The role of slags and other by-products within circular economy in the steel industry

- Steel slags utilization as multipurpose and low-cost catalysts
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ESTEP Focus Group Circular Economy & FEhS-Institute

European Steel Technology Platform

INSTITUT FÜR BAUSTOFF FORSCHUNG

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Introduction: Acciaierie d’Italia

Acciaierie d'Italia is one of the largest steel groups in Italy. The company operates **eight sites** across the country, with its facilities covering a total area of over 17 million square meters and employing more than 10,000 people, in addition to workers from related industries.

Novi Ligure works
Capacity 1.750.000 ton
Cold rolled coils (batch annealing or continuous annealing)
HDGalvanized coils
HDAlluminazed coils
Electrogalvanized coils

Paderno Service Center
Narrow strips and sheets

Genova works
Capacity 1.250.000 ton
HDGalvanized coils
Tinplate and TFS
Pickled coils

The **Taranto plant** is strategically important in the production route of Acciaierie d'Italia and represents the **core of its production**.

ADI Taranto plant is the only Italian steel plant with an integrated route. **Other facilities** include:

- two hot strip mills and a plate mill;
- a tandem cold rolling mill;
- two hot galvanizing plants;
- pipe mills plants.

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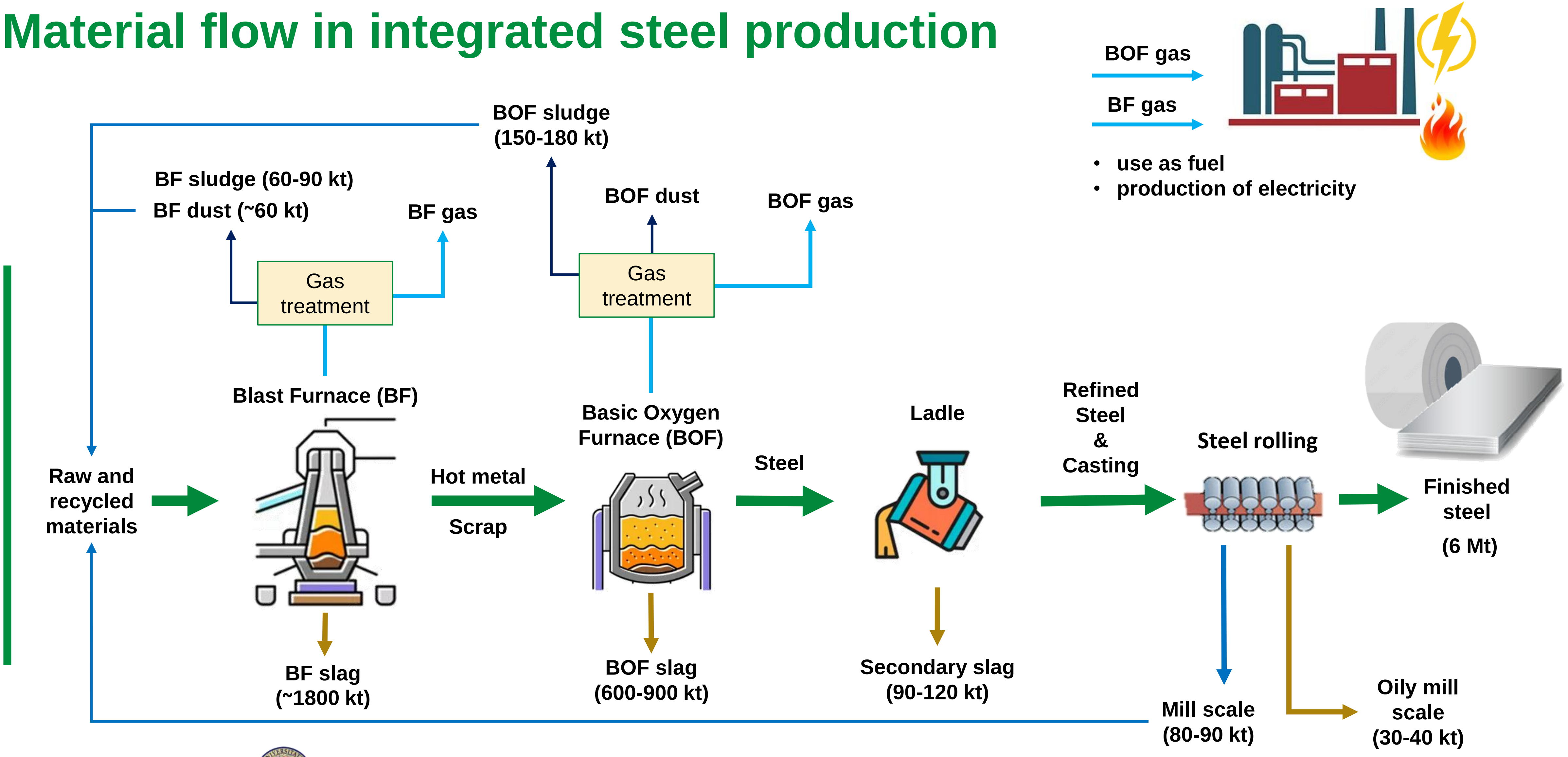
Material flow in integrated steel production



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*The quantities of materials refer to the production of **6 Mt** of finished steel per year

Introduction: the topic

Steel slags, due their content of various metal oxides and minerals, have the potential to act as sustainable **catalysts for the production of renewable fuels**, even **without the application of chemical, thermal, and doping treatments**.

