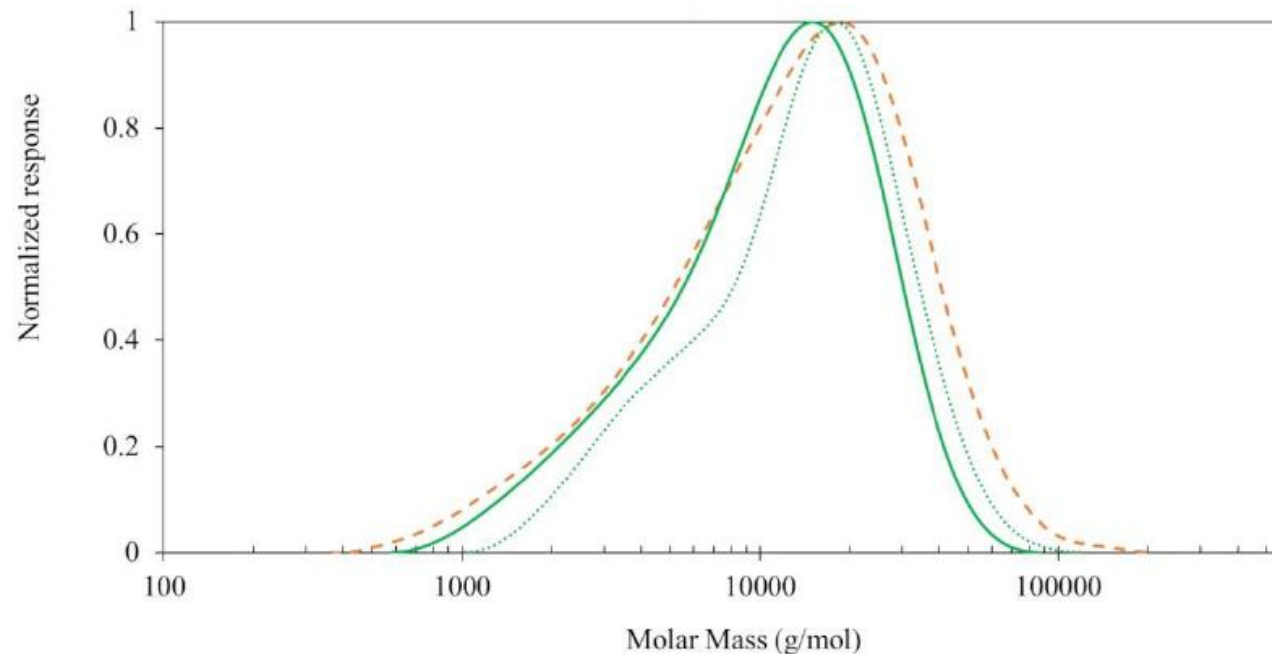
Manuscript Number:	JOOE-D-21-00464
Full Title:	Preparation of Polymer Microparticles Through Non-aqueous Suspension

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Journal of Polymers and the Environment

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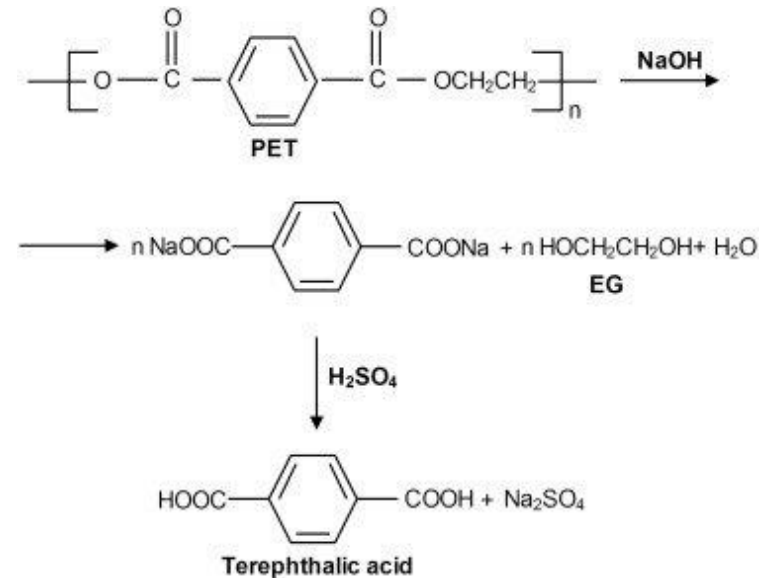
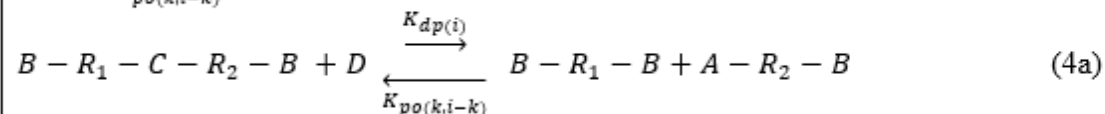
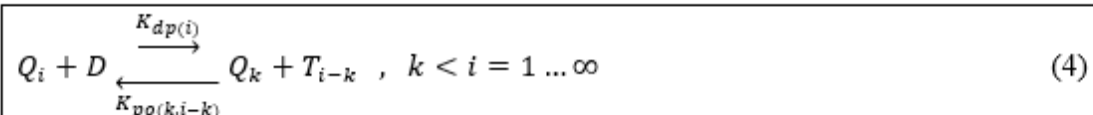
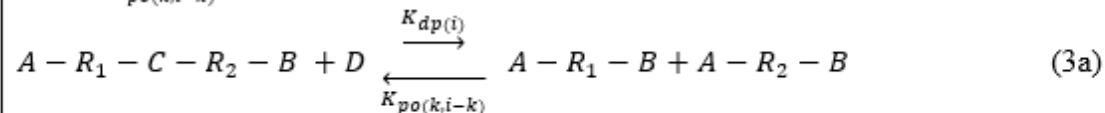
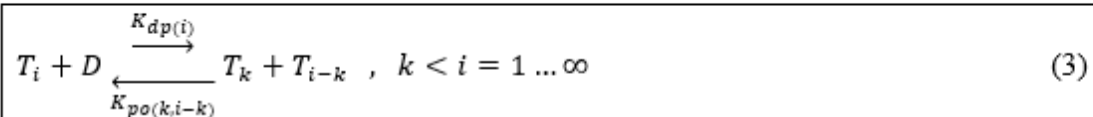
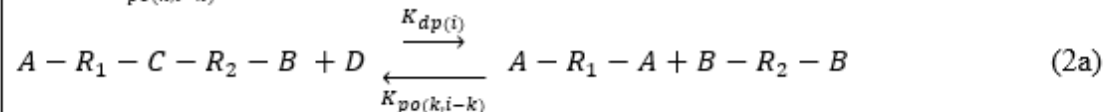
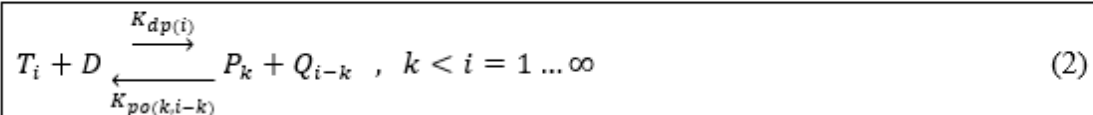
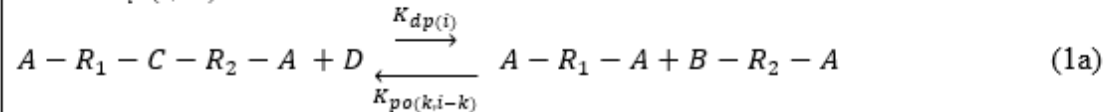
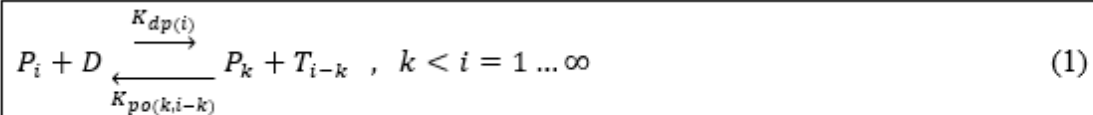
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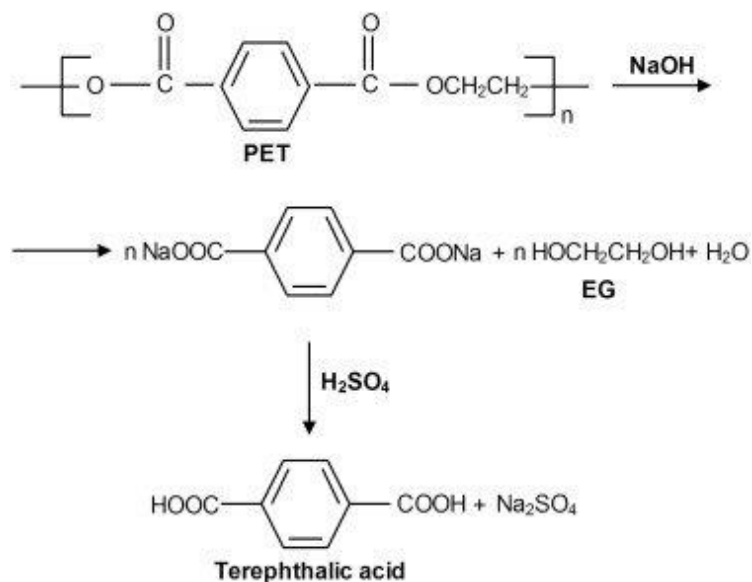
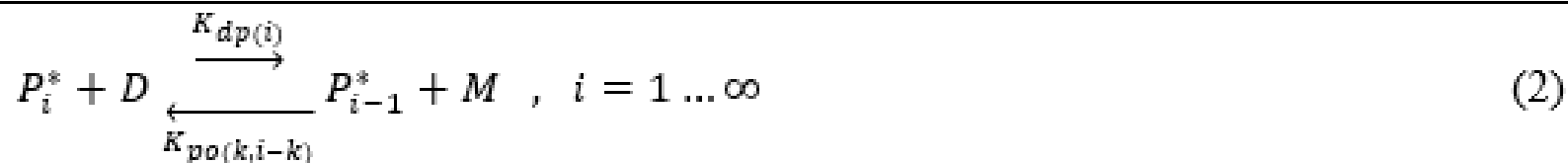


