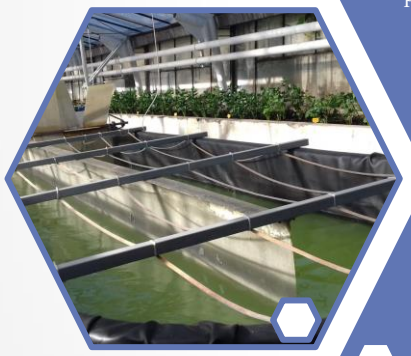
UNIVERSITATEA PETROL-GAZE DIN PLOIEȘTI
ROMÂNIA
Fondată în 1948

The importance of algal biomass production for obtaining value-added compounds



It is important to highlight that algae and microalgae are a primary source of polyunsaturated fatty acids, and they are considered a vegan source of these compounds

Microalgae are microorganisms easily adaptable to environmentally changing conditions, present high biomass

Productivity per unit area and their cultivation does not use arable land, not competing with food production.

There are interesting sources of carotenoids (lutein, β-carotene,zeaxanthin), and lipids rich in essential fatty acids, such as linoleic (C:18:2n6) and α-linolenic (C18:3n3) acids.

Compound (g/L)	Sample ID					
	C	1	2	3	4	5
KNO_3	1	**0.5**	1	1	1	1
KH_2PO_4	0.076	0.076	0.076	0.076	0.076	0.076
$NaHCO_3$	0.54	0.54	**0.27**	0.54	0.54	0.54
NaCl	15	15	15	15	15	15
$MgSO_4 \cdot 7H_2O$	3.055	3.055	3.055	**1.5275**	3.055	3.055
$MgCl_2 \cdot 6H_2O$	2.8	2.8	2.8	2.8	**1.4**	2.8
$CaCl_2 \cdot 2H_2O$	0.75	0.75	0.75	0.75	0.75	**0.375**

Porphiridium Purpureum sp.

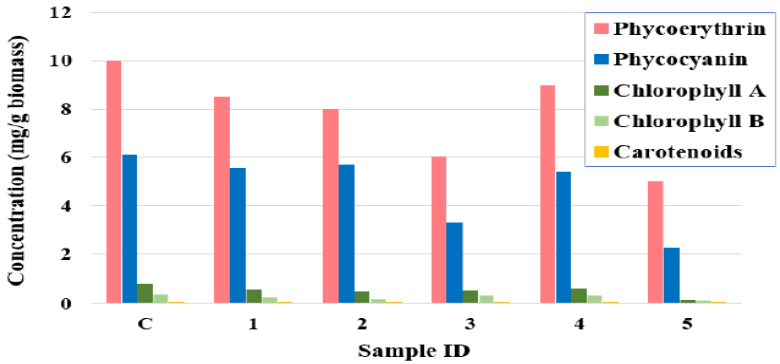


Figure 2. Phycobiliproteins and pigments concentrations in *Porphyridium purpureum* samples grown on modified ASW medium

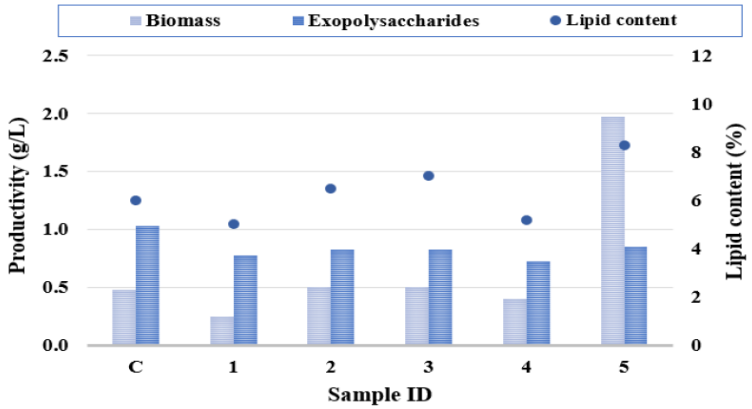


Figure 1. Biomass and exopolysaccharides productivities and lipid content of *Porphyridium purpureum* samples grown on modified ASW medium

The stress factors in the growth medium led to a decrease in both pigment accumulation and phycobiliprotein production as seen in figure 2, especially when the amounts of magnesium sulphate and calcium chloride were reduced. This behavior is consistent with microalgae's tendency to accumulate lipids under limited nutrients conditions, as opposed to pigments. Pigments are mainly synthetized under stress factors such as high light intensity, extreme temperature or excess nutrients. Even though potassium nitrate was essential for microalgae cell growth and proliferation, these results show that it plays a less significant role in the case of pigment and phycobiliproteins accumulation. Proposed stress factors led to different effects regarding lipid content, with a notable relationship between pigment and lipid accumulation. Therefore, stress factors which favour pigment accumulation have an opposite effect on lipid production.

The proposed stress factors show in figure 1, present a decrease or similar results as the control sample in terms of biomass productivity, while exopolysaccharides productions for all cases are roughly 20% lower than the control sample. The lower availability of nitrogen as a result of using a smaller amount of potassium nitrate has the most significant impact on biomass productivity.

International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 2021, EFFECTS OF STRESS FACTORS IN THE GROWTH MEDIUM ON BIO-COMPOUNDS PRODUCTION BY PORPHYRIDIUM PURPUREUM

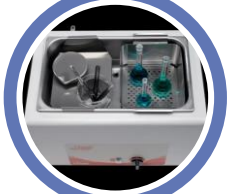
Extraction of bioactive compounds from microalgae

Carotenoids consumption has been associated with health benefits, as cancer, cardiovascular and chronic diseases prevention due to their antioxidant capacity.Besides these nutraceutical properties, carotenoids have potential as food colorants and pharmaceutical and cosmetic usages

The fatty acids, also known as ω-3 and ω-6 fatty acids, develop an important function in immune and inflammatory cells, decreasing risk of cardiovascular diseases.