Once industrialized, these applications will contribute to:

- **Decarbonization of fuel-based systems**, substituting fossil fuels with renewable ones produced using slag-catalyzed processes.
- **Reduce costs and emissions** from the production and disposal **of traditional catalysts**. They are often made of precious materials while slag is a cheap and abundant material.
- **Decrease the residues production of steelmaking sector** using a part of slag as secondary raw material in catalytic systems.

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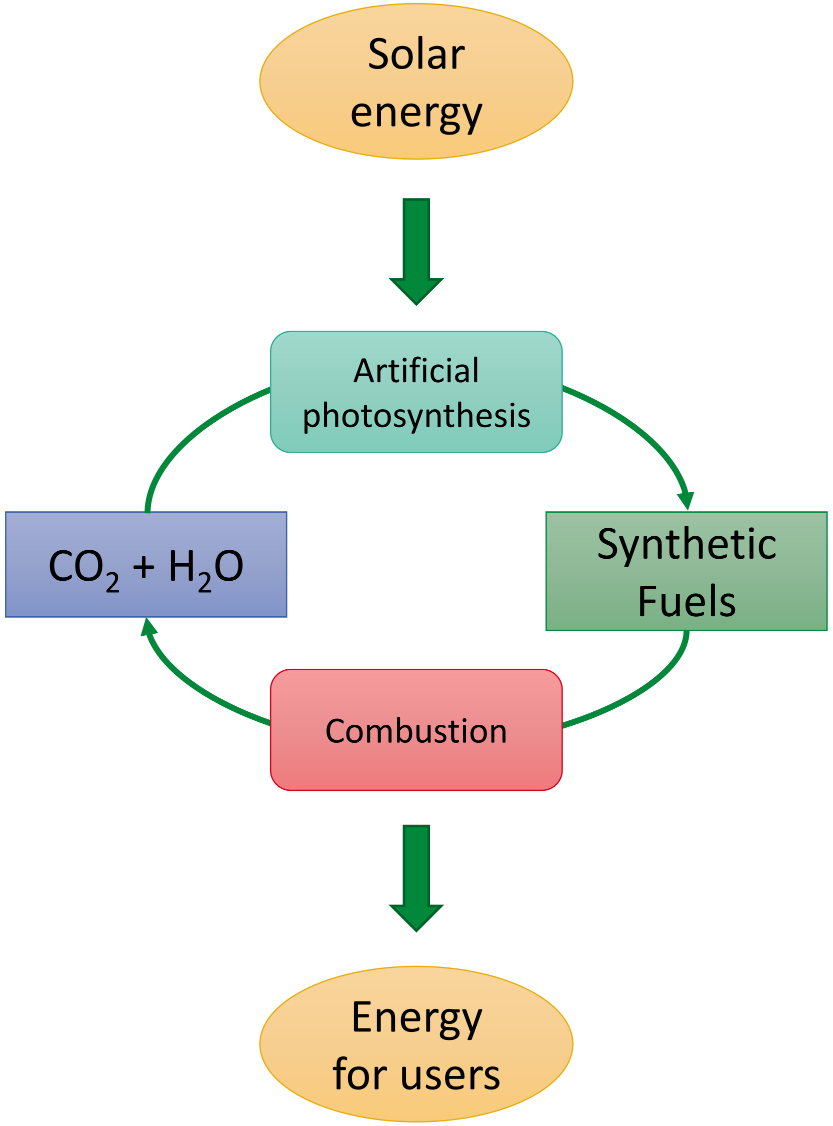
Introduction: renewable fuels

“Renewable fuels” are fuels produced using renewable energy or biological resources:

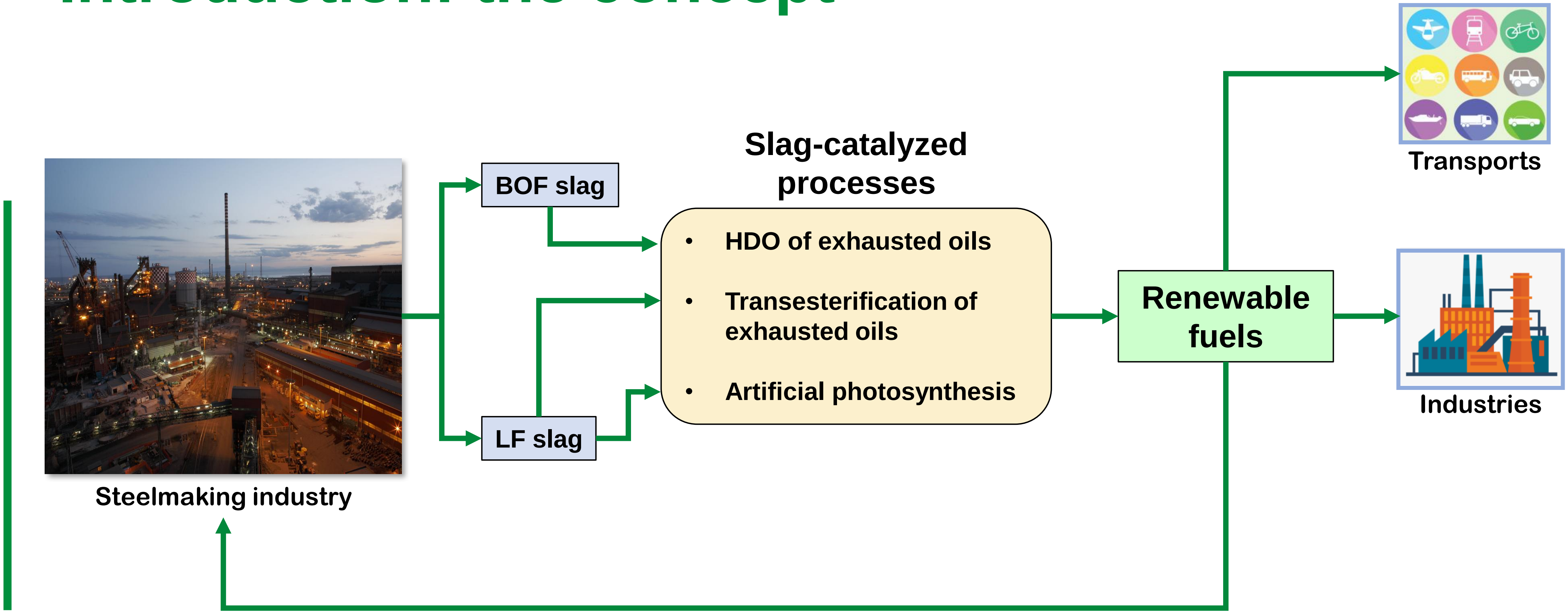
Biological fuels: produced by vegetable sources and waste (like exhausted oils).