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Solvólise



Solvólise



A maior parte dos polímeros é de adição.

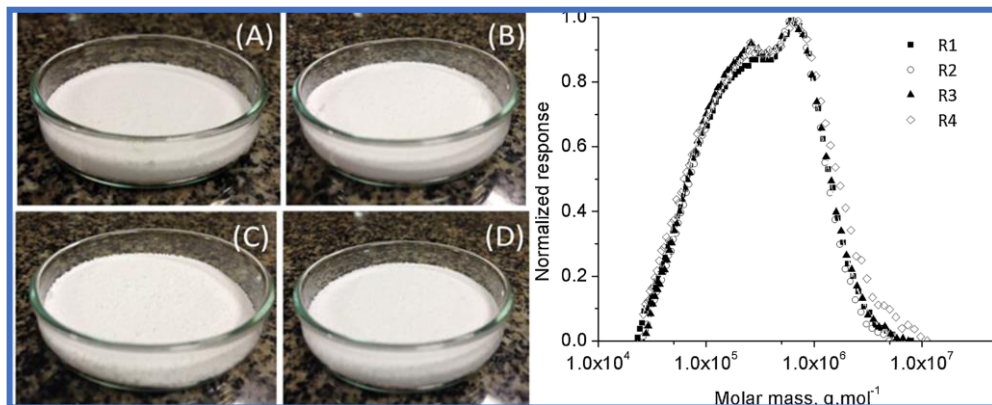
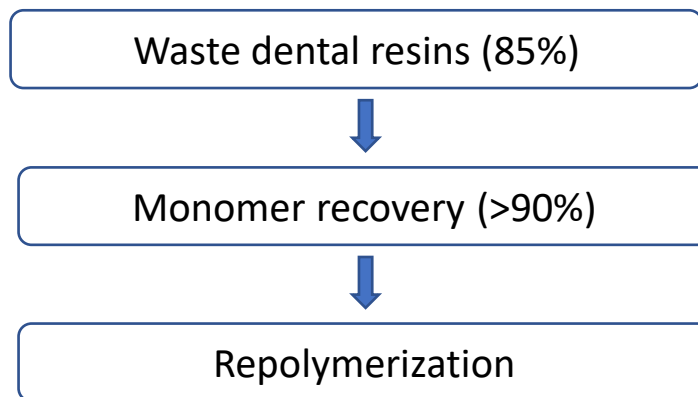


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Alguns materiais despolimerizam.



(A) 100:0; (B) 90:10; (C) 50:50; (D) 0:100 (virgin/recycled)



Chemical recycling of crosslinked poly(methyl methacrylate) and characterization of polymers produced with the recycled monomer



Modelling the chemical recycling of crosslinked poly (methyl methacrylate): Kinetics of depolymerisation

Simón Da Ros^{a,*}, Rayany Stocco Braido^a, Nathany Lisboa de Souza e Castro^a, Amanda L.T. Brandão^b, Marcio Schwaab^c, José Carlos Pinto^a

^aPrograma de Engenharia Química/COPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP:68502, Rio de Janeiro, 21941-972, RJ, Brazil

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A temperatura teto.

Thermodynamics of polymerization [\[edit\]](#)

At constant temperature, the reversibility of polymerization can be

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

where ΔS_p is the change of [entropy](#) during polymerization. The

$$\Delta H_p = E_p - E_{dp}$$

where E_p and E_{dp} denote the activation energies for polymerization and depolymerization, respectively.

Entropy is the measure of randomness or chaos. A system has a higher entropy when it is more disordered. Because the process of depolymerization involves a decrease in order, the entropy term is negative. Enthalpy drives polymerization. At the ceiling temperature, the enthalpy term and the entropy term become zero.^[1] Above the ceiling temperature, the rate of depolymerization is greater than the rate of polymerization. The ceiling temperature can be defined by

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

Ceiling temperatures of common monomers [\[edit\]](#)

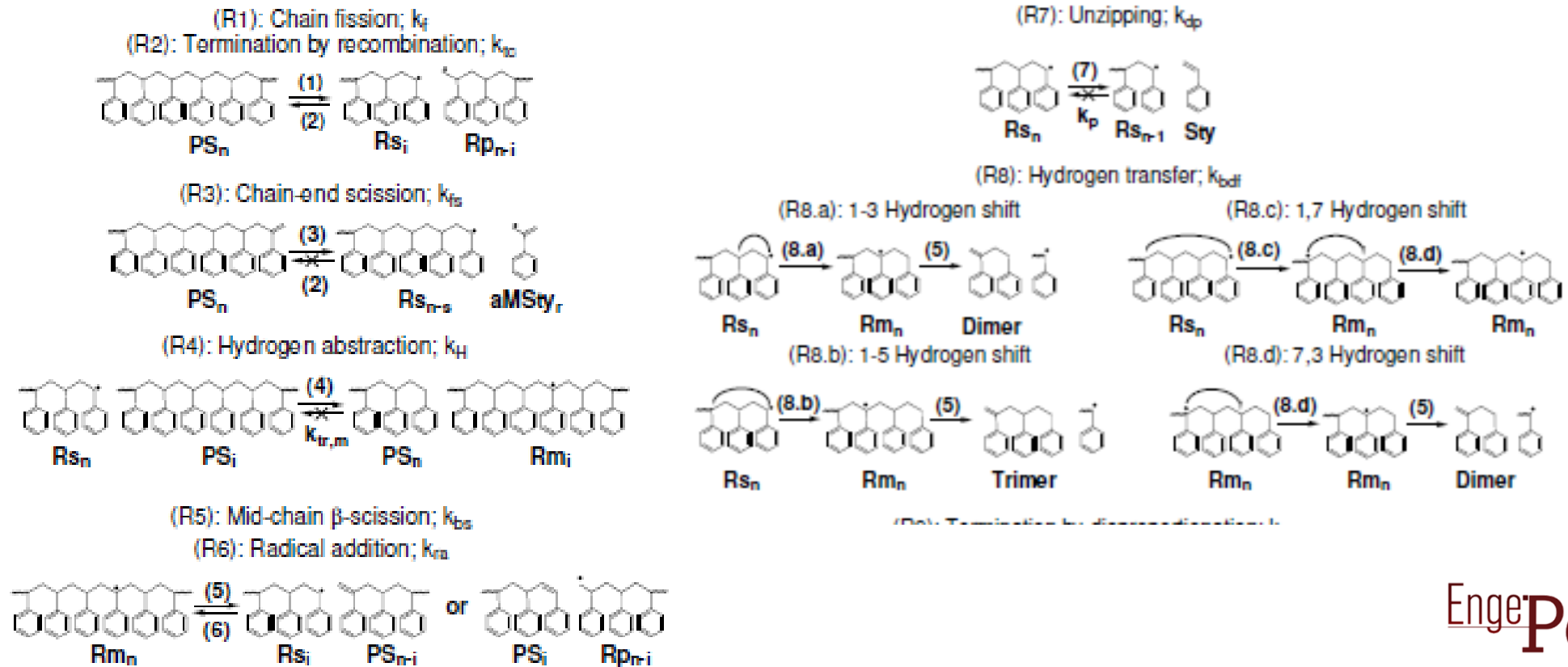
Monomer	Ceiling temperature (°C) ^[6]	Structure
1,3-butadiene	585	$\text{CH}_2=\text{CHCH}=\text{CH}_2$
ethylene	610	$\text{CH}_2=\text{CH}_2$
isobutylene	175	$\text{CH}_2=\text{CMe}_2$
isoprene	466	$\text{CH}_2=\text{C}(\text{Me})\text{CH}=\text{CH}_2$
methyl methacrylate	198	$\text{CH}_2=\text{C}(\text{Me})\text{CO}_2\text{Me}$
α -methylstyrene	66	$\text{PhC}(\text{Me})=\text{CH}_2$
styrene	395	$\text{PhCH}=\text{CH}_2$
tetrafluoroethylene	1100	$\text{CF}_2=\text{CF}_2$