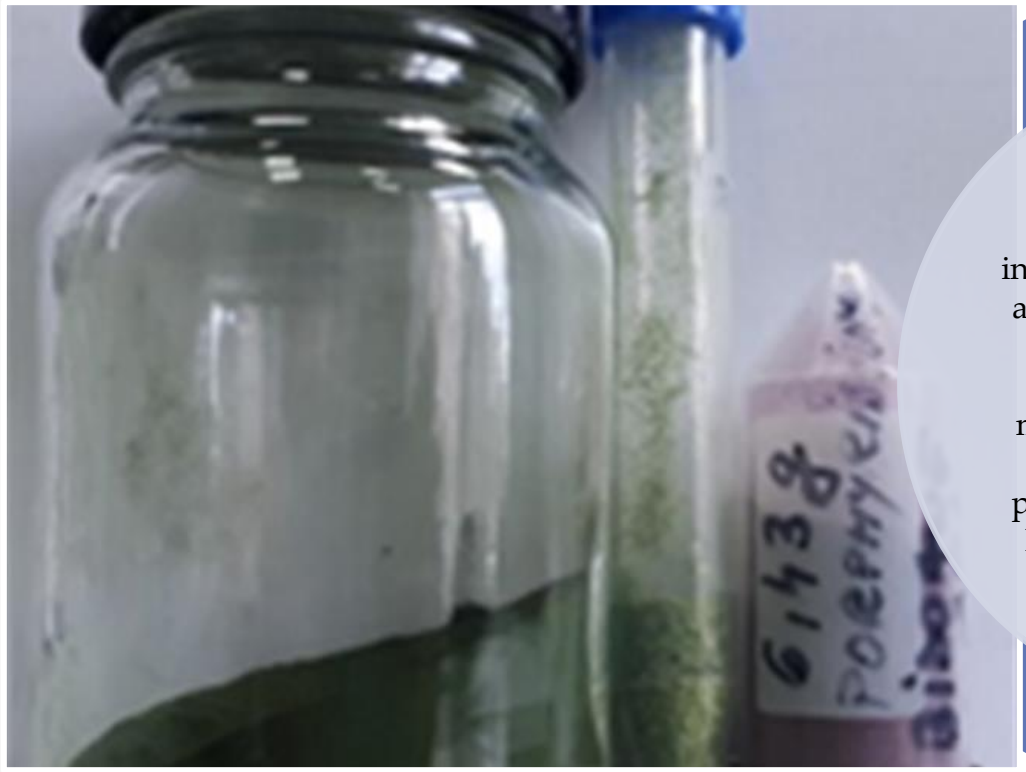
Several methods have been applied for extraction of carotenoids and lipids from microalgae biomass.

The conventional extraction methods such as maceration andsoxhlet extraction



The most innovative employed technics are: subcritical fluid extraction (SFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE) and high pressure homogenization (HPH) treatment

Evaluation of ultrasound assisted extraction(UAE) of bioactive compounds from microalgae



The effect of ultrasound assisted irradiation was investigated on the carotenoids and lipids extraction from the Chlorella vulgaris and Porphyridium purpureum microalgae in the presence of three solvents with various polarities (water, ethanol, and hexane) allowed in the food industry.

Vintila, A.C.N; Vlaicu, A; Radu, E; Ciltea-Udrescu, M.; Enascuta, E.C; Banu, I., **Oprescu, E.-E.,** Evaluation of ultrasound assisted extraction of bioactive compounds from microalgae, Journal of Food Measurement and Characterization, 2022, 16, 2518–2526.

The effect of the independent variables (extraction intensity (power), sample to solvent ratio, solvent concentration and ethanol to hexane ratio in the solvent on the performance of the extraction process (characterized by the total carotenoid content) was evaluated.

Exp. No.	Power (%)	Ethanol concentration (%)	Biomass to solvent ratio (w/v) g/mL	Ethanol to hexane ratio (v/v) mL/mL	Total carotenoid in ethanol phase (µg/g)	Total carotenoid in hexane phase (µg/g)	Total carotenoid (µg/g)	Total lipids (mg/g)
1	60	25	1/8	2/1	14.44	810.52	824.96	22.67
2	60	25	1/8	1/2	506.00	138.71	644.71	15.68
3	60	25	1/4	1/2	83.02	647.68	730.70	16.37
4	60	25	1/4	2/1	178.79	944.99	1123.78	16.01
5	60	70	1/8	1/2	1154.26	1529.10	2683.35	13.64
6	60	70	1/8	2/1	279.84	2827.89	3107.74	14.59
7	60	70	1/4	1/2	1671.81	3020.57	4692.38	25.87
8	60	70	1/4	2/1	673.53	5762.08	6435.60	29.07
9	80	47.5	1/8	1.25/1	51.76	1529.44	1581.20	18.27
10	80	47.5	1/4	1.25/1	52.36	3145.79	3198.15	24.02
11	80	47.5	1/5.33	1/2	69.17	1518.58	1587.75	17.49
12	80	47.5	1/5.33	2/1	60.25	2598.05	2658.30	20.65
13	80	25	1/5.33	1.25/1	49.43	1440.25	1489.68	16.31
14	80	70	1/5.33	1.25/1	383.45	3216.69	3600.13	17.73
15	100	25	1/8	1/2	749.23	568.55	1317.78	16.01
16	100	25	1/8	2/1	380.10	773.47	1153.57	18.94
17	100	25	1/4	2/1	194.12	2699.94	2894.06	23.64
18	100	25	1/4	1/2	153.73	1542.08	1695.81	20.36
19	100	70	1/8	1/2	229.56	1630.64	1860.20	14.96
20	100	70	1/8	2/1	1282.33	2432.44	3714.77	16.54
21	100	70	1/4	1/2	1744.13	2803.17	4547.30	20.44
22	100	70	1/4	2/1	748.77	4883.28	5632.05	11.78
23	80	47.5	1/5.33	1.25/1	66.04	2189.24	2255.28	15.31
24	60	47.5	1/5.33	1.25/1	59.55	2074.89	2134.44	17.27
25	60	1/5.33	47.5	1.25:1	139.94	1980.5	2120.44	17.05
26	100	47.5	1/5.33	1.25/1	51.67	1186.96	1238.63	17.09
27	100	1/5.33	47.5	1.25:1	49.72	1190.6	1240.32	17.45
28	70	100	1/4	1/0	2027.72	0	2027.72	13.68
29	70	70	1/4	1/0	1109.2	0	1109.2	12.23
30	70	25	1/4	1/0	40.02	0	40.02	10.67
31	70	0	1/4	0/1	0	226.87	226.87	24.83
32	70	70	1/4	2/1	1239.56	4787.00	6026.56	28.47

Vintila, A.C.N; Vlaicu, A; Radu, E; Ciltea-Udrescu, M.; Enascuta, E.C; Banu, I., **Oprescu, E.-E.,** Evaluation of ultrasound assisted extraction of bioactive compounds from microalgae, Journal of Food Measurement and Characterization, 2022, 16, 2518–2526.