Synthetic fuels: obtained converting renewable energy into chemical energy transforming H_2O, CO_2 or both.

The figure shows how **renewable synthetic fuels act as vectors of renewable energy** avoiding emission of CO_2, which is locked in a cycle.



Introduction: the concept



There are ongoing studies to recycle exhausted catalyst for civil applications.

Introduction: state of the art and innovations

Catalyst	Main Solar fuel	$\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$	Reference
CdS, ZnS	HCOOH	320	Nanomaterials 2020, 10 (12), 2422
CuO/ZnO/zeolite	HCOOH	907	J. Phys. Chem. Solids 2021, 151, 109917
Eu-MOF	HCOOH	304	J. Am. Chem. Soc. 2021, 143, 16, 6114–6122
Steel slag	HCOOH	480	[2]

Comparison table of catalysts in **artificial photosynthesis** for the production of formic acid

Metal	support	feedstock	Conditions	Conversion	Hydrocarbon Yield (%) / Selectivity	Reference
Noble metals						
Pd	C	Stearic acid	280 °C, 18 bar	>99%	HDO/DCN 0:100	Appl. Catal. A Gen. 355 (1–2) (2009) 100–108
Pt	ZrO_2	Palmitic acid	260 °C, 12 bar	>99%	HDO/DCN 29/61	Chem. - A Eur. J. 19 (15) (2013) 4732–4741
Non-noble metals						
Ni	ZrO_2	Palm oil	300 °C, 30 bar	92%	88% (C15-C18)	Fuel Process. Technol. 209 (August) (2020),
Co	SiO_2 or Al_2O_3	Palmitic acid	260 °C, 20 bar	99%	52% (C15)	Catal. Commun. 129 (December) (2018) 2019
Fe	-	Oleic acid	350 °C, 40 bar	80%	78% (C15-C18)	J. Anal. Appl. Pyrolysis 155 (2021) 105044,
Steel slag		Palmitic acid	340 °C, 16 bar	>99%	90% (HDO-C16)	In progress

Comparison table of catalysts in **HDO** for the production of green diesel

Regarding the **transesterification** process, steel slag would allow the replacement of current industrial basic catalysts such as NaOH and KOH.

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Experimental campaigns in cooperation with University of Bari

Various experimental campaigns were conducted at laboratory scale and the following results are published in scientific papers:

1. For the first time, **secondary slag** is used as a catalyst without undergoing any preliminary chemical or thermal modifications for **biodiesel production** by transforming vegetable oils. [1]
2. **Secondary slag** has also demonstrated its catalytic effectiveness in the CO_2 photoreduction process, exploiting the so-called **artificial photosynthesis.** [2]
3. Instead, **BOF slag** has been successfully used in the laboratory to produce **green diesel**, through the hydrodeoxygenation (HDO) of vegetable oils. [3]

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1. Steel Slag as New Catalyst for the Synthesis of FAMEs from Soybean Oil

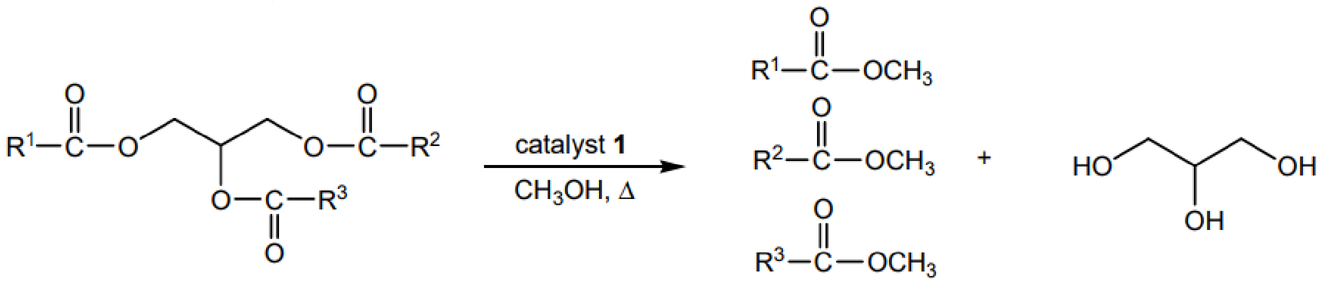
General information

Catalyst: In this work, **secondary slag** was used as catalyst without any chemical or thermal treatment but exclusively ground below 60 microns.

Raw materials: **Soybean oil** (used as a reference with the aim of using exhausted oils) and methanol

Process and conditions: The selected process is **transesterification** in a batch reactor. Each test is conducted using 0.5 mL (0.415 g) of soybean oil and 4 mL of methanol (MeOH/oil ratio = 8), while the controlled parameters are time, temperature and catalyst concentration. The biodiesel yield is considered for the process evaluation.