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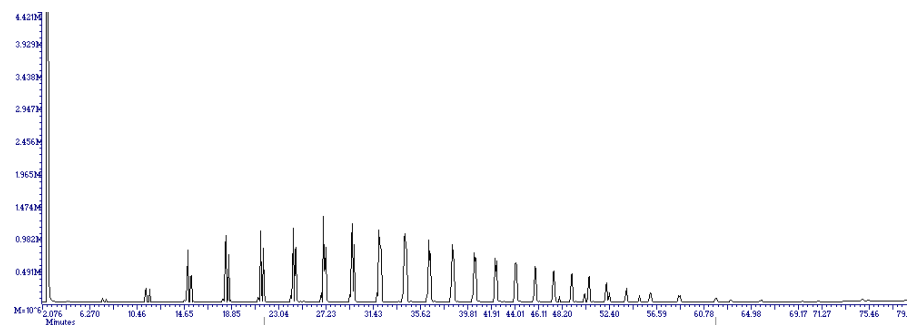
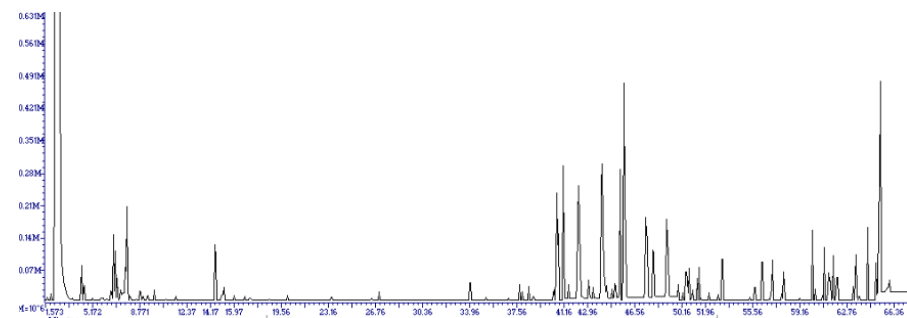
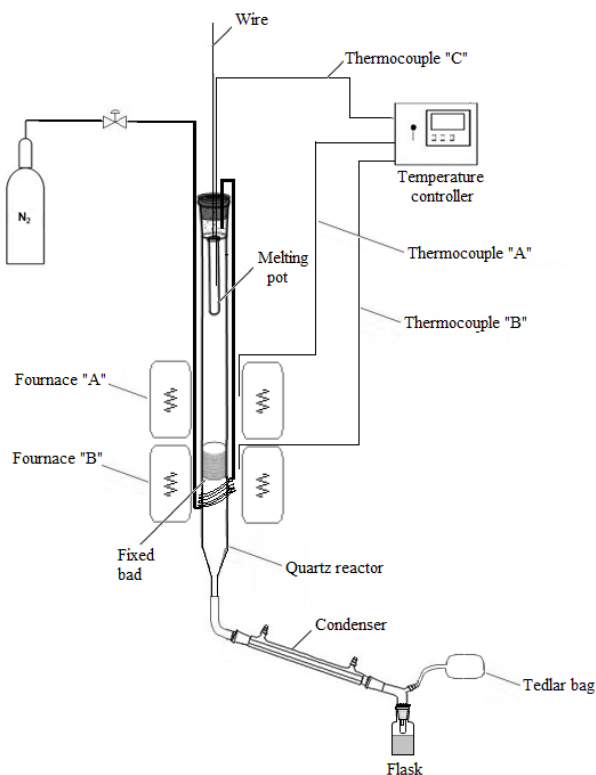
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O mecanismo de radicais livres.



A pirólise.



D.V. Miranda et al. (2021), to be submitted.

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A pirólise.

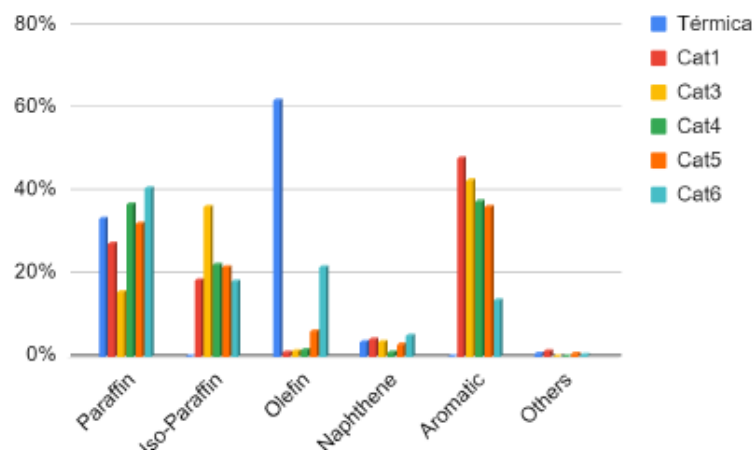
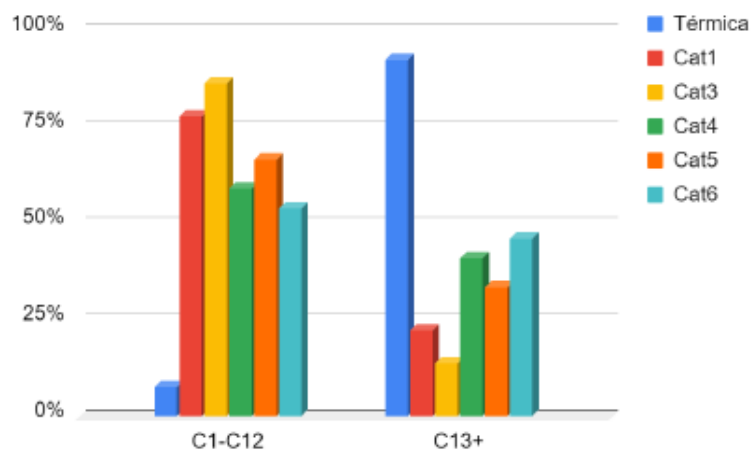
▪ Avaliação comparativa



	Térmica	Cat1	Cat3	Cat4	Cat5	Cat6
C1-C12	7.53	77.57	86.08	59.14	66.35	53.98
C13+	92.46	22.41	13.92	40.86	33.59	46.02

Ação: Abordagem analítica

Ação: Fechar BMs



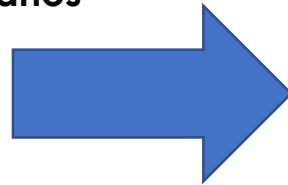
A pirólise.



Resíduos marinhos



Resíduos sólidos urbanos



Resíduos eletro-eletrônicos



O problema dos contaminantes.



Made for minds.

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SCHEDULE AND RECEPTION TV PROGRAMS

TV / ECO INDIA

ECO INDIA

The recycling myth: What really happens to our plastic

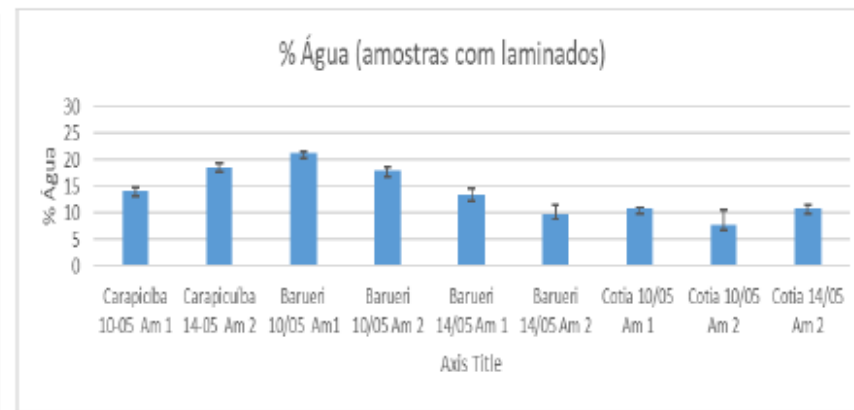
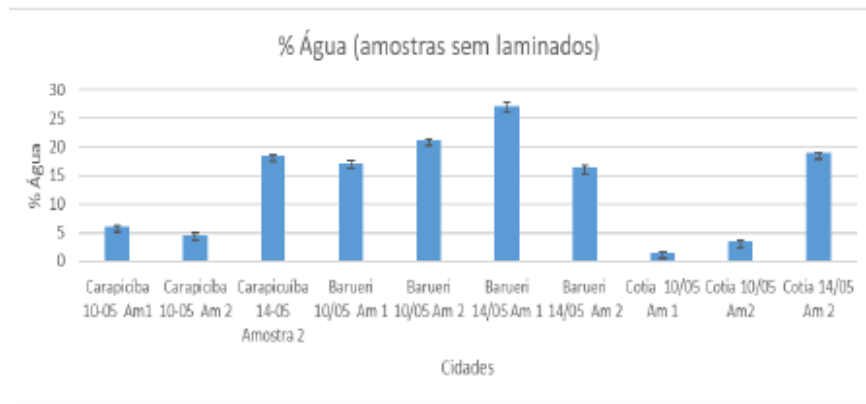
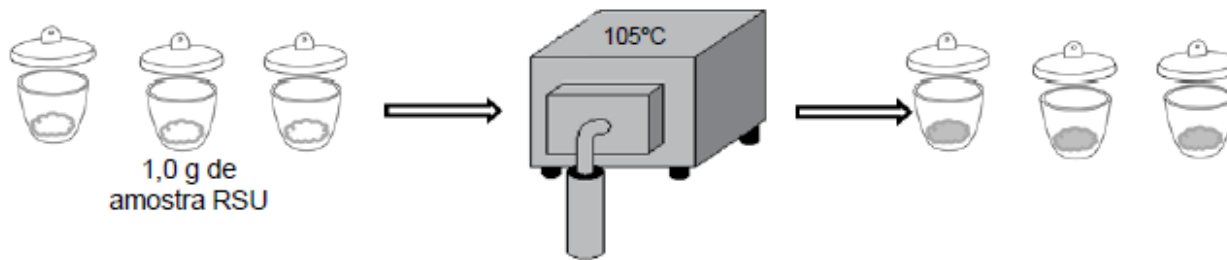
Recycling is the way to save us from plastic pollution. But not even recycling champion Germany has got it right. DW reporter Kai Steinecke follows the plastic stream into the heart of the German recycling industry to find out what's wrong with it.

