

Recycling of food byproducts: Waste Cooking Oils exploitation for industrial purposes

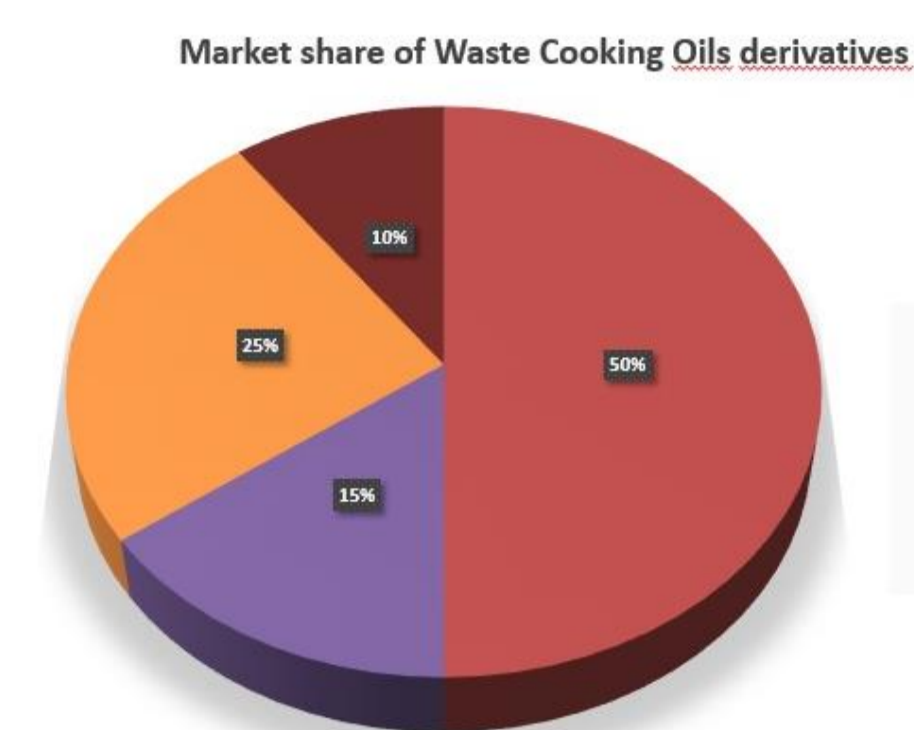
Alberto Mannu,¹ Monica Ferro,¹ Greta Colombo Dugoni,¹ Maria Enrica Di Pietro,¹ Andrea Mele^{1,2}

¹Department of Chemistry, Materials and Chemical Engineering 'G. Natta', Politecnico di Milano, Milano, Italy

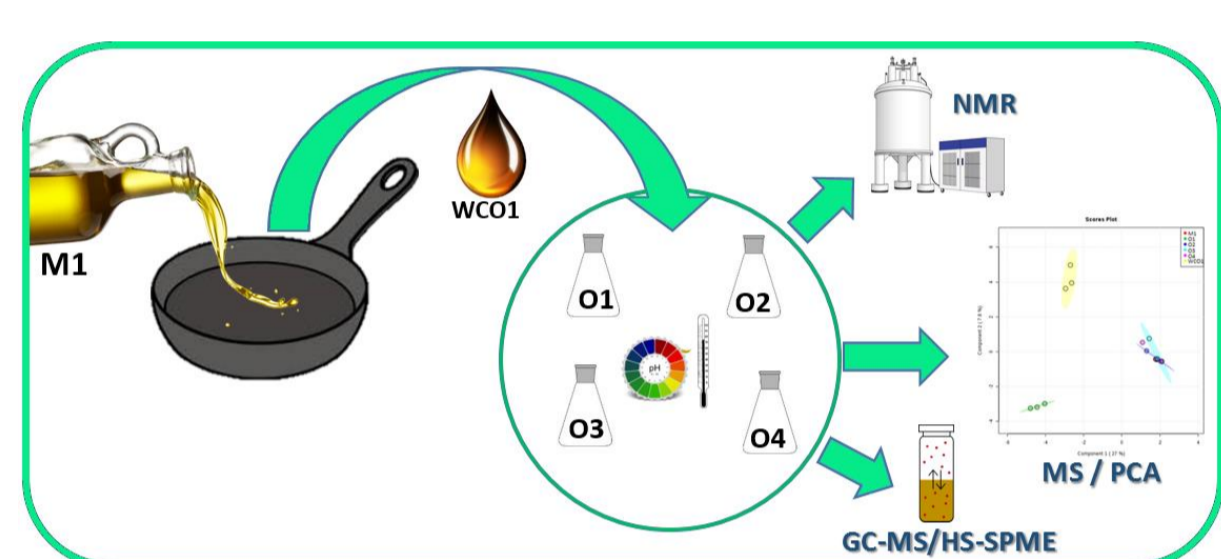
²CNR-ICRM Istituto di Chimica del Riconoscimento Molecolare, 'U.O.S. Milano Politecnico', Milano, Italy