Products: **Biodiesel** (FAMEs - Fatty Acid Methyl Esters) and glycerol



triglycerides FAMEs glycerol

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1. Steel Slag as New Catalyst for the Synthesis of FAMEs from Soybean Oil

Results

Temperature	Reaction Time	Catalyst Weight	Yield*
°C	Hrs	mg	%
95	12	25	55,5
95	12	25	56,0
95	12	25	54,3
120	12	10	91,9
120	18	25	100,0
120	6	25	21,5
70	18	25	18,4
95	6	10	4,0
95	18	40	100,0
70	12	10	9,2
70	6	25	2,5
95	18	10	96,7
95	6	40	6,5
120	12	40	71,2
70	12	40	3,5

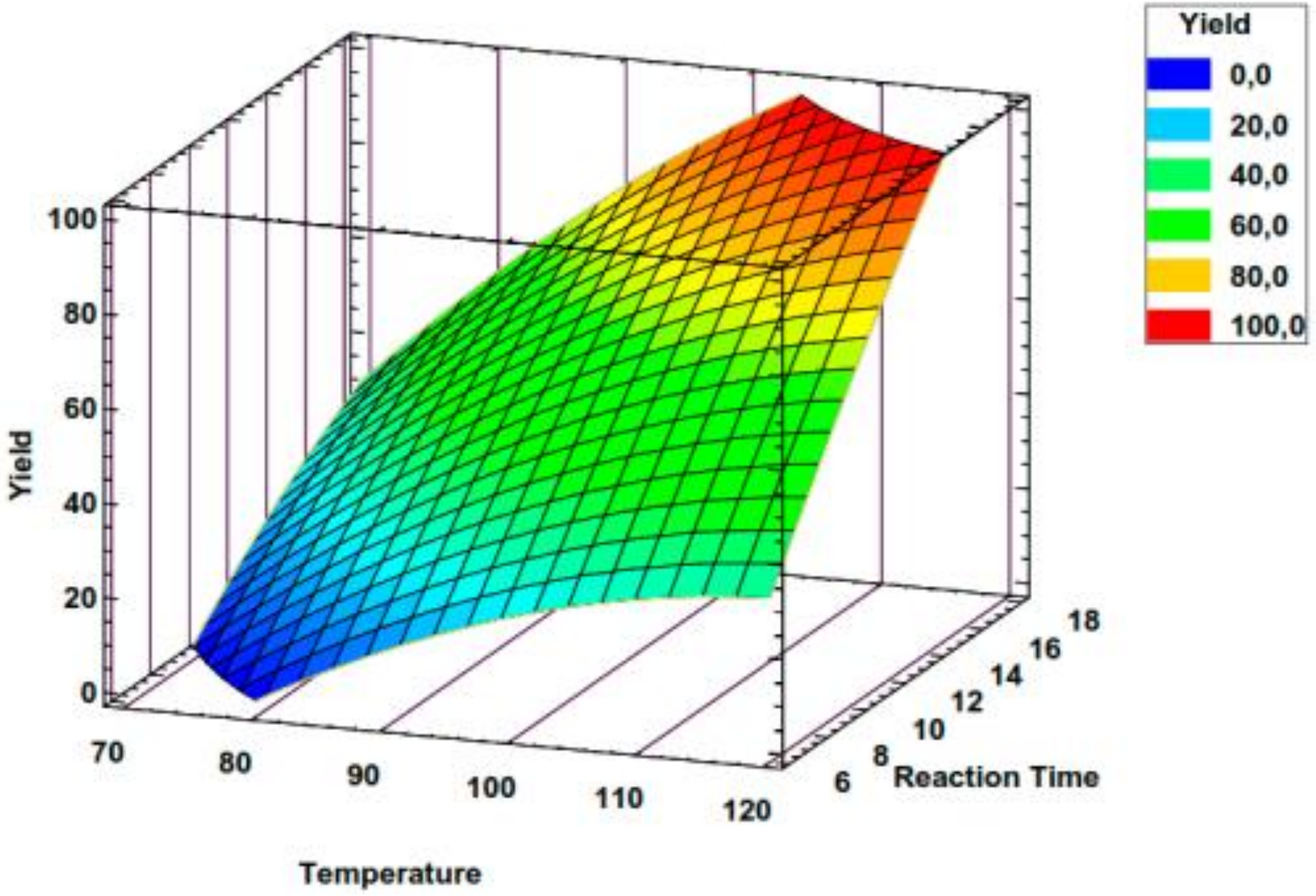
0.5 mL (0.415 g) of soybean oil and 4 mL of methanol (MeOH/oil ratio = 8)

1. Steel Slag as New Catalyst for the Synthesis of FAMEs from Soybean Oil

Results

Cycles	Yield %
1	100
2	70
3	67
4	13
5	15

Time = 18 h
Temperature = 100 °C
After each test, the catalyst was washed with methanol, dried at 50 ◦C, and reused for the next run.