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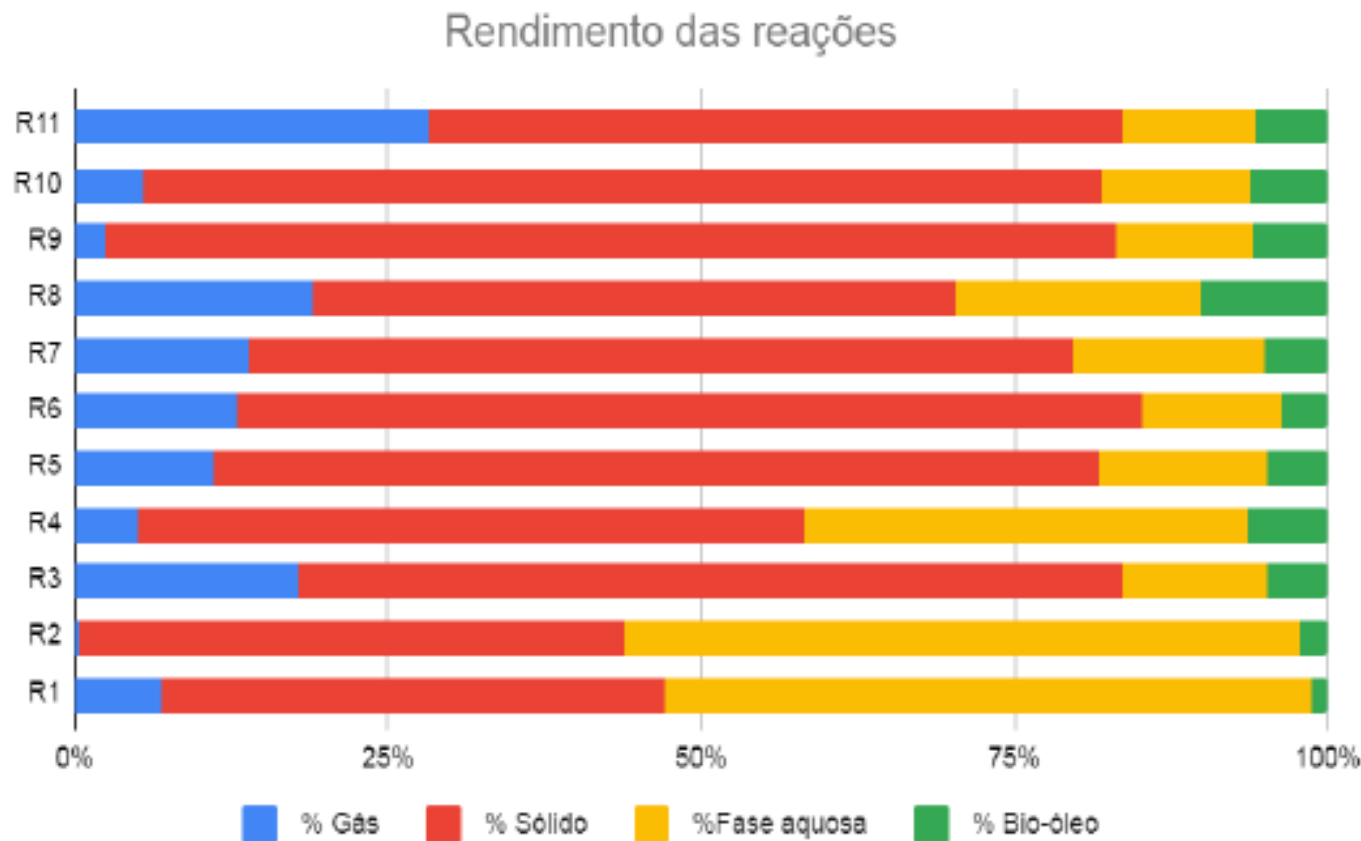


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O problema dos contaminantes (água).



O problema dos contaminantes (biomassa).



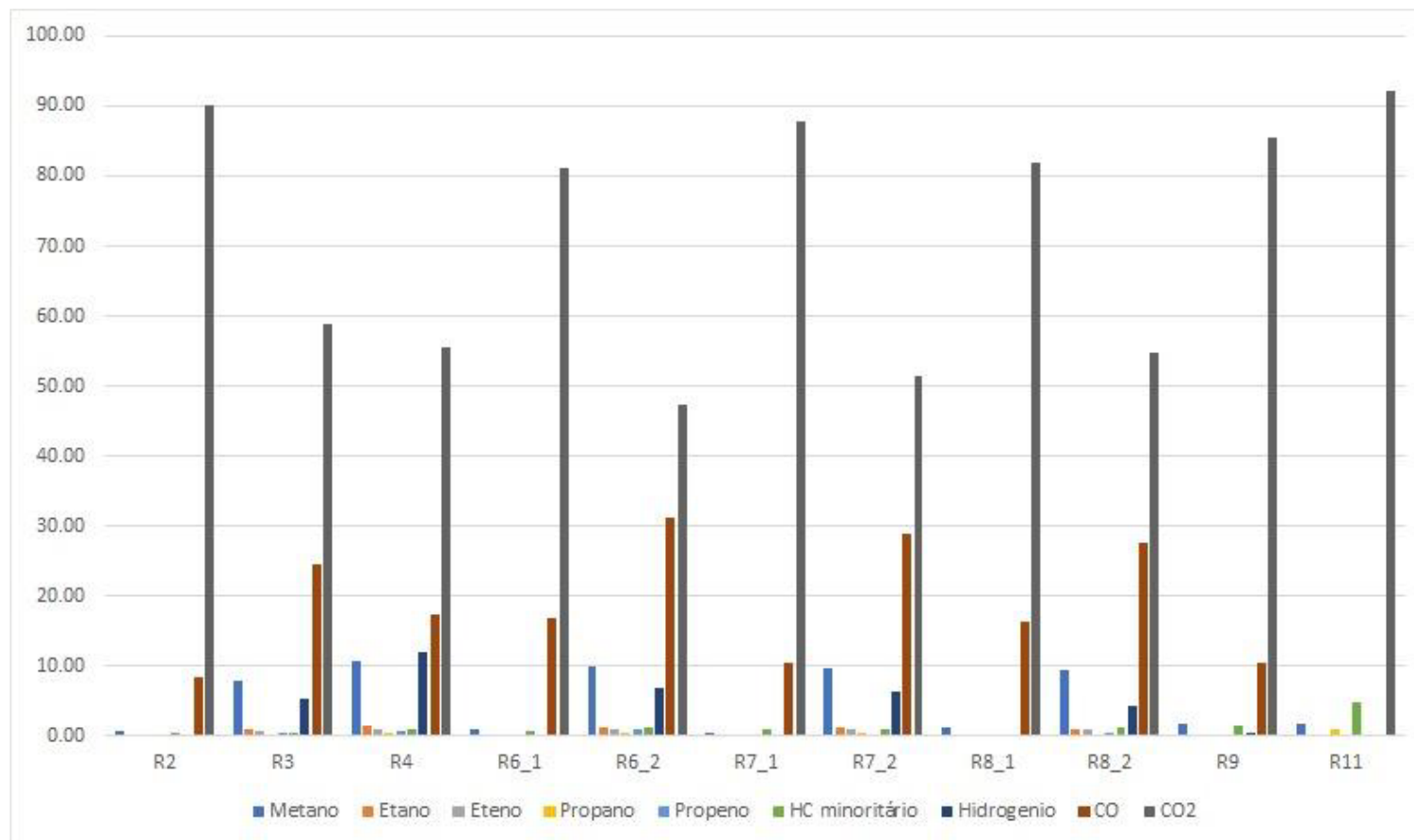
L. Almeida et al. (2021), to be submitted.