Fatty acid methyl esters profiles

Fatty acid profile of *Porphyridium purpureum* in ethanolic and hexane phase

Fatyy acid	70% Ethanol (%)	Hexane (%)
Palmitic acid (C16:0n)	54,82	40,92
Linoleic acid C18:2n (9,12)	0	43,21
12,15-octadecadiynoic Acid	9,38	15,87
5,8,11,14 -eicosapentanoic Acid	11,72	0
5,8,11,14,17-eicosapentanoic Acid	16,14	0
5,8,11,14,17-eicosapentanoic Acid	7,94	0

Fatty acid profile of Chlorella vulgaris in ethanolic and hexane phase

Fatyy acid	70% Etha-nol (%)	Hex-ane (%)
Palmitic acid (C16:0n)	18.26	30.35
Hexadec-11-enoic acid (C16:1n (11))	3.67	4.91
Palmitoleic acid (C16:1n (9))	3.84	0
Palmitlinoleic acid (C16:2n (7,10))	12.18	7.97
Palmitlinolenic acid (C16:3n (7,10,13))	10.92	3.41
Hexadeca-4,7,10,13-tetraenoic acid (C16:4n (4,7,10,13))	1.26	0
Stearic acid (C18:0n)	1.04	3.2
Oleic Acid (C18:1n (9))	1.65	0
Vaccenic acid (C18:1n (11))	3.82	11.72
Linoleic acid (C18:2n (9,12))	25.64	28.23
Linolenic acid (C18:3n (9,12,15))	17.72	10.21

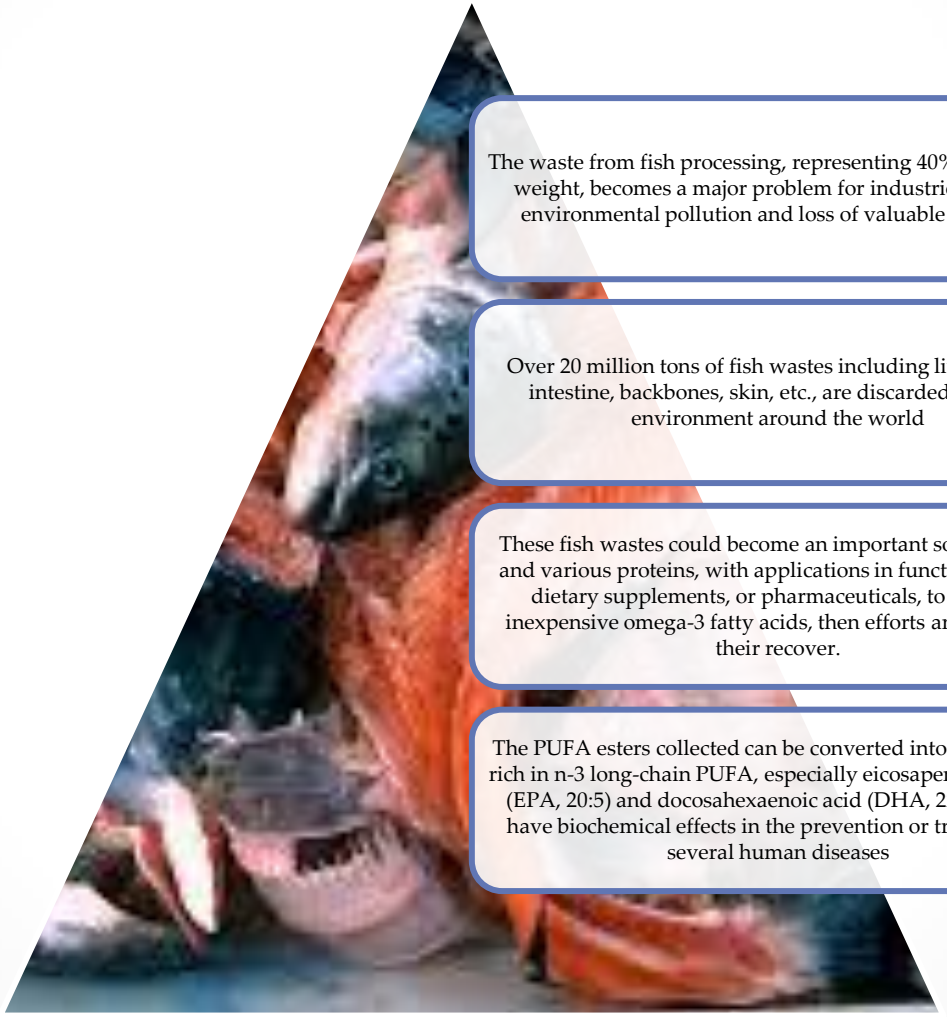
Study of the antioxidant activities of the extracted compounds

Antioxidant activity determined for exopolysaccharides, Chlorella vulgaris and Porphyridium purpureum

Concentration (µg/ml)	Antioxidant activity (%)		
	Exopolysaccharides	Chlorella vulgaris	Porphyridium purpureum
0,05	58.64	53.95	50.79
0,1	66.06	56.14	53.93
1	73.36	58.57	54.78
10	73.60	62.94	56.59
100	73.97	64.52	58.89

Vintila, A.C.N; Vlaicu, A; Radu, E; Ciltea-Udrescu, M.; Enascuta, E.C; Banu, I., **Oprescu, E.-E.,** Evaluation of ultrasound assisted extraction of bioactive compounds from microalgae, Journal of Food Measurement and Characterization, 2022, 16, 2518–2526.