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2. Steel slag as low-cost catalyst for artificial photosynthesis to convert CO_2 and water into hydrogen and methanol

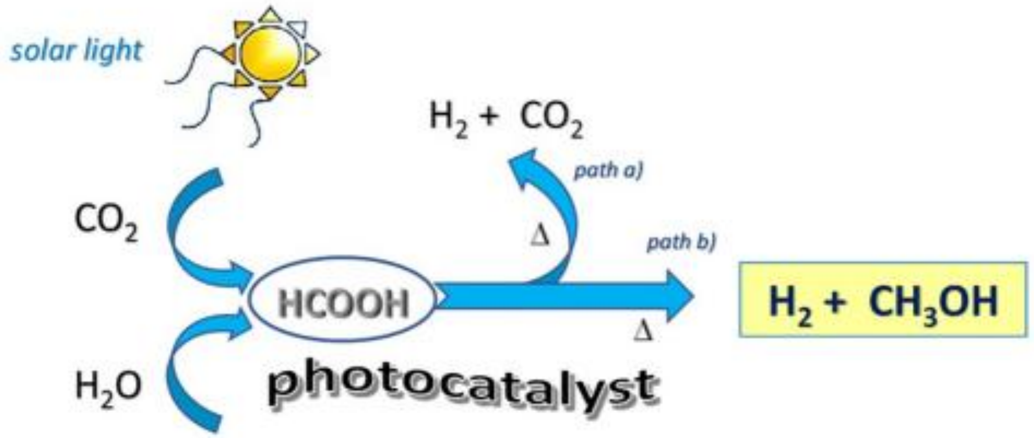
General information

Catalyst: Ground **secondary slag**

Raw materials: CO_2, Water

Process and conditions: **Artificial photosynthesis** to produce formic acid and its **thermal decomposition**.
Artificial photosynthesis conditions: 30 mg of catalysts in water (saturated with CO_2) suspension volume=20 mL, T=25 °C, irradiation time=5 h. Irradiation source: Sanolux (UV/Vis), Halogen (Vis)
Thermal decomposition conditions: 100 mL of Formic acid 0.44 M, T=250 °C, t=6 h. TOF evaluated as mmol of HCOOH converted/mmol of cat.

Products: **Formic acid, Hydrogen-rich syngas**



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2. Steel slag as low-cost catalyst for artificial photosynthesis to convert CO_2 and water into hydrogen and methanol

Results

Entry	Catalyst	Irradiation source[a]	HCOOH[b] μmol g^{-1} h^{-1b}
1	Slag	Sanolux (UV/Vis) Halogen (Vis)	480
2	**1**	Sanolux (UV/Vis) Halogen (Vis)	540

Entry	Catalyst	Conv[a]	Gas phase composition (%)			CH_3OH (Yield%)[a]	TOF[b]
			H_2	CO	CO_2		
1	–	70	46	3.5	42	–	–
2	Steel slag	95	39	11	38	–	–
3	**1**	95	32	traces	27	6	9

Recycling tests

a) Reaction conditions: saturated CO_2-bidistilled water (30 mL), catalyst 1 (45.32 mg), T = 25 °C, irradiation time = 5 h.

b) Reaction conditions: formic acid suspension of 1st step heated in an autoclave reactor at 250 °C for 6 h

Cycle	1st step: CO_2 photoreduction[a]	2nd step: thermal conversion of HCOOH[b]		
			Products yields(%)	
	HCOOH (M)[c]	HCOOH Conv. (%)	CH_3OH	H_2
1	2.9×10^{-3}	98	43	31
2	3.5×10^{-4}	53	32	21

Catalyst 1 is slag doped with palladium

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3. Steel Slag as Catalyst for Green diesel production

General information

Catalyst: **BOF slag** was ground and sieved in the following fractions: >1600 µm, 800-600 µm, 800-500 µm, 500-210 µm, and 210-90 µm, without any chemical or thermal treatment. The fraction 90-0 µm obtained is negligible.

Raw materials: **Palmitic and stearic acids,** hydrogen

Process and conditions: The involved process is **hydrodeoxygenation (HDO).** The experimental set-up was calibrated to handle 100 - 500 mg of fatty acid, under a hydrogen pressure of 16 bar, reaction time = 10h. The effect of temperature, solvent, substrate and slag fraction was evaluated.

Products: **Green diesel** (alkanes C16 and C18)

Hydrogen (g)/Palmitic acid (wt/wt) = 1/42.7

Hydrogen (g)/Hexadecane (wt/wt) = 1/37.7

$$C_{15}H_{31}\text{-}COOH + 3\,H_2 \xrightarrow{\text{slag catalyst}} C_{16}H_{34} + 2\,H_2O$$