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O problema dos contaminantes (biomassa).



L. Almeida et al. (2021), to be submitted.

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O problema dos contaminantes (biomassa).

Resultados – Caracterização

- Poder Calorífico

Amostras	Repetição	PCS, MJ/Kg
RPR	A	9,9
	B	10,0
	Média	10,0
Resíduo Sólido	A	21,9
	B	21,7
	Média	↑ 21,8

Bio-óleo = 25 MJ/ kg

Diesel = 45 MJ/kg

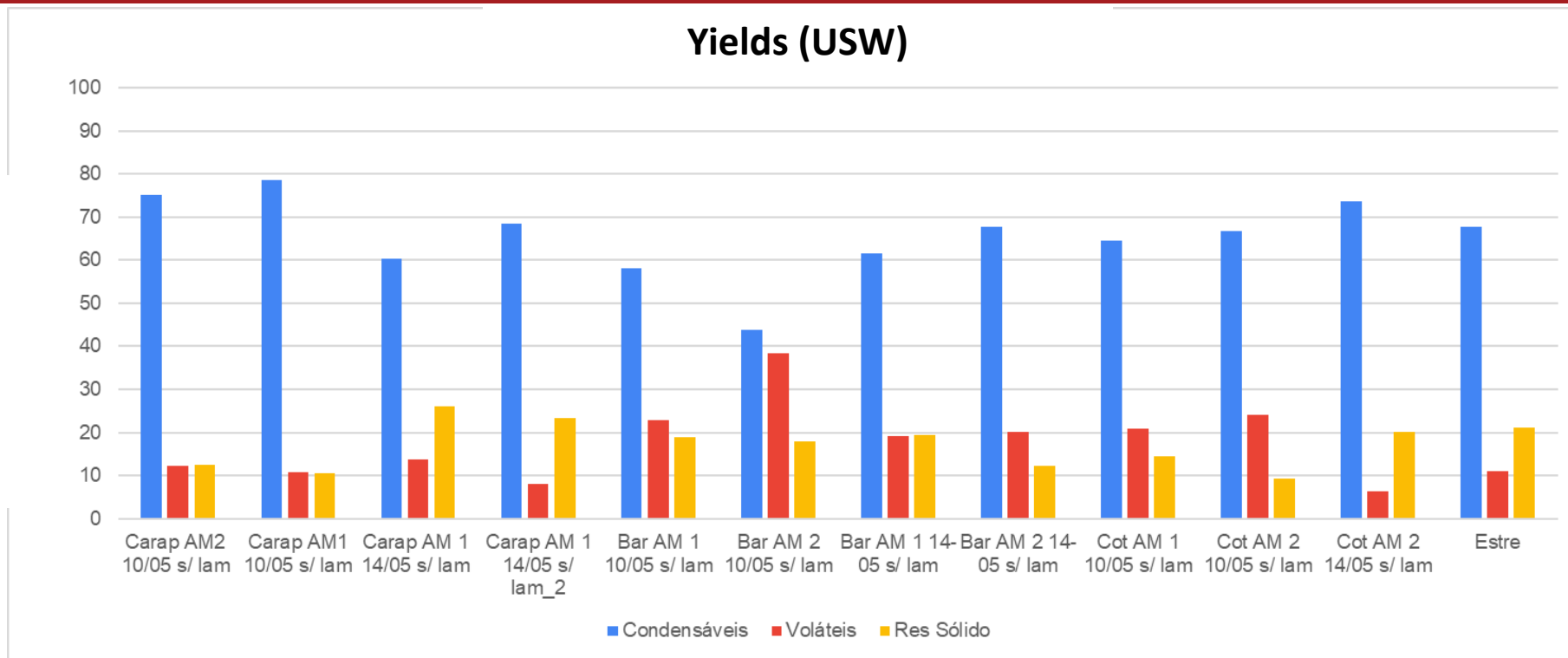
L. Almeida et al. (2021), to be submitted.

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O problema dos contaminantes (RSU).



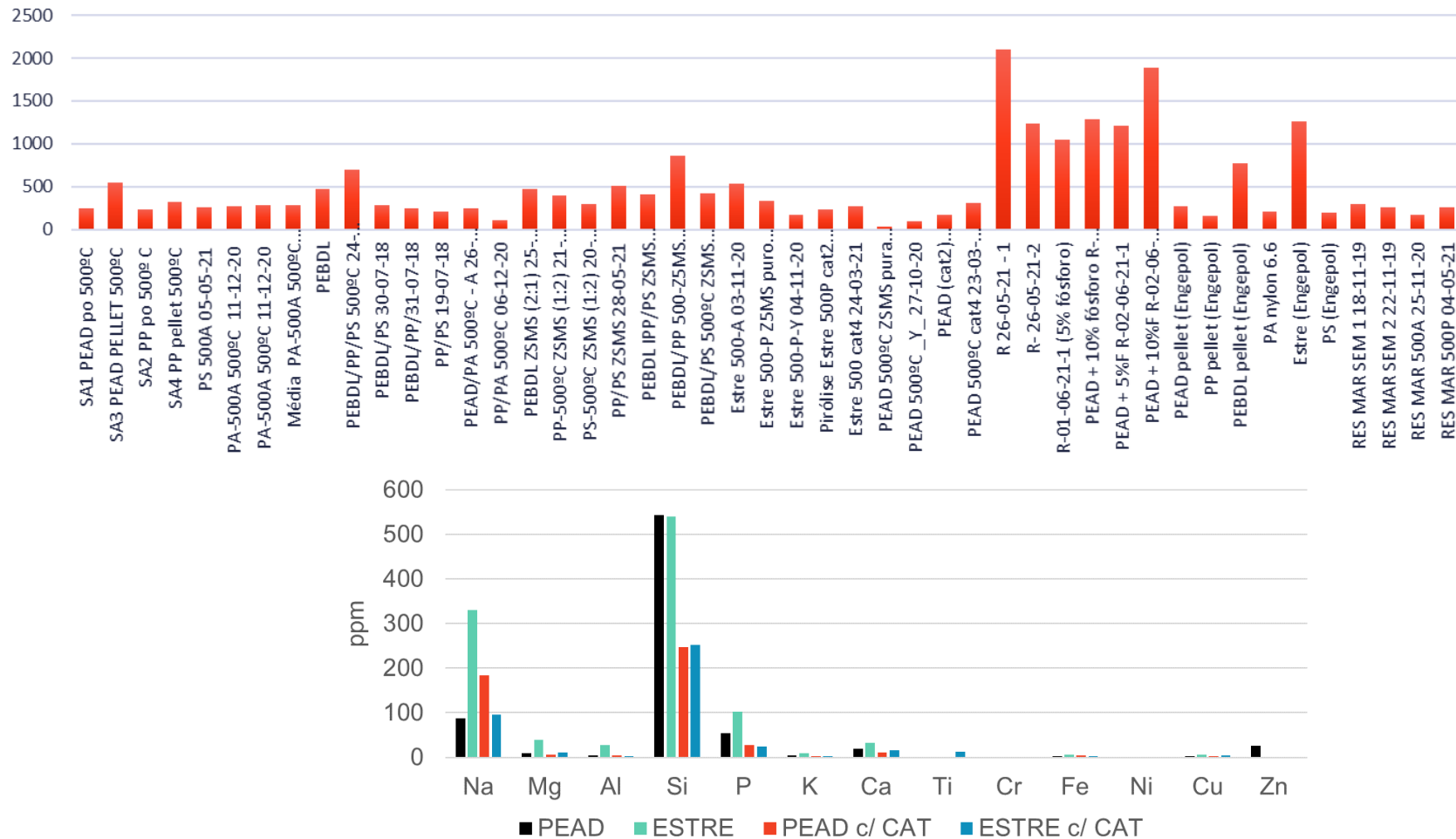
L. Almeida et al. (2021), to be submitted.