Overview

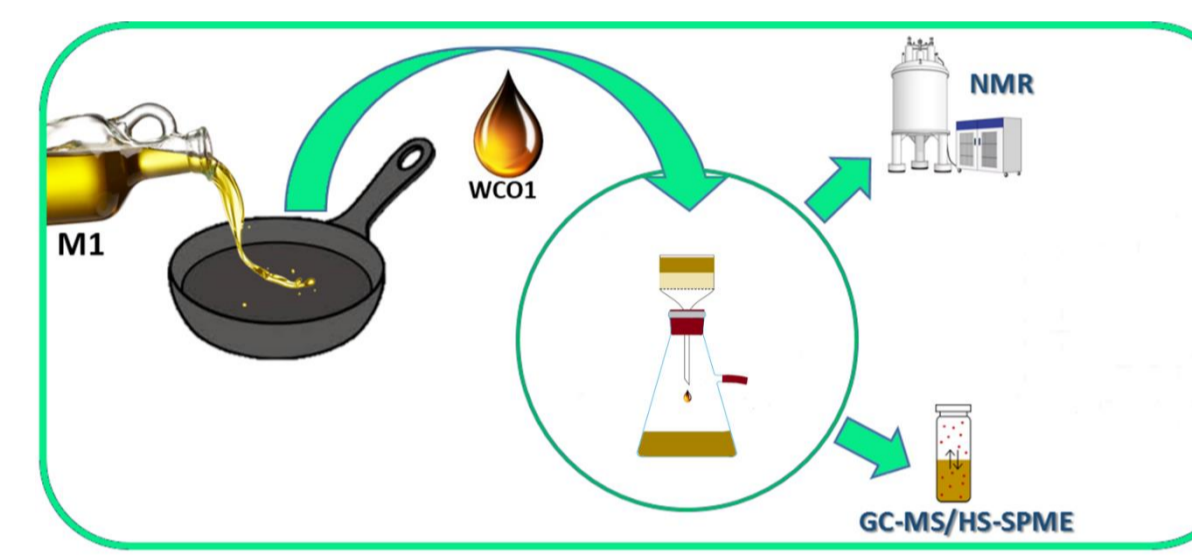
Waste Cooking Oils (WCOs) are a mixture of exhausted vegetable oils, by-products of the food chain, which arise from private kitchens and catering industries. Most of WCOs are originated from cooking processes, usually by deep frying. The amount of available WCOs is impressive: only in the European Union (EU), more than 4 million tons of WCOs are produced yearly and despite the high amount of available oil, only the 25% is collected. It has been estimated that the amount of collected WCOs could increase from the current 1.2 L of WCO/capita/year to 8 L and that about 15 million tons of WCOs are inadequately disposed every year worldwide, main through public sewerage. The production of natural biolubricants represents the second main application of recycled WCOs, after the biodiesel formulation, with a positive estimated trend during the next years. Nevertheless, a customized and optimized recycling process for obtain biolubricants from WCOs has never been proposed.