Simultaneous production of oil enriched in ω-3 polyunsaturated fatty acids and biodiesel from fish wastes

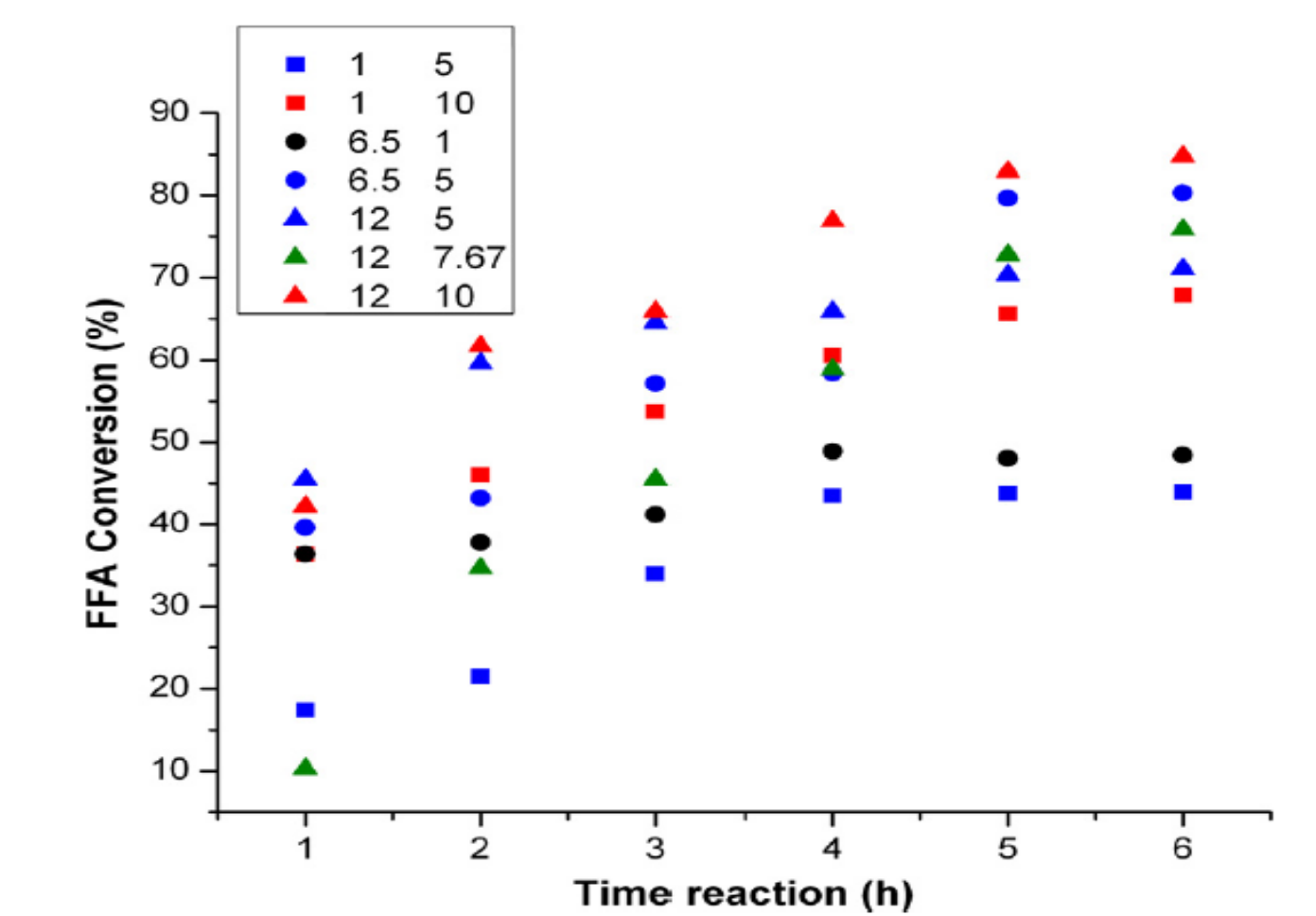


The waste from fish processing, representing 40% of the body weight, becomes a major problem for industries causing environmental pollution and loss of valuable nutrients

Over 20 million tons of fish wastes including liver, heads, intestine, backbones, skin, etc., are discarded into the environment around the world

These fish wastes could become an important source of oils and various proteins, with applications in functional foods, dietary supplements, or pharmaceuticals, to provide inexpensive omega-3 fatty acids, then efforts are made for their recover.

The PUFA esters collected can be converted into compounds rich in n-3 long-chain PUFA, especially eicosapentaenoic acid (EPA, 20:5) and docosahexaenoic acid (DHA, 22:6), which have biochemical effects in the prevention or treatment of several human diseases



