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HYDROTHERMAL TREATMENT OF BIO-OIL FOR THE PRODUCTION OF BIODIESEL ANTIOXIDANTS

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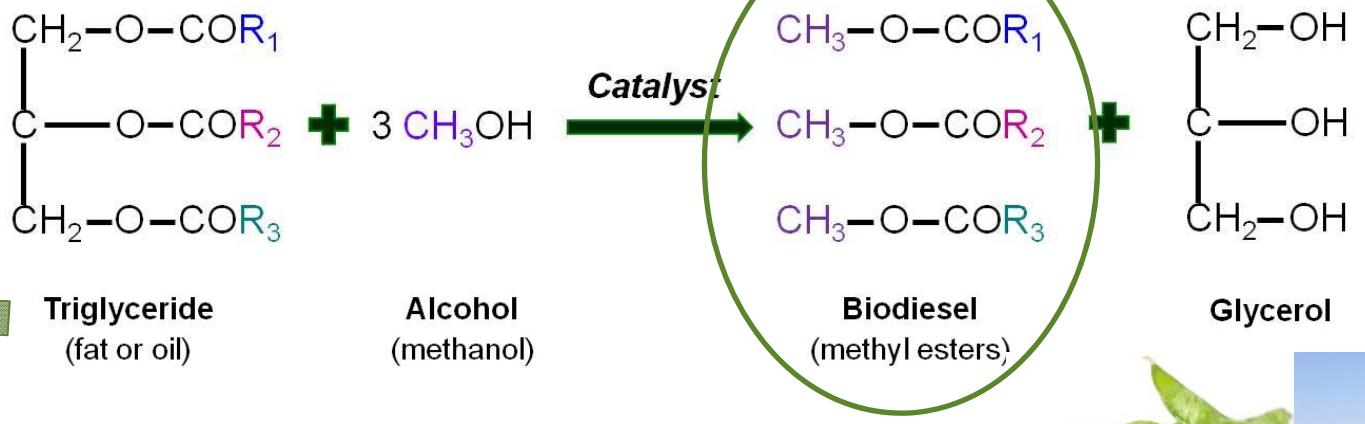
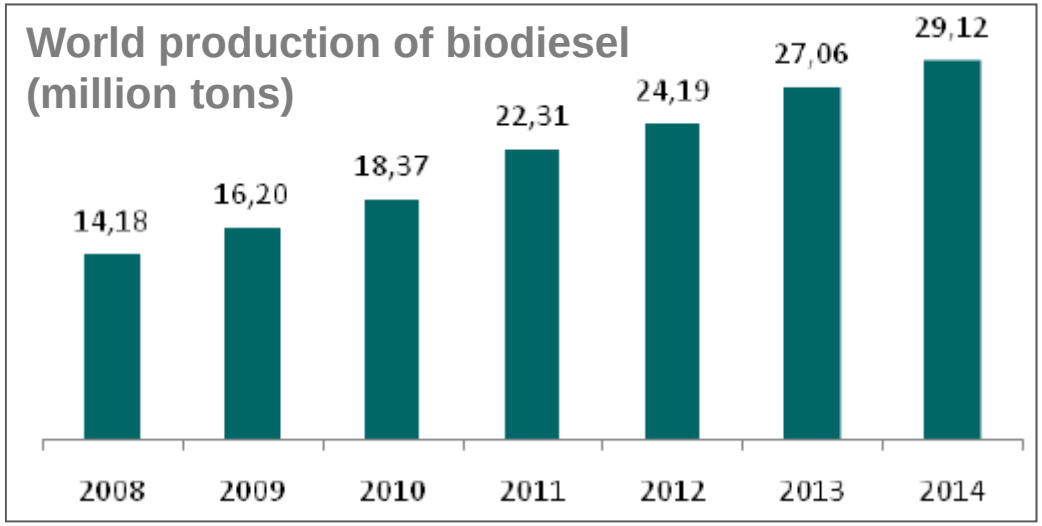
BIODIESEL

- ✓ Renewable alternative to fossil diesel.
- ✓ Less harmful emissions.
- ✓ Carbon neutral.

Transesterification process



- o Feed crops: Soybean, rapeseed, and palm oil.
- o Non-food oil: Waste oil, Jatropha, and algae.
- o Animal fat.