Proposed recycling process of WCOs for the production of natural biolubricants



SAMPLE	CONDITIONS
M1	Sunflower commercial oil
WCO1	M1 subjected to several frying cycles
O1	WCO1 after treatment at pH = 3 and T = 25 °C
O2	WCO1 after treatment at pH = 9 and T = 25 °C
O3	WCO1 after treatment at pH = 3 and T = 80 °C
O4	WCO1 after treatment at pH = 9 and T = 80 °C



Selected Bibliography

- Mannu, A. et al. *Science Progress*, **2019**, *102*, 153.
- Mannu, A. et al. *Resources*, **2019**, *8*, 108.
- Vlahopoulou, G. et al. *J. Food Process. Preserv.*, **2018**, *42*(3), e13533.
- Mannu A. et al. "Improving the recycling technology of Waste Cooking Oils: chemical fingerprint as tool for non-biodiesel application", *submitted*.

Water treatment

Table 1: selected volatiles compounds detected by Gas-Chromatography

Entry	RT	M1	WCO	O1	O2	O3	O4	Analyte
1	19.573	n.d.	0.7684	-	0.4901	-	0.4494	Limonene
2	20.354	n.d.	1.8623	1.0677	1.2202	-	0.4494	Furan, 2-pentyl-
3	25.183	n.d.	4.0382	3.8689	4.0172	2.8489	2.4767	Nonanal
4	27.052	n.d.	0.6783	-	0.5719	0.0791	0.1544	Furfural
5	29.158	n.d.	0.5625	0.4577	0.4587	0.1700	0.5569	Cyclohexanol, dimethyl
6	29.475	n.d.	0.4908	0.4230	0.4550	0.2407	0.2646	benzaldehyde
7	29.692	n.d.	0.6348	0.6042	0.5006	0.4925	0.7101	2-Nonenal
8	32.423	n.d.	1.4988	1.4236	1.4708	1.3255	1.5066	2-Decenal
9	34.587	n.d.	1.0504	1.0649	1.0810	1.0060	0.6942	2-Undecenal