The influence of reaction parameters over conversion of FFA

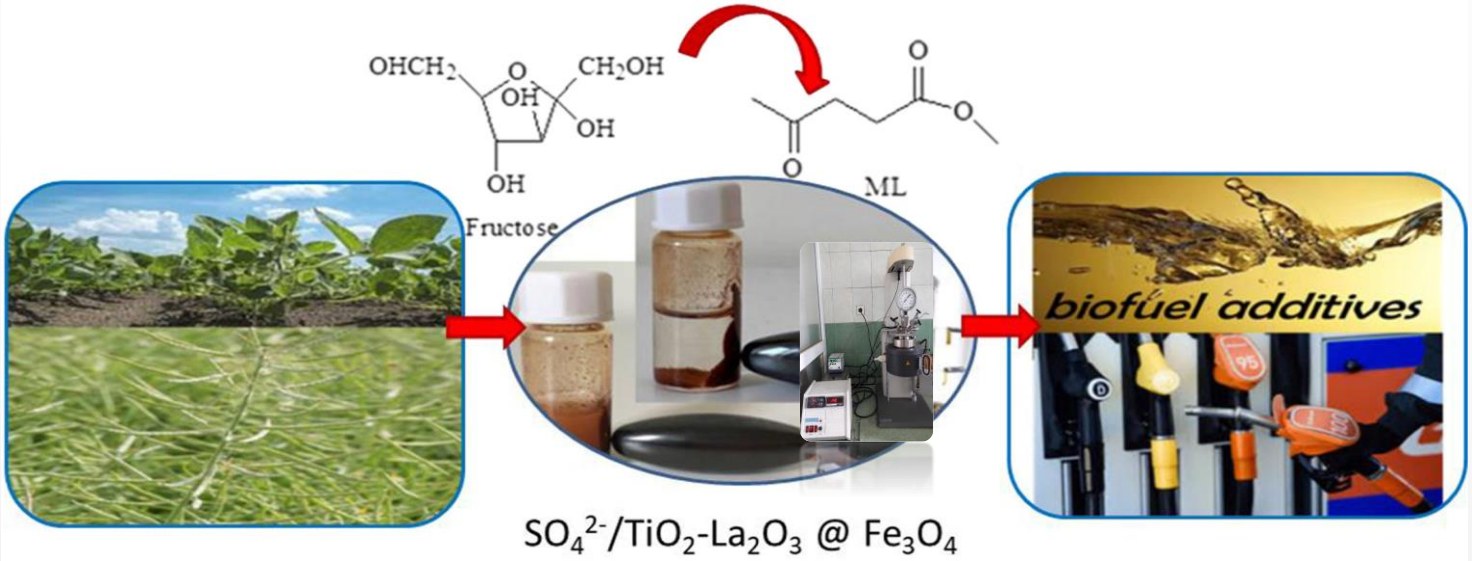
FAEE, weight %	Before distillation	After distillation
C14:0	5.7	-
C16:4	1.96	-
C16:1	10.81	-
C16:0	17.83	-
C18:4	2.5	0.53
C18:2	7.17	-
C18:1	20.81	5.5
C18:0	6.7	2.58
C20:5	9.43	34.03
C20:4	3.2	5.34
C20:1	2.02	2.43
C22:6	5.68	40.18
C22:5	1.9	9.41
C22:1	0.46	-
other	3.83	-

Enascuta C.E., Stepan E., Bolocan I., Bombos D., Calin C., **Oprescu E.-E.,** Vasile L., , Simultaneous production of oil enriched in ω-3 polyunsaturated fatty acids and biodiesel from fish wastes, Waste Management, 2018, 75, 205-214 ;
Enascuta, C., Stepan, E., Plesu, V., Iancu, P., Stefan, N., 2017. Process for preparing an oil with high content of polyunsaturated fatty acid and a diesel biofuel. RO129836 (B1).

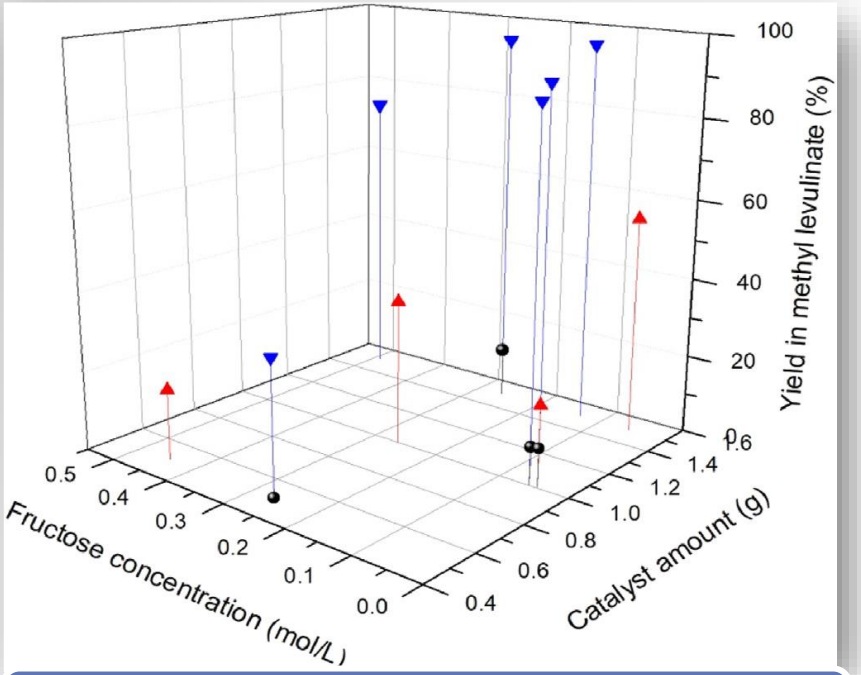
Synthesis of methyl levulinate from biomass carbohydrates

Carbohydrates are abundant, inexpensive, and naturally available carbonaceous resources, that cand be convert into usefully compounds such as 5-hydroxymethylfurfural (HMF), lactic acid, levulinic acid (LA), levulinic acid esters, and others.

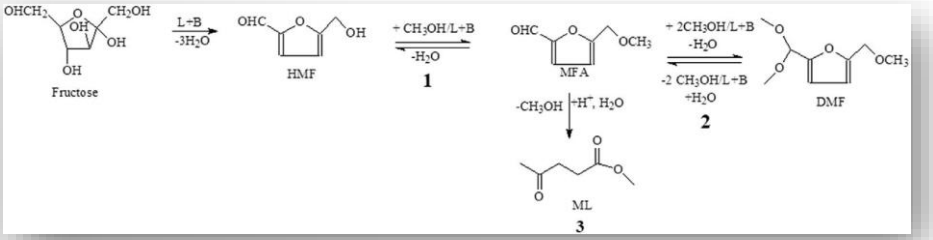
In recent years, significant attention has been dedicated to converting carbohydrates into alkyl levulinates (ALs). Methyl levulinate, ethyl levulinate, or butyl levulinate are known as fuel oxygenates, due to properties such as a high ignition temperature, high oxygen content (33%), and clean high efficiency combustion. Ethyl levulinate can be used as an additive in diesel fuel at up to 5% w/ w and has excellent properties, such as clean combustion and low toxicity, compared to other oxygenated fuel additives.