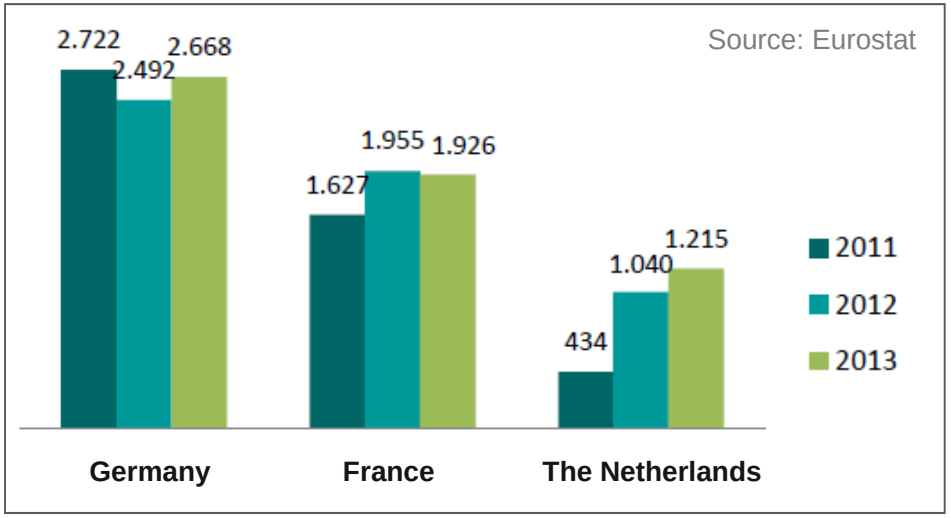


Source: Oil World Statistic Update

World ranking

1st: USA
2nd: Indonesia
3rd: Brazil
4th: Germany
5th: Argentina

Major producer countries of biodiesel in Europe (thousand tons)



Wide variety of feedstock

Different properties of biodiesel

Standardization to ensure customer´s acceptance

European FAME Standard EN 14214:
Quality requirements for biodiesel commercialization

Properties	Units	Limits					
		Lower			Upper		
FAME Content	% (w/w)	96,5			-		
Oxidation stability (110 ^{o}C)	h	8			-		
Viscosity at 40 ^{o}C	mm^2 / s	3,50			5,00		
Water content	mg / kg	-			500		
CFPP	^{o}C, max	Grade A	Grade B	Grade C	Grade D	Grade E	Grade F
		+5	0	-5	-10	-15	-20

× **Poor oxidation stability**
(unsaturated fatty acids)

→ **USE OF ANTIOXIDANTS**

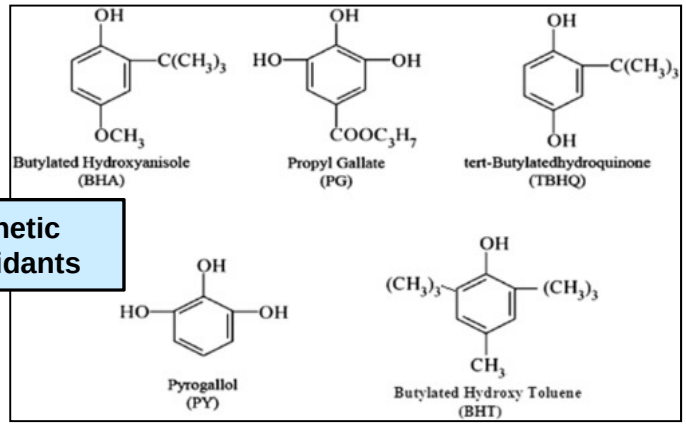
Chain-breaking

$$A\text{–}H + ROO^{\bullet} \rightarrow A^{\bullet} + ROO\text{–}H$$

$$A^{\bullet} + ROO^{\bullet} \rightarrow \text{non-radical products}$$

Mono- or poly- hydroxylated phenolic compounds with varying substituents on one or several phenol rings (labile hydrogen in OH-group)