palmitic acid — hexadecane

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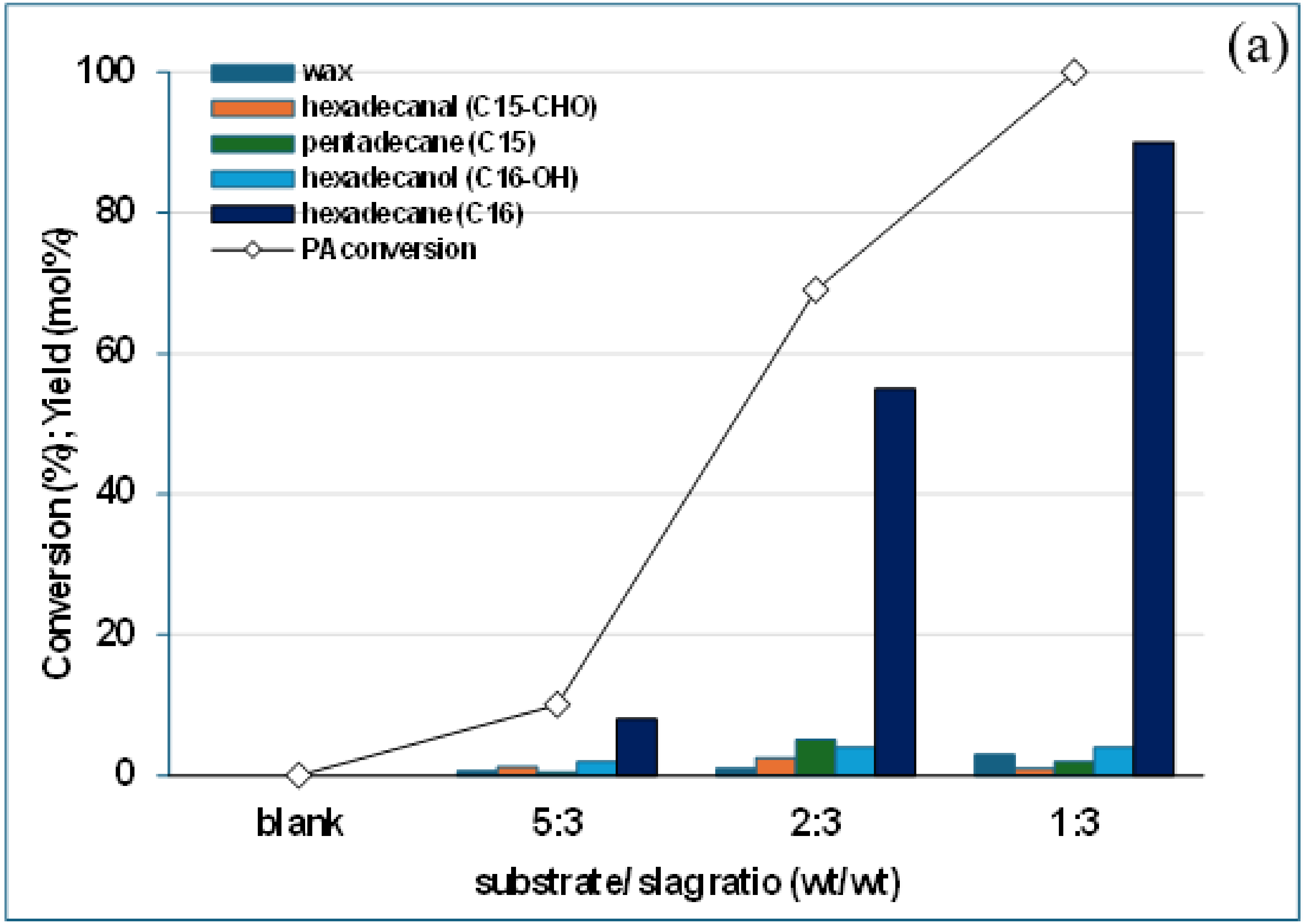
3. Steel Slag as Catalyst for Green diesel production

Results

Influence of the substrate/slag ratio (wt/wt): substrate (PA) 100 – 500 mg, slag catalyst (sizes > 1600 µm) 300 mg, solvent (hexane) 5 mL, T= 260°C.



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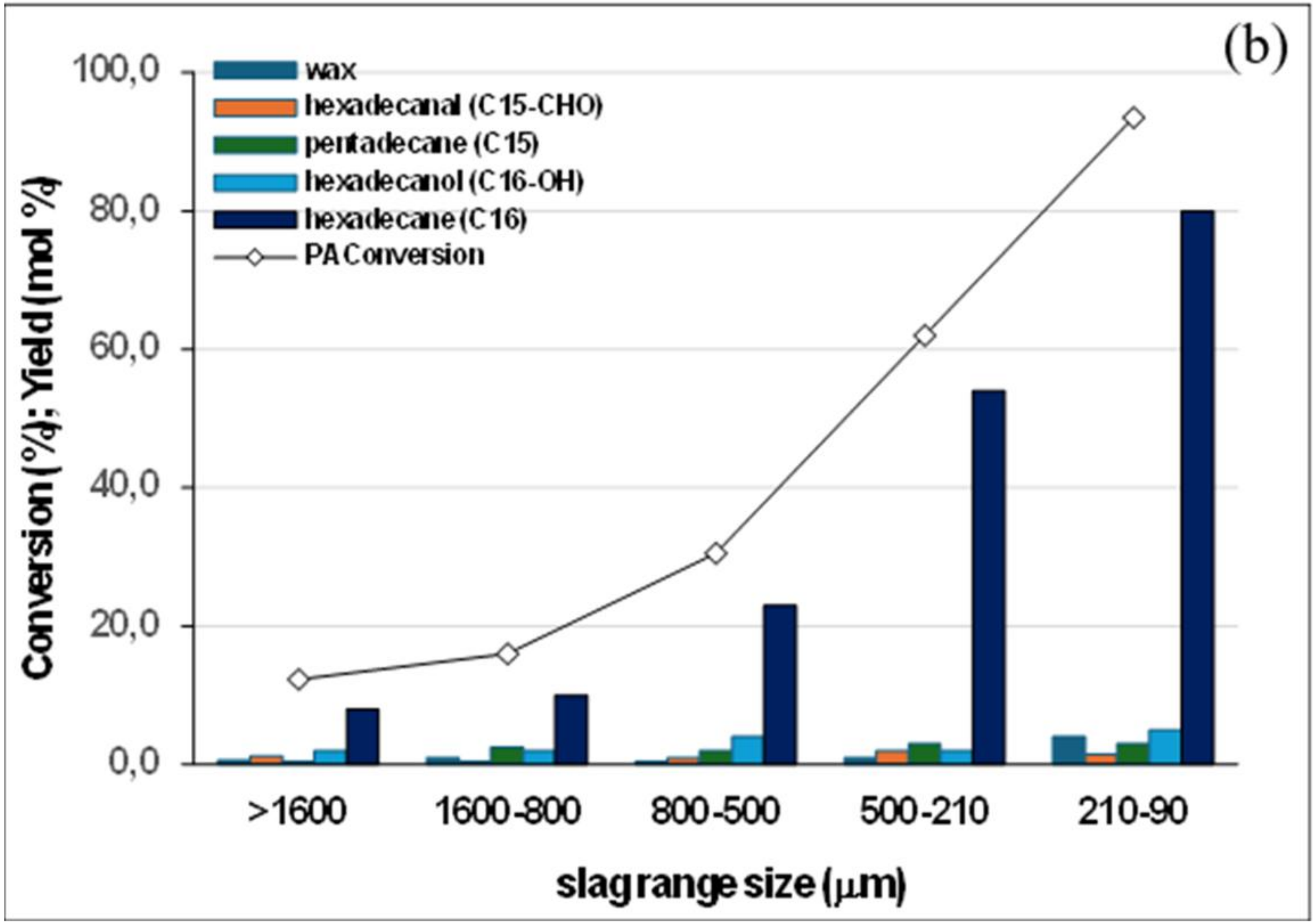
3. Steel Slag as Catalyst for Green diesel production