Figure 1: ¹H NMR zoom of aldehyde region

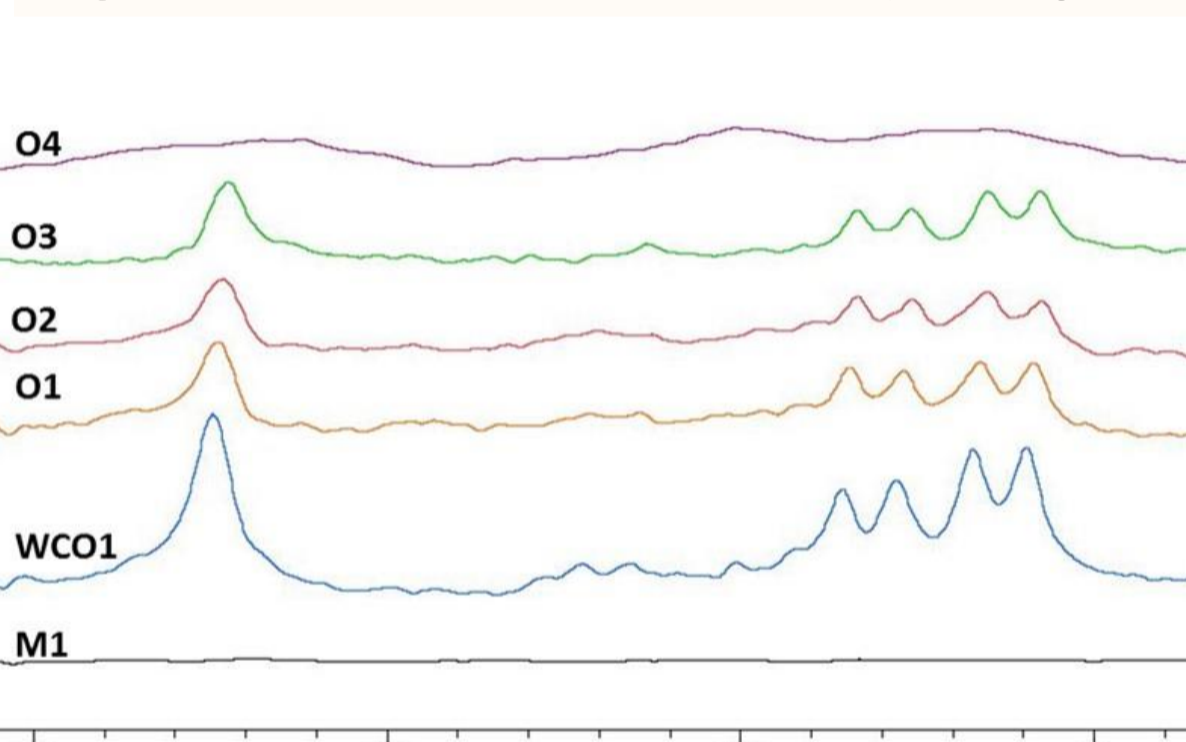
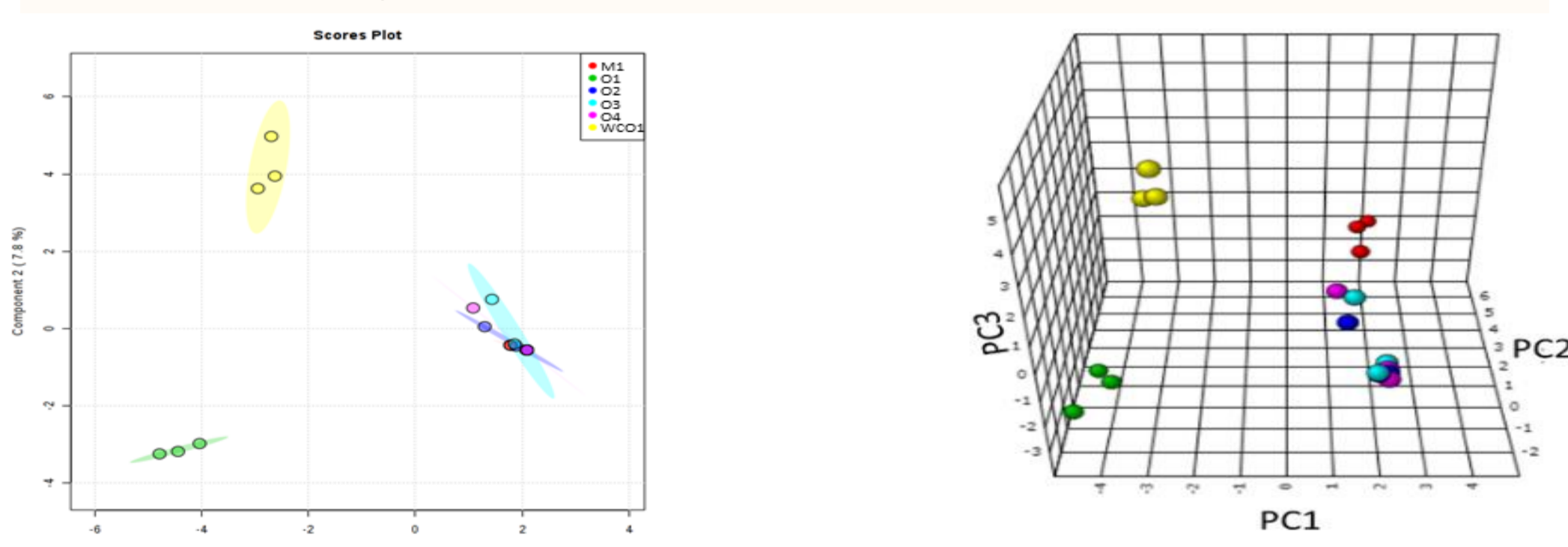


Table 3: main composition of samples calculated by ¹H NMR spectroscopy

Entry	Sample	Linolenic acid	Linoleic acid	Oleic acid	SFA	Iodine number
1	M1	1.9%	35.7%	46.4%	14.0%	106
2	WCO1	1.7%	19.1%	62.2%	15.4%	91
3	O1	1.8%	17.0%	63.7%	15.7%	88
4	O2	1.7%	17.6%	63.6%	15.4%	89
5	O3	1.9%	18.4%	62.1%	15.8%	90
6	O4	3.7%	14.7%	63.4%	14.1%	85

Water treatment affect the fatty acids profile of the waste vegetable oil at pH = 9 and at 80 °C (O4)