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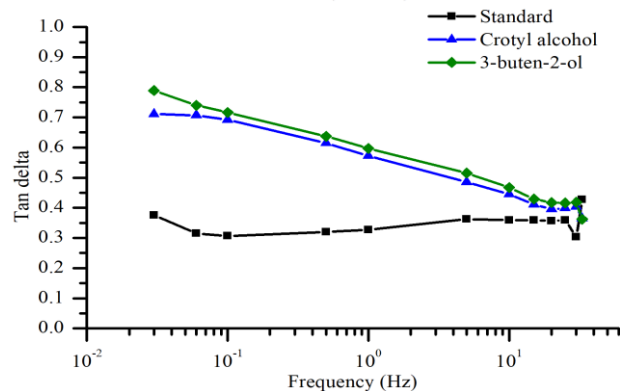
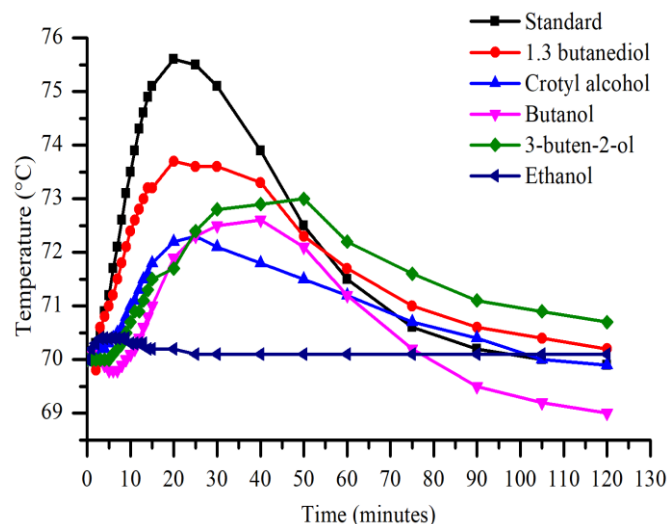
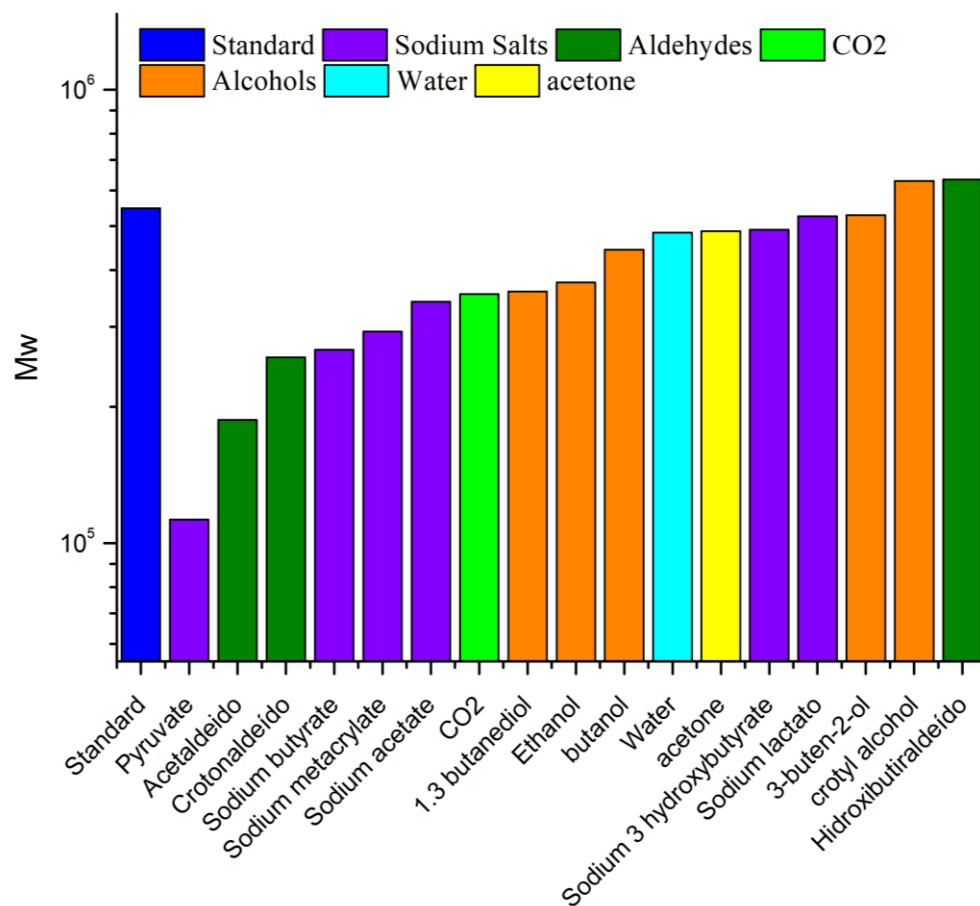
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O problema dos contaminantes (metais).



D.V. Miranda et al. (2021), to be submitted.

O problema dos (bio) contaminantes.



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A planta piloto.

Planta Piloto de Pirólise



Apoiado por:



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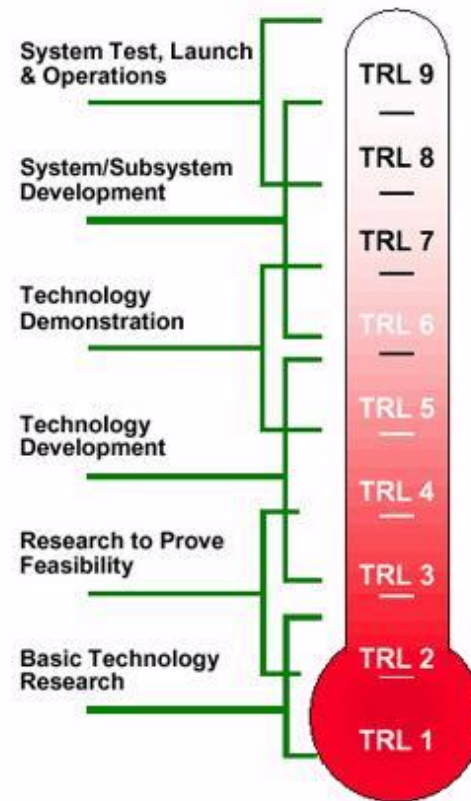
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Maturidade Tecnológica

A Escala TRL (Technological Readiness Level)



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Tecnologia	Vantagens	Desvantagens	Escala	Temperatura (°C)	Sensibilidade	TRL	Plantas em operação
Pirólise (craqueamento térmico)	○ Simplicidade ○ Flexibilidade do Processo ○ Possibilita que resíduos plásticos “não recicláveis” sejam despolimerizados	○ Reações complexas ○ Alta demanda energética ○ Baixa tolerância a PVC ○ Sensível a contaminantes na matéria-prima ○ Produtos requerem etapa de beneficiamento e “upgrade” antes do uso	Comercial	300–700	Alta	9	Mogami-Kiko, Japan, 3 tonnes/day, commercial scale operation
Pirólise Catalítica (craqueamento termocatalítico)	○ Em comparação à pirólise térmica: ○ Baixa temperatura de processo ○ Elevado rendimento do óleo ○ Menor tempo de reação ○ Pode reduzir custos de produção ○ Pode reduzir consumo energético ○ Produto com propriedades similares a combustíveis fósseis ○ Catalisador ajuda a otimizar a distribuição e seletividade do produto final ○ Possibilita 100% de conversão de resíduos plásticos	○ Sensível a contaminantes na matéria-prima ○ Cloreto e nitrogênio podem desativar o catalisador ○ Materiais inorgânicos presentes no resíduo (matéria-prima) podem bloquear os poros do catalisador ○ Requer pré-tratamento	Comercial	450–550	Alta	9	Sapporo/Toshiba, Japan 14.8 ktonnes mixed waste plastic/year, commercial scale operation
Pirólise por plasma	○ Temperatura alta o suficiente para decompor compostos tóxicos em produtos gasosos ○ Adequado para tratar RSU ○ Produtos gasosos com baixo teor de alcatrão e elevado poder calorífico ○ Formação de cloro livre de HCl	○ Alta demanda energética	Bancada	1800–10000	Baixa	4	Escala de bancada
Pirólise assistida por microondas	○ Distribuição uniforme de calor ○ Adequado para tratar RSU Em comparação com a pirólise convencional: ○ Taxas de aquecimento mais altas ○ Mais controle sobre o processo ○ Aumento da velocidade de produção	○ Sensível a grandes flutuações na composição de resíduos ○ Desafio do uso eficiente de absorventes dielétricos em escala industrial ○ Requer grandes volumes de matéria-prima para ser viável	Bancada	> 1000	Média	4	Escalas piloto e de bancada

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Tecnologia	Vantagens	Desvantagens	Escala	Temperatura (°C)	Sensibilidade	TRL	Plantas em operação
Gaseificação	○ Possível quebra de polímero muito detalhada: para hidrogênio e metano ○ Múltiplas aplicações do gás do produto ○ Adequado para resíduos plásticos mistos ○ Tecnologia bem estabelecida ○ A gaseificação de oxigênio puro gera syngas quase livres de nitrogênio atmosférico ○ A gaseificação a vapor resulta em syngas livres de nitrogênio que podem ser usados para aplicações de síntese e produção de novos produtos plásticos ○ Possível produção de hidrogênio a partir da gaseificação a vapor	○ O gás do produto requer melhoria da qualidade antes de ser usado novamente ○ Requer altos volumes de matéria-prima para ser viável ○ Alcatrão e carvão em produtos gasosos ○ Intensivo em custos e energia ○ A gaseificação pura de oxigênio requer separação de oxigênio do ar, o que custa muito dinheiro	Comercial	700–1200	Média	9	Enerkem, Edmonton, Canada, 100 ktonnes RDF/year, commercial scale operation
Gaseificação de plasma	Em comparação com a gaseificação convencional: ○ Maior pureza do gás do produto ○ Nível reduzido de alcatrão ○ Alta tolerância a matéria-prima de baixa qualidade ○ Controle de temperatura independentemente das flutuações nas propriedades da matéria-prima e na qualidade e fornecimento de agente gaseificador ○ Tecnologia bem estabelecida	○ Nenhuma operação comercial na indústria WTE, amplamente utilizada para decompor resíduos perigosos em escala comercial ○ Alto investimento e custos operacionais ○ Exigência de eletricidade muito alta	Comercial (na decomposição de resíduos perigosos)	1200–15000	Baixa	8	Comercial (na decomposição de resíduos perigosos)
Pirólise com reforma em linha	○ Produção de hidrogênio a partir do processo ○ Gás do produto isento de alcatrão ○ As impurezas nos resíduos de plástico não têm contato com o catalisador de reforma ○ Em comparação com a gaseificação convencional: ○ Temperatura mais baixa do processo ○ Menor custo de produção ○ Maior produção de hidrogênio do que a partir da gaseificação a vapor	○ O problema de desativação do catalisador precisa ser mais pesquisado e resolvido	Piloto	500-900	Média	8	Escala piloto
Hidrocraqueamento	Alta qualidade do produto de craqueamento	○ Alto custo de hidrogênio ○ Efeito de envenenamento após hidrocracking de PVC ○ Alto investimento e custos operacionais	Piloto	375–500	Alta	7	Escala piloto