Results

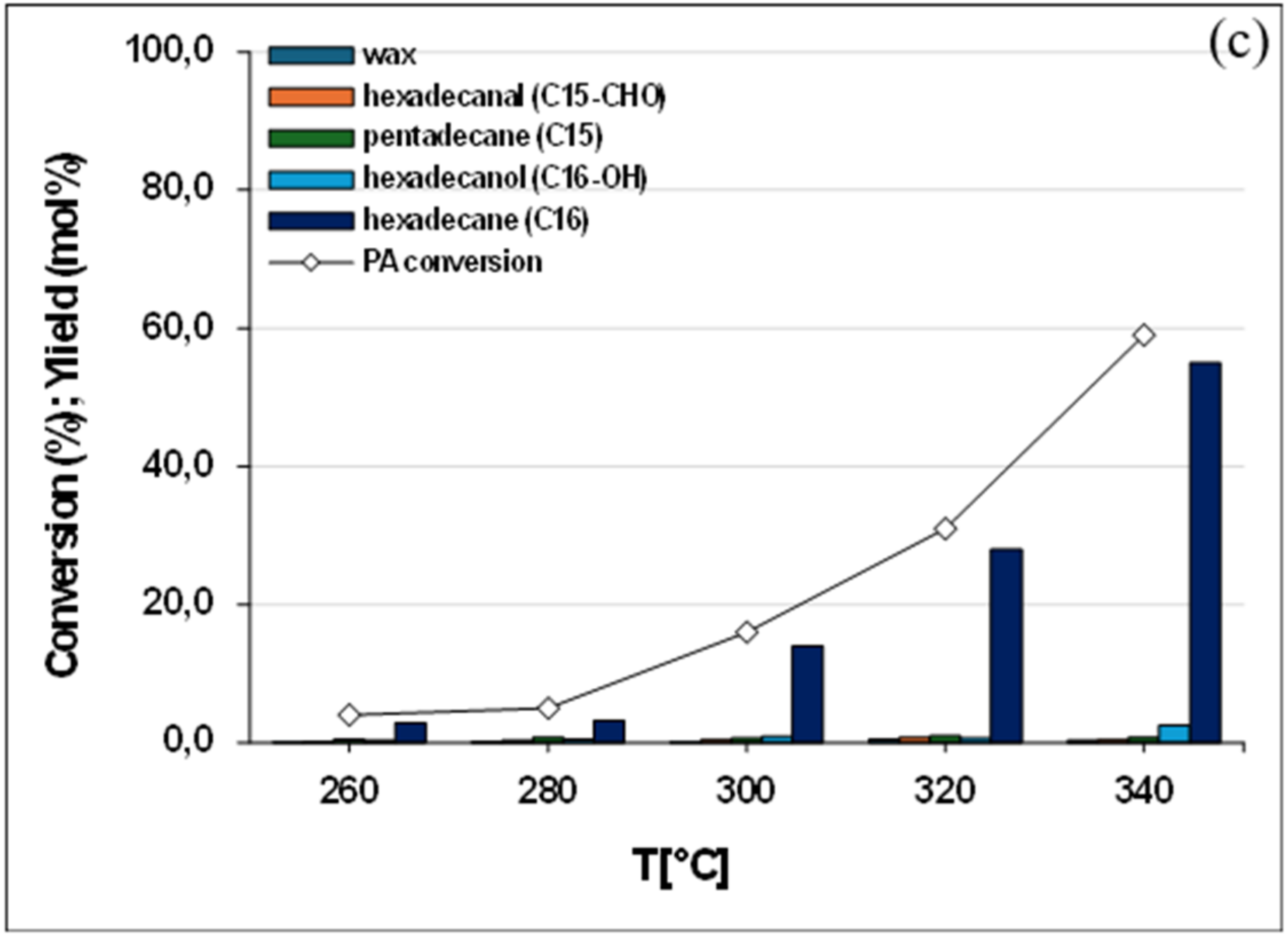
Influence of the slag particle sizes: substrate (PA) 500 mg; slag catalyst 300 mg, solvent (hexane) 5 mL, T= 260°C.



3. Steel Slag as Catalyst for Green diesel production

Results

Temperature dependence: substrate (PA) 500 mg, slag catalyst (210-90 µm) 100 mg (5:1 wt/wt), solvent (hexane) 10 mL.