Figure 2: 2D (left) and 3D (right) PCA score plot obtained from MS-ESI data for the comparison of samples M1 (red), WCO1 (yellow), O1 (green), O2 (dark blue), O3 (light blue), and O4 (pink)



Filtration on bentonite pad

Table 2: selected volatiles compounds detected by Gas-Chromatography

Entry	RT	WCO	Treated oil WCO1	Compound
1	10.132	0.72	0.43	Butanal, 3-methyl-
2	10.579	0.14	n.d.	Butyl-cyclopentane
3	26.756	11.05	n.d.	Acetic acid
4	27.498	12.72	0.17	Furfural
5	31.011	1.32	0.08	2-Furancarboxaldehyde, 5-methyl-
6	32.627	2.00	1.07	2-Decenal, (E)-
7	32.695	1.21	n.d.	Furanmethanol
8	34.497	2.27	1.66	α-Farnesene
9	34.857	1.06	0.35	2-Undecenal
10	35.117	1.01	0.29	2,4-Decadienal, isomer 1
11	35.997	4.48	0.39	2,4-Decadienal, isomer 2
12	36.215	1.91	n.d.	Hexanoic acid

Table 4: main composition of samples calculated by ¹H NMR spectroscopy

Analyte	Prior to Filtration (WCO)	After Filtration (WCO1)
Linolenic acid	<3%	<3%
Linoleic acid	13%	10%
Oleic acid	70%	70%
SFA ^a	16%	16%
Iodine number	83.2	83.8

Treatment with bentonite does not affect the fatty acids profile of the waste oil as observed in the case of the water treatment.

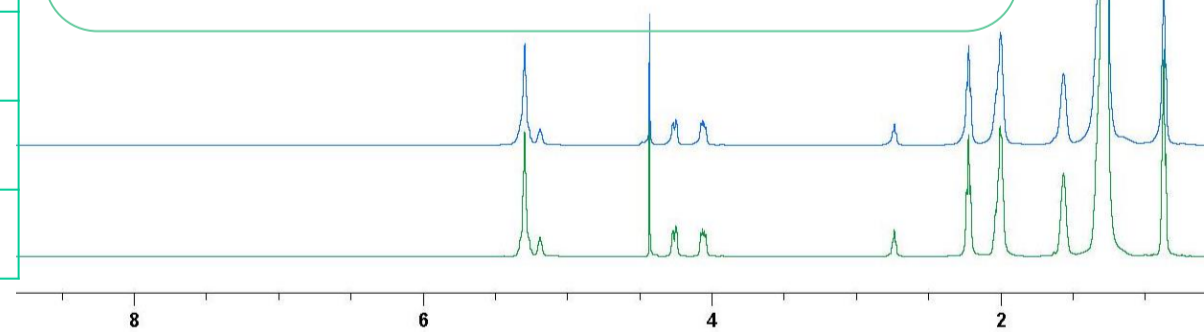


Table 5. Color coordinates for crude and filtered samples of WCOs. a Commission Internationale de l'Eclairage; b The values reported were calculated as results of four measurements; the standard deviation is indicated. c L, lightness; d a, green-red; e b, blue-yellow; e E: total color difference

Entry	Sample	Color (CIE) ^a (S) ^b			
		L ^c	a ^d	b ^e	ΔE (ΔS)
1	WCO	23.11 (0.02)	3.25 (0.05)	9.33 (0.04)	
2	WCO1	27.17 (0.01)	0.21 (0.05)	15.25 (0.05)	7.79 (0.05)

After filtration on bentonite the lightness increases as well as the yellow component (a), while the red contribute results reduced.

Natural Biolubricant

2nd full factorial design was employed in order to screen the effect of the main factors (pH, oil/H₂O ratio, Temperature and Time) on the density and the flash point.