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Pirólise (craqueamento térmico)	○ Simplicidade ○ Flexibilidade do Processo ○ Possibilita que resíduos plásticos “não recicláveis” sejam despolimerizados	○ Reações complexas ○ Alta demanda energética ○ Baixa tolerância a PVC ○ Sensível a contaminantes na matéria-prima ○ Produtos requerem etapa de beneficiamento e “upgrade” antes do uso	Comercial	300–700	Alta	9	○ Fração líquida/pesada (óleos, combustíveis, monômeros) ○ Fração sólida ○ Fração gasosa (C1 – C4)	Mogami-Kiko, Japan, 3 tonnes/day, commercial scale operation
Pirólise Catalítica (craqueamento termocatalítico)	○ Em comparação à pirólise térmica: ○ Baixa temperatura de processo ○ Elevado rendimento do óleo ○ Menor tempo de reação ○ Pode reduzir custos de produção ○ Pode reduzir consumo energético ○ Produto com propriedades similares a combustíveis fósseis ○ Catalisador ajuda a otimizar a distribuição e seletividade do produto final ○ Possibilita 100% de conversão de resíduos plásticos	○ Sensível a contaminantes na matéria-prima ○ Cloreto e nitrogênio podem desativar o catalisador ○ Materiais inorgânicos presentes no resíduo (matéria-prima) podem bloquear os poros do catalisador ○ Requer pré-tratamento	Comercial	450–550	Alta	9	○ Fração líquida/pesada (óleos, combustíveis, monômeros) ○ Fração sólida ○ Fração gasosa (C1 – C4)	Sapporo/Toshiba, Japan 14.8 ktonnes mixed waste plastic/year, commercial scale operation
Gaseificação	○ Possível quebra de polímero muito detalhada: para hidrogênio e metano ○ Múltiplas aplicações do gás do produto ○ Adequado para resíduos plásticos mistos ○ Tecnologia bem estabelecida ○ A gaseificação de oxigênio puro gera syngas quase livres de nitrogênio atmosférico ○ A gaseificação a vapor resulta em syngas livres de nitrogênio que podem ser usados para aplicações de síntese e produção de novos produtos plásticos ○ Possível produção de hidrogênio a partir da gaseificação a vapor	○ O gás do produto requer melhoria da qualidade antes de ser usado novamente ○ Requer altos volumes de matéria-prima para ser viável ○ Alcatrão e carvão em produtos gasosos ○ Intensivo em custos e energia ○ A gaseificação pura de oxigênio requer separação de oxigênio do ar, o que custa muito dinheiro	Comercial	700–1200	Média	9	○ Enriquecido em H₂, CO e CH₄	Energkem, Edmonton, Canada, 100 ktonnes RDF/year, commercial scale operation

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Reactor	Advantages	Disadvantages
Fixed bed reactors	- Simple construction and easy to build - Economical operation and maintenance of the unit - Two staged process for selective productions - Both thermal and catalytic processes are possible	- Temperature controls are difficult - Batch operation and scale up issues - Bed channelling causes uneven distribution of products - Coke deposition causes blockages and increase pressure drop
Fluidized bed reactors	- High heat and mass transfer and solid mixing regimes - Significant versatility on gas residence times - Liberty in product distribution – residence time - Continuous operation possible (scalable) - Both thermal and catalytic processes are possible - Maintenance costs are moderate	- Complex design and operation - Bed defluidization may occur - Melt plastic attaches to the surface of the bed particles. - A pilot plant is often necessary for scale up - Attrition of particle can be serious in CFB - Capital costs are higher for CFB than BFB
Fluid Catalytic Cracking (FCC)	- Widely used in conventional refinery (VGO to gasoline) - Two zones in the reactor - Hot particulate catalyst contact with feed creating cracking products and coked catalyst - Catalyst is regenerated by burning - Hot catalyst is recycled to the riser for additional cracking of feed - Feedstocks are cracked to gaseous components and further separated to fuel gas - Good solid polymer mixing	Large energy requirement
Screw/Auger kiln reactors	- Typically made up of tubular reactor and a screw conveyor. - Residence time can be varied by the varying the speed of the screw and length of the reactor - Spheres (metal/ceramic) avoid coke build up and improves heat transfer. - High amounts of thermoset materials (e.g. WEEE) can be pyrolyzed - Efficient removal of chlorine from the mixed waste - Selective zone heating from outside. - Several Rotary kiln commercial process are online (feedstocks biomass, municipal solid waste, Tires, shredder light fractions, WEEE, cables etc.)	Maintenance
Microwave thermolysis	- Attractive for efficient heat transfer - Temperatures can reach up to 1000 °C - Short residence time	- Plastic has to be mixed with heat adsorbent such as graphitic carbon or inorganic oxides - Poor mixing - Scale up is questionable

	Temp. control	Heat transfer	Particle size flexibility	Residence time flexibility	Process flexibility	Thermal mode operation	Catalytic mode operation	Value of obtained products	Scale-up flexibility	Economic feasibility
Fixed Bed	Red	Red	Orange	Orange	Red	Orange	Orange	Green	Red	Orange
BFB	Orange	Green	Orange	Orange	Green	Green	Green	Green	Orange	Orange
CFB	Orange	Green	Orange	Orange	Green	Green	Orange	Green	Orange	Red
Rotary kiln	Red	Red	Orange	Green	Orange	Green	Orange	Orange	Orange	Orange
Melting vessel	Red	Red	Orange	Green	Orange	Green	Orange	Orange	Orange	Red
Extruder	Orange	Red	Red	Red	Green	Orange	Orange	Green	Green	Orange

Green = good

Orange = satisfactory

Red = Poor

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Technology provider	Capacity (TPD)	Temperature (oC)	Products	Reactor
VadXX	60	365 - 488	Syncrude, diesel	Rotary kiln
Nexus	50		Light crude, diesel, gasoline, Kerosene blendstock, wax	Melting Vessel
Agilyx	10-50	400 - 530	Light synthetic crude oil	Dual screw reactor
Recycling Technologies	20	400 - 600	Low sulphur hydrocarbon Plaxx – wax	Fluidized Bed
Plastic Energy	20	300 - 450	raw diesel, light oil, synthetic gas components	Stirred-tank reactor (Vertical stirred with sieve membrane)
Susteen Technologies	12		Green Crude, Diesel, Gasoline and Jetfuel	Screw with recirculation
			Green Hydrogen	Thermo-Catalytic Reforming
			Anthracite Coal	
PHJK	12-14		Light crude oil	Rotary kiln
			Diesel	
Renewology	0.24	400 - 550	Crude oil	Rotary kiln
	10			
Pyrovac	1.2	< 550	Diesel and gasoline	Multiple Hearth Vacuum Reactor
	12		Diesel and gasoline	
				Idem
Re-oil (OMV)	2.4		Synthetic crude oil	Melting vessel
BP	1	500	Light and heavy wax	Fluidized bed
Pyrowave (600 CMD)	0.1-0.2		Styrene monomers from PS	microwave catalytic depolymerization
BASF	0			Tubular
NKT				
Berliner	55			
Plastic Advanced Recycling Corporation – PARC*	30	280 - 500	Oil and gas	