Oprescu, E.-E., Enascuta C.-E., Doukeh, R., Calin, C., Lavric, V., Characterizing and using a new bi-functional catalyst to sustainably synthesize methyl levulinate from biomass carbohydrates, Renewable Energy, 2021, 176, 651-662

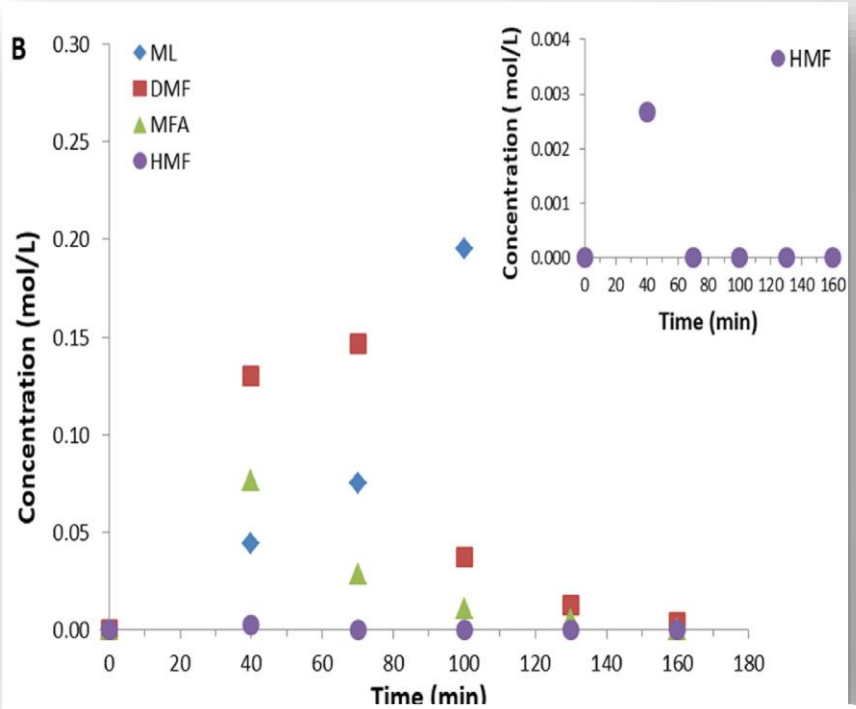


The effect of the operating parameters on ML yield (black 110 °C, red 130 °C, blue 160 °C).



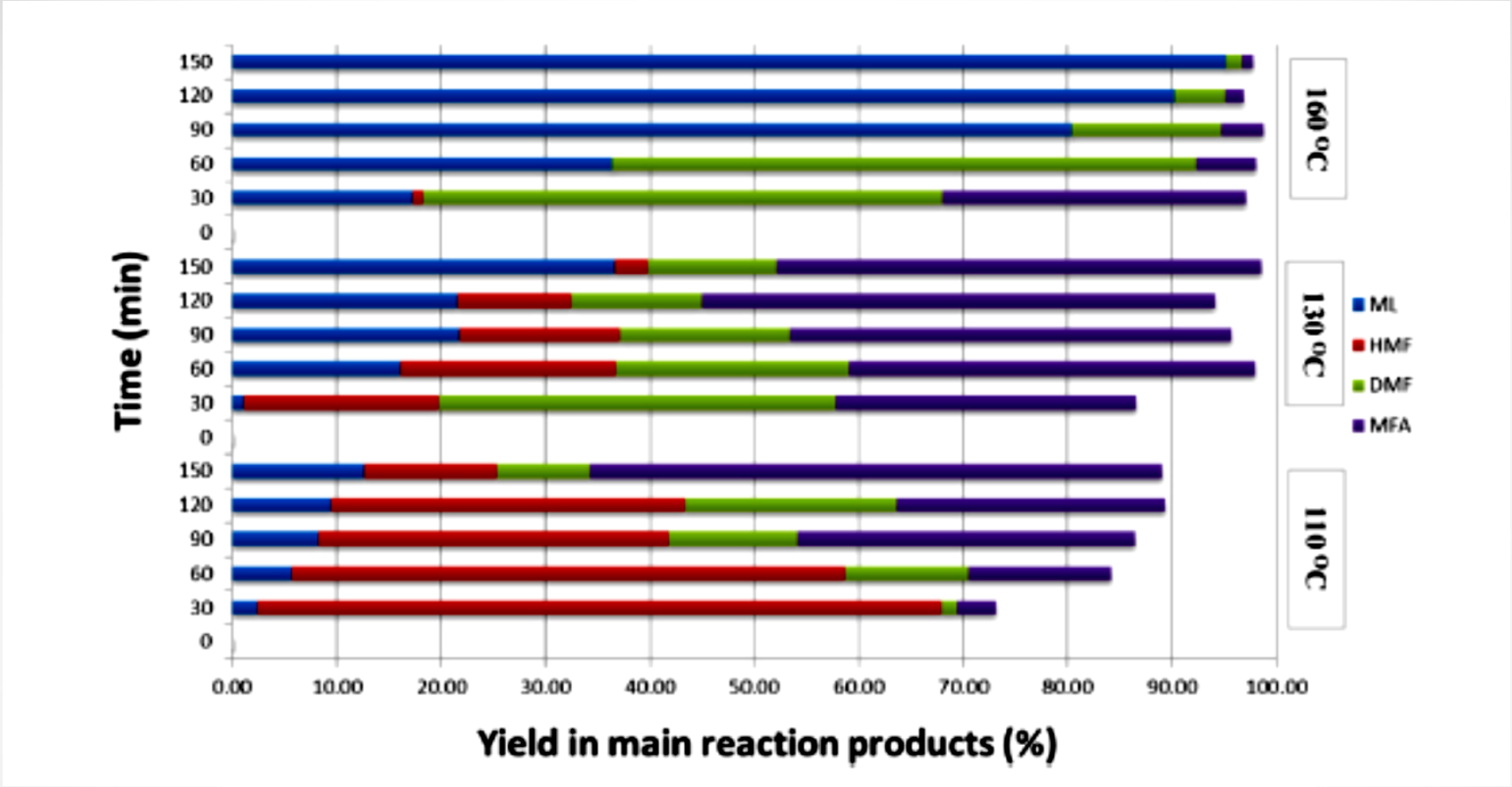
The proposed reaction pathway for the synthesis of ML from fructose

- 2-(dimethoxymethyl)-5-(methoxymethyl)furan(DMF),
- 5-(methoxymethyl)-2-furancarboxadhyde(MFA),
- 5-(hydroxymethyl)furfural (HMF)
- Methyl levulinate (ML)



The highest ML concentrations obtained in the experimental design (160 °C ,1.5g catalyst mass, and 0.489 mol/L fructose concentration.