Figure 3: Main effect plot for density

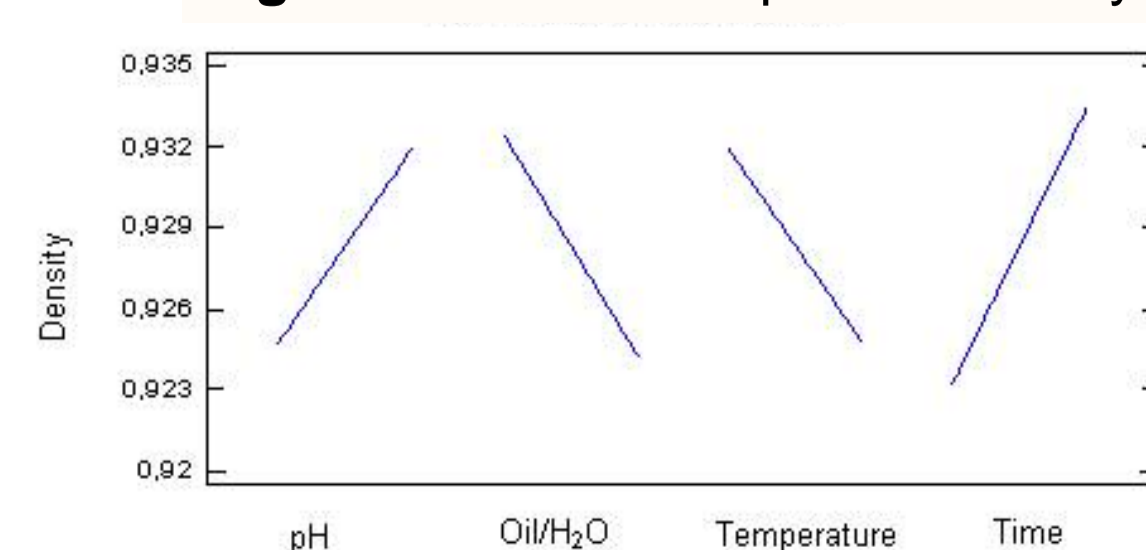


Table 6: Prevision of the best experimental conditions for minimum and maximum density

Parameter	minimum (0.913 g/mL)	maximum (0.965 g/mL)
pH	4.0	6.0
Oil/H ₂ O ratio	30.0	30.0
Temperature	60.0	20.0
Time	5.0	24.0

Figure 4: Main effect plot for flash point

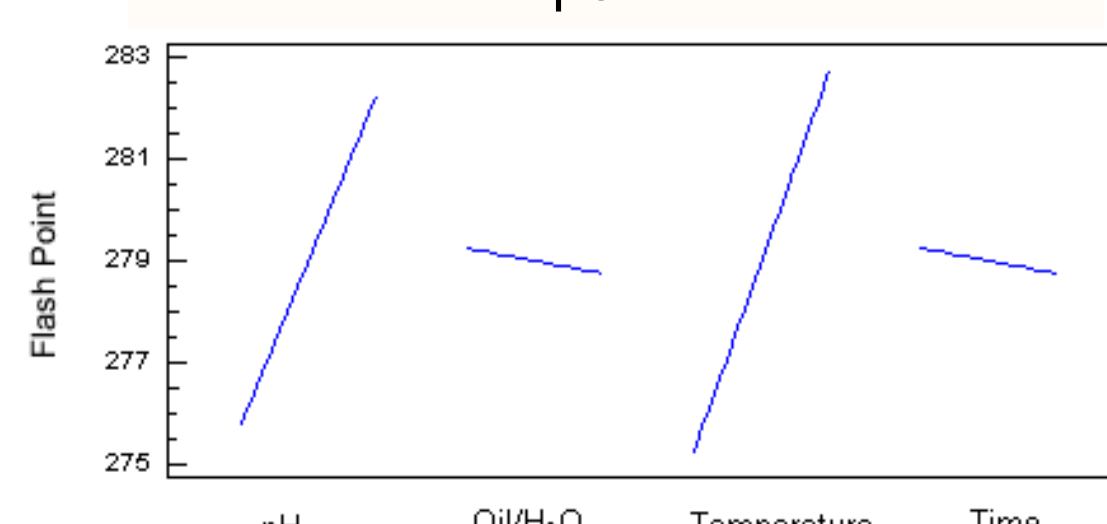


Table 7: Experimental conditions corresponding to the maximum and the minimum flash point value

Factor	Minimum (262.9 °C)	Maximum (289.5 °C)
pH	4.0	6.0
Oil H ₂ O	30.0	30.0
Temperature	22.4	60.0
Time	23.9	5.0