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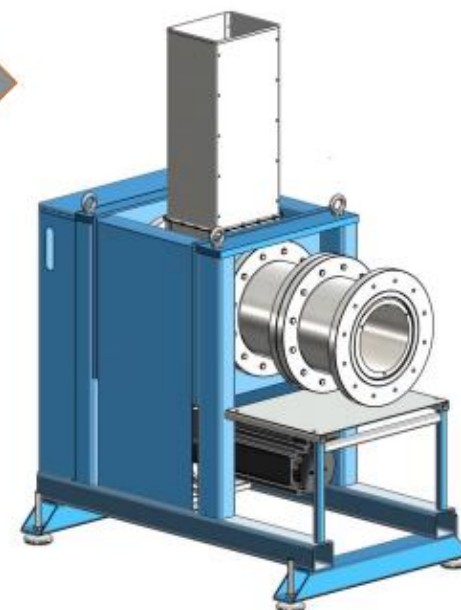
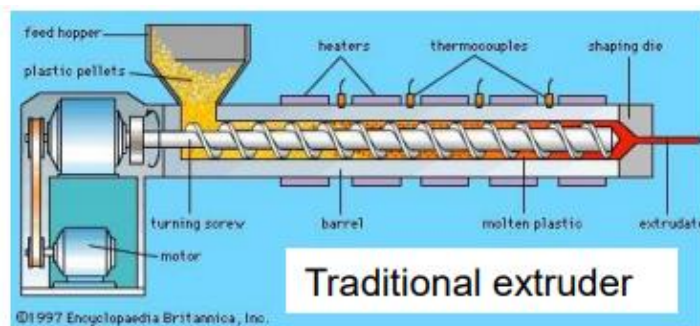
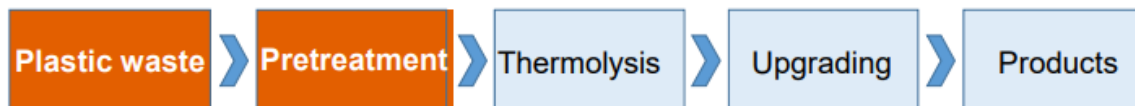
Technology provider	Capacity (TPD)	Temperature (oC)	Products	Reactor
Noell	40			
Serpac	45			
Pacific Pyrolysis	10		Biochar	Rotary Klin
Spainex Ltd	20		Tyre oil, gas	Rotary Klin
Kouei Industries	16		Tyre oil, gas, and char	Fixed bed / batch
T-Technology (POL)/ Polymer Energy (USA)	0.03	180 - 300oC (1st stage), 350 - 400 oC (2o stage)		
Fuji	14	390	Gasoline, kerosene, diesel oil	Two-stage / Extruded plastics mixed with returning uncracked plastics and transported to cracking reactor
MCC	1 - 2		Pyrolysis oil	STR (induction heating, batch or continuous reactor available. Reformer optional)
NiuTech	80	380 - 500	Oil, carbon black	Rotatory
Res Polyflow	Unknown	315 - 650	Oil, gas, carbon black	Rotatory
Agylix	10	400 - 530	Oil and gas	Stirred
Recycling Rechnologies	25	400 - 600	Plaxx and gas	Fluidized bed
Cassandra Oil	20 - 40	490 - 550	Oil, gas, carbon black	Rotatory or fluidized bed
Resynergy				
Recenso		400	Oil, gas	Rotatory
Thermofuel / Cynar	20	300 - 425	Oil, gas, coke	STR
Klean Industries	50	350 - 450	Oil, gas, carbon black	Rotatory or fluidized bed
Plastic2Oil				
PyroMelt		500 - 600		
Beston	6 - 30	280 - 350	Oil, carbon black	Rotatory
PYROPLEQ		450 - 500	Energy	
Akzo Novel	0,72	700 - 900	HCl, CO, H2, CH4	
PKA-Kiener	70	450 - 500	Gas, energy	

Technology provider	Capacity (TPD)	Temperature (oC)	Products	Reactor
Siemens - KWU		450 - 500		
DBA process		450 - 500	energy	
Kobe Steel		450 - 500	oil and gas	
Ebara		unknown	energy	
Mogami-Kiko	1 - 3	unknown	Pyrolysis oil	Stirred Tank Reactor (STR) (dechlorination in situ, vertical char vacuum line, fractionated condensation)
Hitachi-Zosen		unknown		Stirred Tank Reactor (STR) (vertical char removal, vacuum line)
Royco Beijing	6	unknown		Infrared ray heating rods, emulsification of heavy oil fraction
Chiyoda / PWMI		unknown		STR (dechlorination in reactive extruder)
Sappro / Toshiba	38 - 50		Pyrolysis oil	Rotary Klin with Ceramic Balls for Char Removal (dechlorination in reactive extruder)
ALTIS	unknown			Batch dry distillation process for medical waste, removable inner vessel, post pyrolysis dechlorination
Gossler Evitec	2			STR with optional catalytic upgrading
Nanofuel		270 - 370		
Reentech	16	350 - 400	Gasoline, kerosene, diesel	Moving bed catalytic cracker (with catalyst regeneration) (catalytic melting and dehalogenation with catalyst impeller)
Nikko		200 - 250		
Mazda		200 - 450		
Amoco		490 - 580		
Smuda-Eko	27	350		STR
Zadgaonkar		350		
Spalinex				Rotary kiln (Pretreatment to remove PVC and PET from MPW)
Kankyo Tec				Batch tank reactor (vacuum residue removal, halogen feedstocks not acceptable)

EngeCol

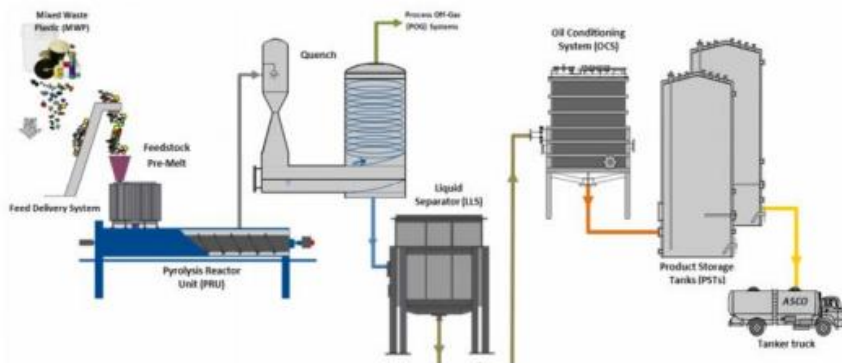


EngePol



agilyx

Reduces. Produces. Creates.



Schematic flow diagram of the Agilyx process

- Continuous non-catalytic
- Self cleaning dual screw reactor
- Currently operational 10 TPD, pilot scale
- Light sweet synthetic crude is the main product sold to a refinery

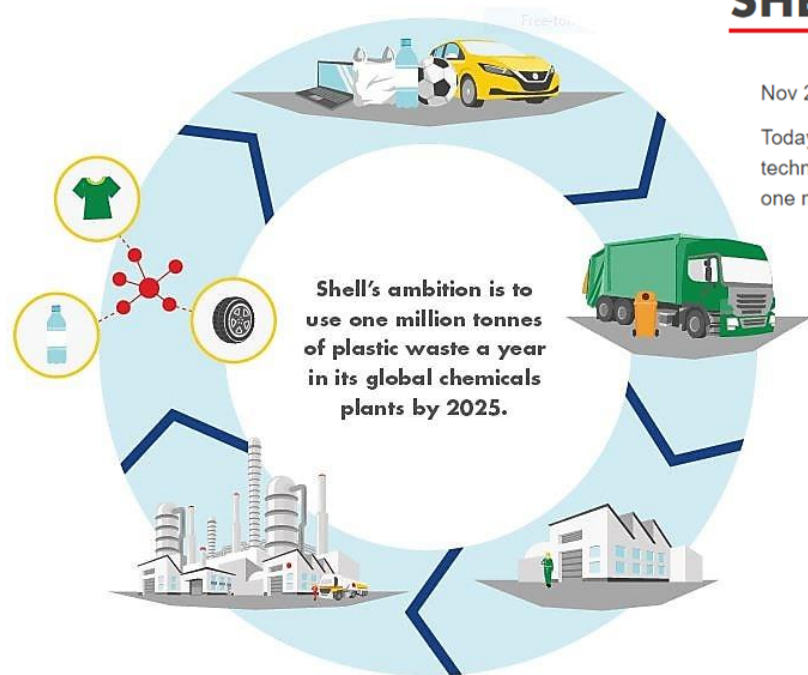
Perspectivas

Pirólise no setor de óleo e gás

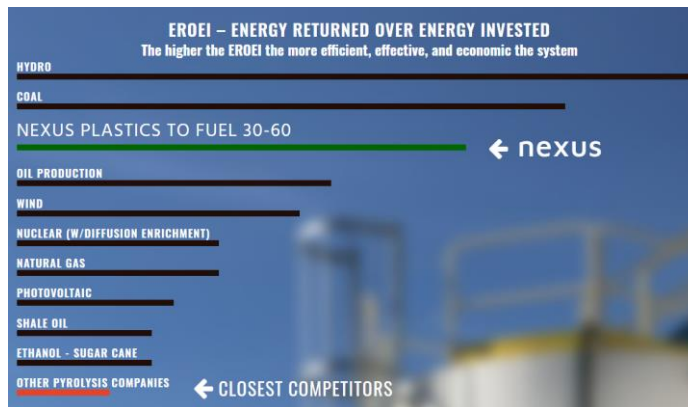
SHELL USES PLASTIC WASTE TO PRODUCE CHEMICALS

Nov 21, 2019

Today Shell announced it has successfully made high-end chemicals using a liquid feedstock made from plastic waste. The technique, known as pyrolysis, is considered a breakthrough for hard-to-recycle plastics and advances Shell's ambition to use one million tonnes of plastic waste a year in its global chemicals plants by 2025.



<https://www.shell.com/business-customers/chemicals/media-releases/2019-media-releases/shell-uses-plastic-waste-to-produce-chemicals.html>



<https://www.nexusfuels.com/>



Contato

Obrigado !!!!

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