Oprescu, E.-E., Enascuta C.-E., Doukeh, R., Calin, C., Lavric, V., Characterizing and using a new bi-functional catalyst to sustainably synthesize methyl levulinate from biomass carbohydrates, Renewable Energy, 2021, 176, 651-662c

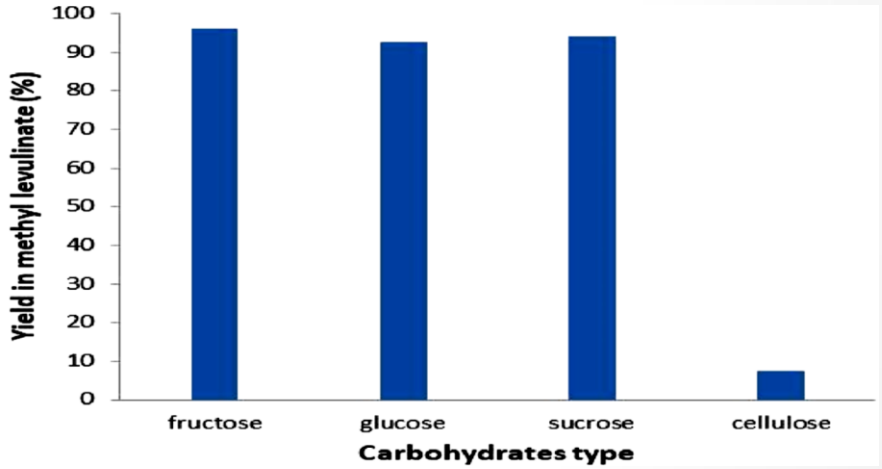


The influence of time and temperature on the reaction product yields

Oprescu, E.-E., Enascuta C.-E., Doukeh, R., Calin, C., Lavric, V., Characterizing and using a new bi-functional catalyst to sustainably synthesize methyl levulinate from biomass carbohydrates, Renewable Energy, 2021, 176, 651-662

Comparison of different sulfonated supports for the synthesis of methyl levulinate from fructose.

Catalyst	Reaction conditions					Methyl levulinate yield (%)	Reference
	Fructose, g	Methanol, mL	Catalyst, g	Temperature, °C	Reaction time, h		
SO_4^{2-}/TiO_2	1.25	25	0.625	200	2	59	[11]
SO_4^{2-}/TiO_2–ZrO_2	0.18	20	0.10	200	1	71	[14]
20- SO_4^{2-}/MMT	0.18	20	0.15	200	4	65	[15]
H_2SO_4	1.18	25	0.375	160	2.5	80.69 ± 0.18	This work
SO_4^{2-}/TiO_2–La_2O_3 coating Fe_3O_4	1.18	25	0.375	160	2.5	95.17 ± 0.21	This work



ML yield using different types of carbohydrates

Oprescu, E.-E., Enascuta C.-E., Doukeh, R., Calin, C., Lavric, V., Characterizing and using a new bi-functional catalyst to sustainably synthesize methyl levulinate from biomass carbohydrates, Renewable Energy, 2021, 176, 651-662

Thermal conversion of biomass into energy

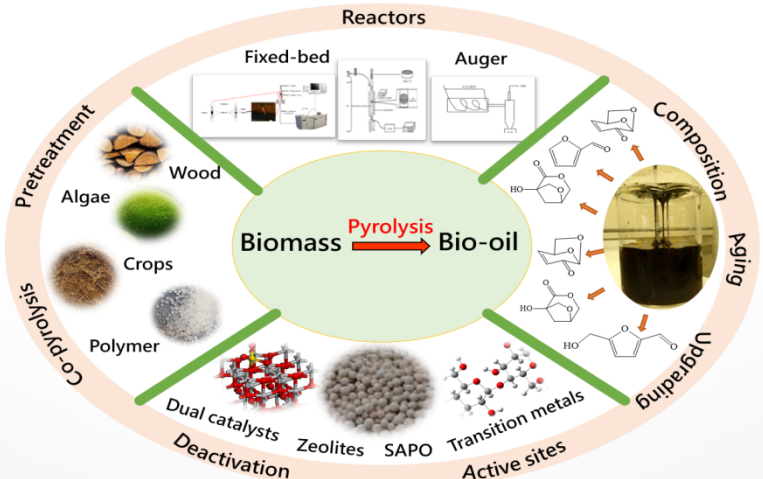
Bio-oil produced from biomass pyrolysis has the potential to become an alternative renewable fuel. However due to the high content of oxygenated compounds is unsuitable as transportation fuel.

Pyrolysis oil contains hundreds of organic compounds including hydrocarbons and oxygenated compounds (i.e. organic acids, aldehydes, ketones and phenolics).

The presents of these compounds cause bio-oil to have low heating value, low solubility in fuels such as diesel/gasoline, poor thermal and chemical stability and high acidity, high viscosity and high corrosiveness than petroleum.

However, pyrolysis oil can be converted to transportation fuel by catalytic treatment. The catalysts and conditions used are very similar to those used in petroleum hydrodesulfurization, hydrotreating, and hydrocracking processes, more generally described as hydroprocessing.

A promising upgrading technology is considered to be catalytic hydrotreatment of bio-oil, which involves treatment of pyrolysis oil with hydrogen in the presence of a heterogeneous catalyst leading to gasoline or diesel like products



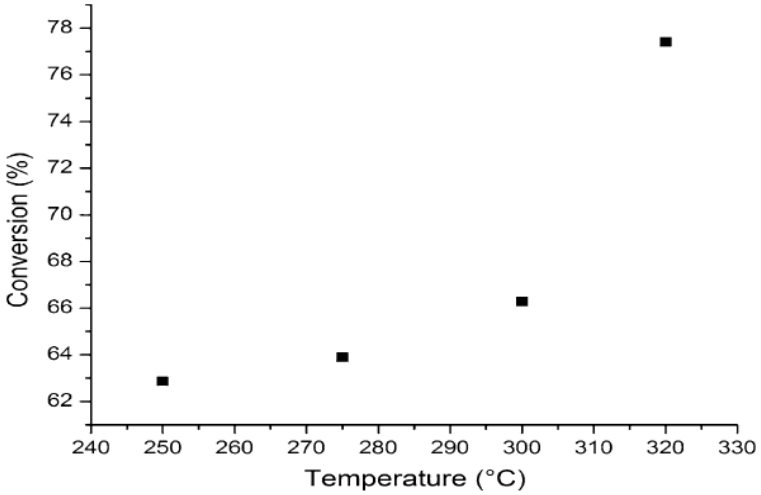
Catalytic hydrotreating of bio-oil and evaluation of main noxious emissions of gaseous phase

The bio-oil used in for catalytic hydrotreating was obtained by pyrolysis of biomass derivate from biogas process and conditioned with waste vegetable oil at 425 °C.