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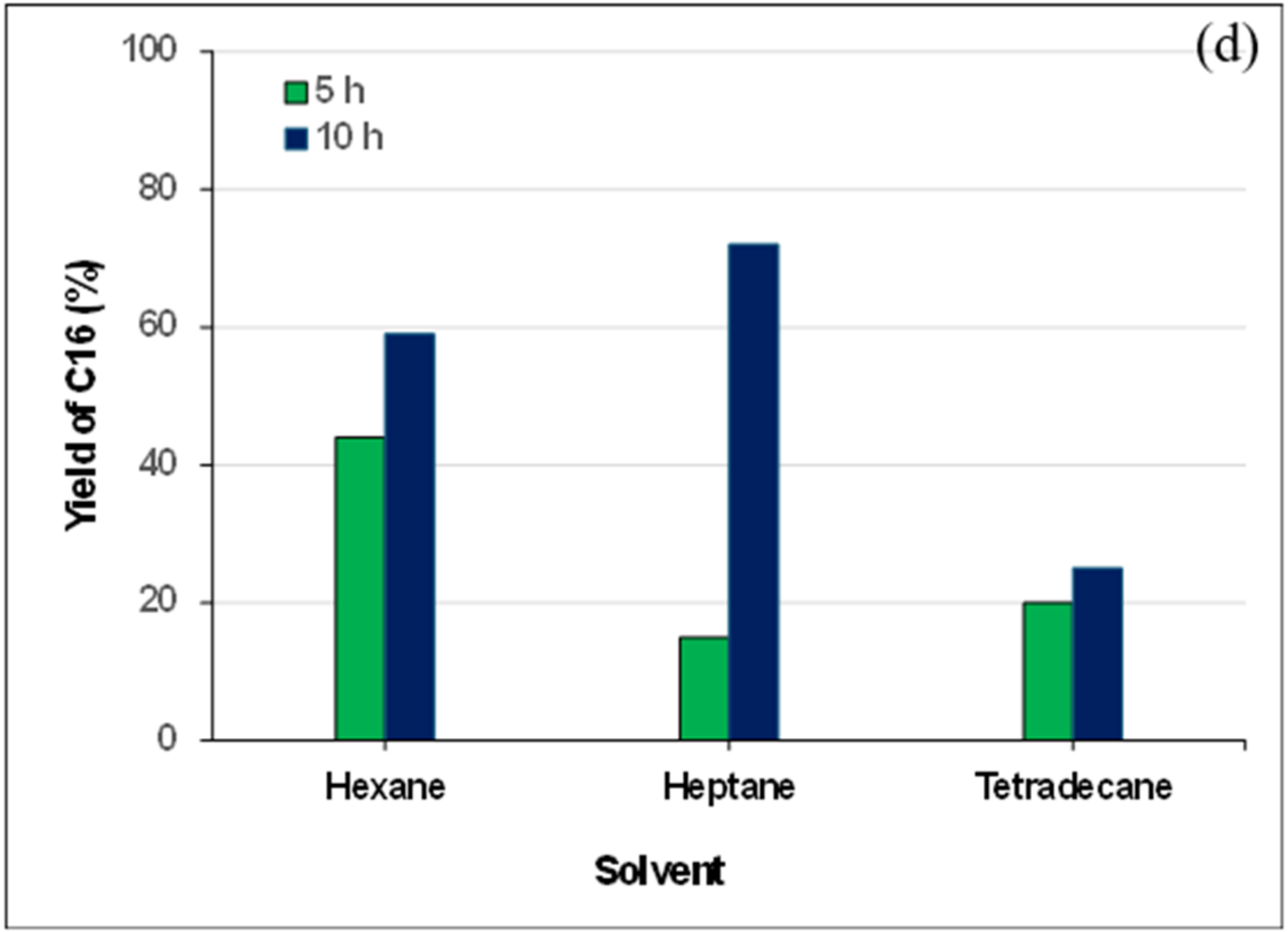
3. Steel Slag as Catalyst for Green diesel production

Results

Solvent and time effect: substrate (PA) 500 mg, slag catalyst (210-90 µm) 100 mg (5:1 wt/wt), solvent 10 mL, T= 340 °C



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Conclusions and future perspectives

From the works carried out, it emerges that **steel slags promote renewable fuel production reactions, acting as catalysts**. This could support the **circular economy** of the steel production and the **decarbonization** of transport and industries. It is of fundamental importance that, for tested processes, BOF and LF **slags do not require doping, chemical or thermal treatments**.
Currently, the use of slags for the applications mentioned has been demonstrated at **laboratory level**.

Therefore, the following studies are underway:

- **Mechanical treatments**, such as grinding and sieving, of slags to optimize their use and increase the production of renewable fuels.

- Possible doping with **non-critical materials**, to increase the reaction yield (for the artificial photosynthesis process)

- Study of the **scalability** of the systems and of the possible economic and environmental benefits.

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References and information

[1] Casiello, M.; Losito, O., Aloia, A.; Caputo, D.; Fusco, C.; Attrotto, R.; Monopoli, A.; Nacci, A.; D'Accolti, L.* Steel slag as new catalyst for the synthesis of fames from soybean oil Catalysts, 2021, 11, 619, **DOI 10.3390/catal11050619**

[2] Fusco, C.; Casiello, M.; Pisani, P.; Monopoli, A.; Fanelli, F.; Oberhuaser, W.; Attrotto, R.; Nacci, A.; D'Accolti, L. Steel slag as low-cost catalyst for artificial photosynthesis to convert CO2 and water into hydrogen and methanol- Scientific Reports 12, 1, 2022
DOI: 10.1038/s41598-022-15554-3

[3] Preliminary Communication in Chemical Catalyst 2024 5th Global Summit on catalysis and chemical engineering Berlin, Germany - July 22nd & 23rd, 2024

Thankyou for your kind attention!!

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