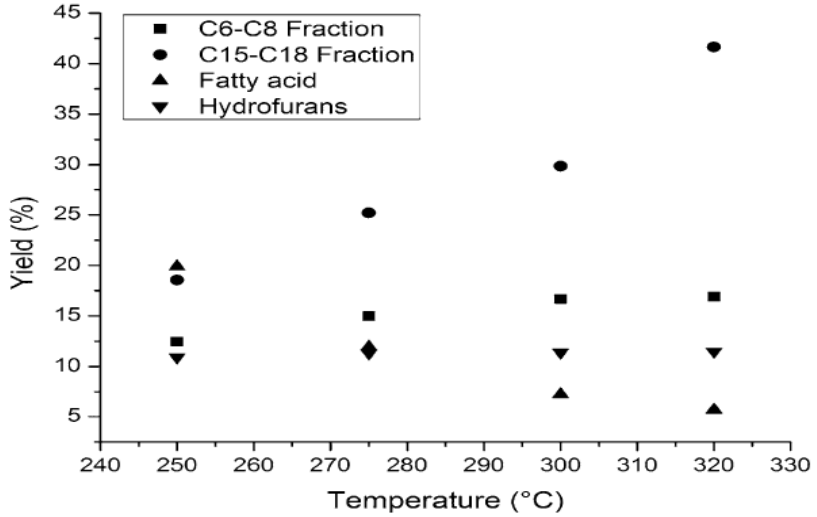
The main compounds identified in the bio-oil fraction were unsaturated organic compounds, carbonyl compounds, furan derivatives, phenols, lower carboxylic acids and unsaturated fatty acids. These compounds have a different polarity and a wide range of boiling point.

Therefore, the catalytic activity of CoMo /γ-Al_2O_3-HMS in the hydrotreating process of biomass pyrolysis bio-oil was investigated in the temperature range of 250–320 °C, pressure between 20–40 bar, and constant LHSV of 3 h−1.

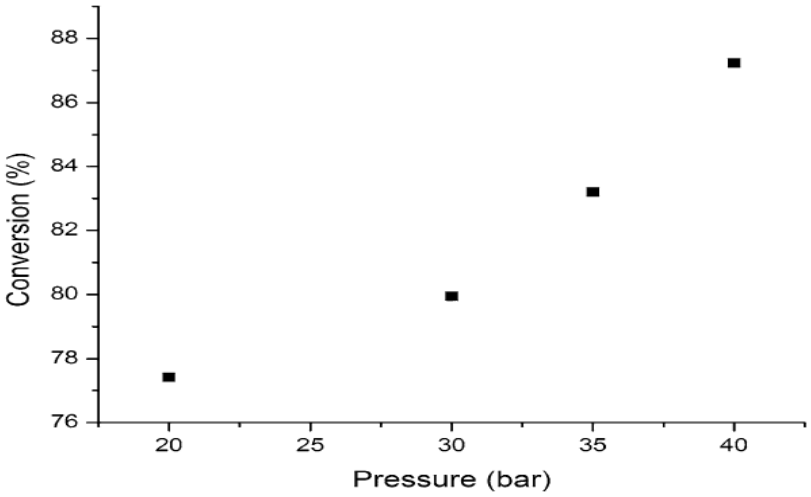
Doukeh, R., Bombos, D., Bombos, M., **Oprescu, E.-E.,** Dumitrascu, G., Vasilievici, G., Calin, C. Catalytic hydrotreating of bio-oil and evaluation of main noxious emissions of gaseous phase, Scientific Reports, 2021, 11(1), 6179



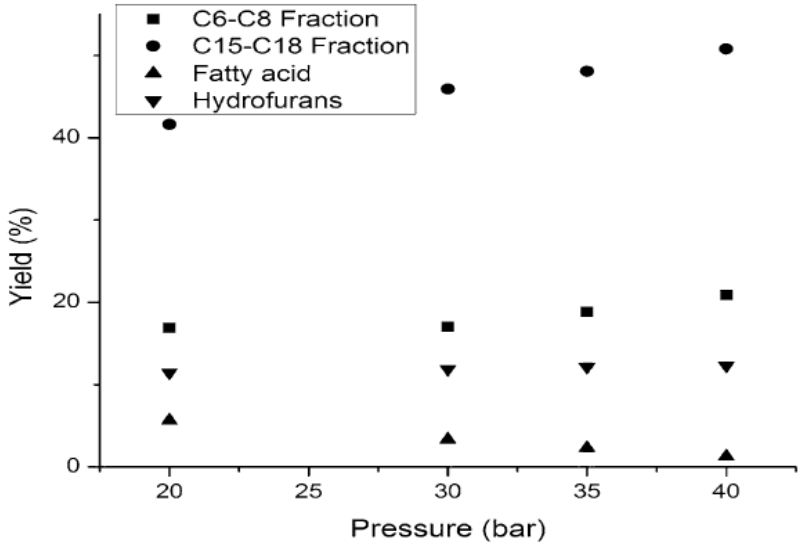
The influence of temperature over bio-oil conversion



The influence of temperature over the yields in products composition of liquid organic phase



The influence of temperature over bio-oil conversion



The influence of temperature over the yields in products composition of liquid organic phase

Doukeh, R., Bombos, D., Bombos, M., **Oprescu, E.-E.,** Dumitrascu, G., Vasilievici, G., Calin, C. Catalytic hydrotreating of bio-oil and evaluation of main noxious emissions of gaseous phase, Scientific Reports, 2021, 11(1), 6179

Thank you for your attention!