Synthetic antioxidants

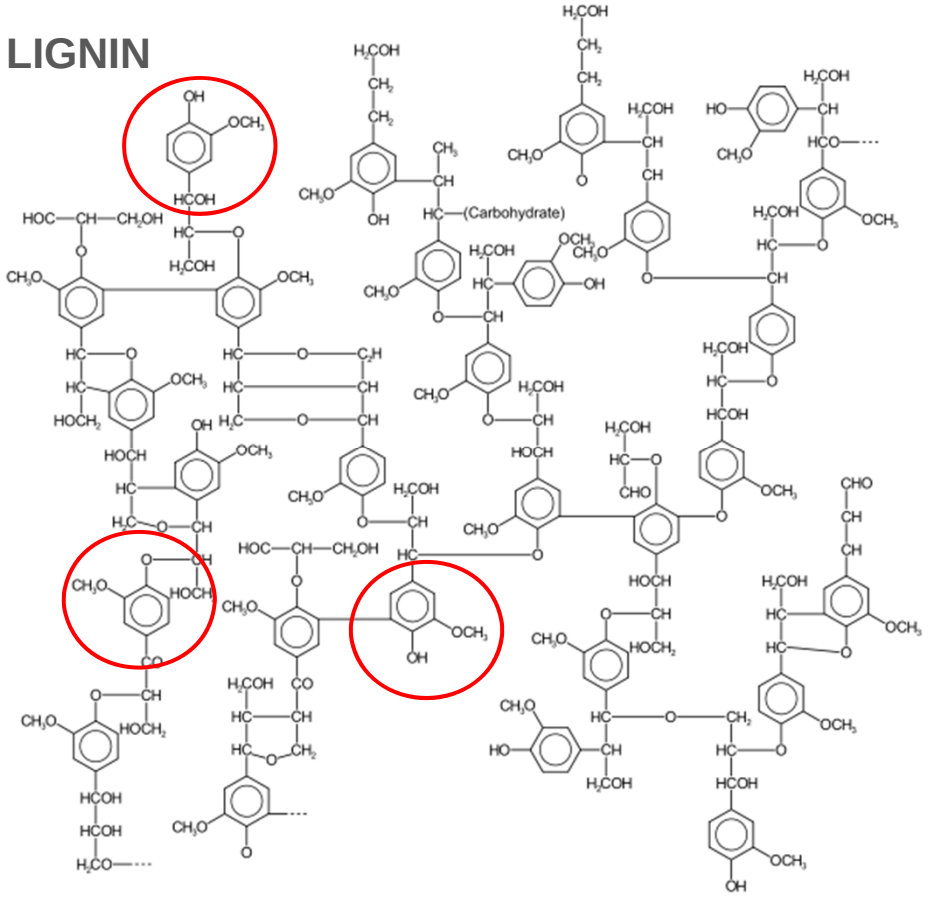


Properties	Units	Limits					
		Lower			Upper		
FAME Content	% (w/w)	96,5			-		
Oxidation stability (110 °C)	h	8			-		
Viscosity at 40 °C	mm^2 / s	3,50			5,00		
Water content	mg / kg	-			500		
POFF	°C, max	Grade A	Grade B	Grade C	Grade D	Grade E	Grade F
		+5	0	-5	-10	-15	-20

Lignocellulosic biomass

PYROLYSIS

LIGNIN



Thermal degradation → Mono-lignols: up to15 % of bio-oil mass.

(García-Pérez et al., Biomass & Bioenergy, 2007; 31:222-242)

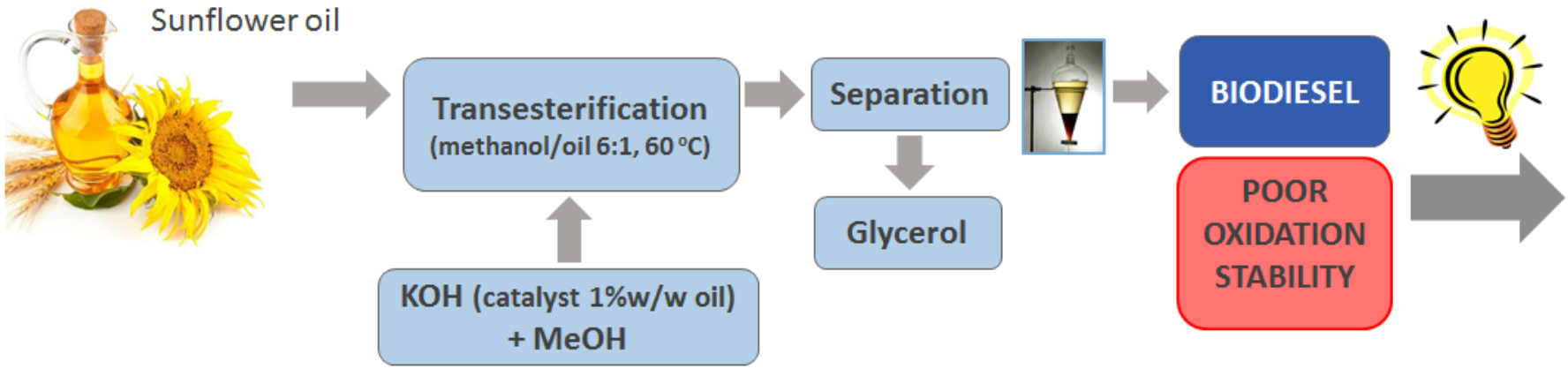
OBJECTIVE OF THE WORK…

- Previous studies from our group have shown that it is possible to obtain great improvements in oxidation stability using additives extacted from pyrolysis bio-oils

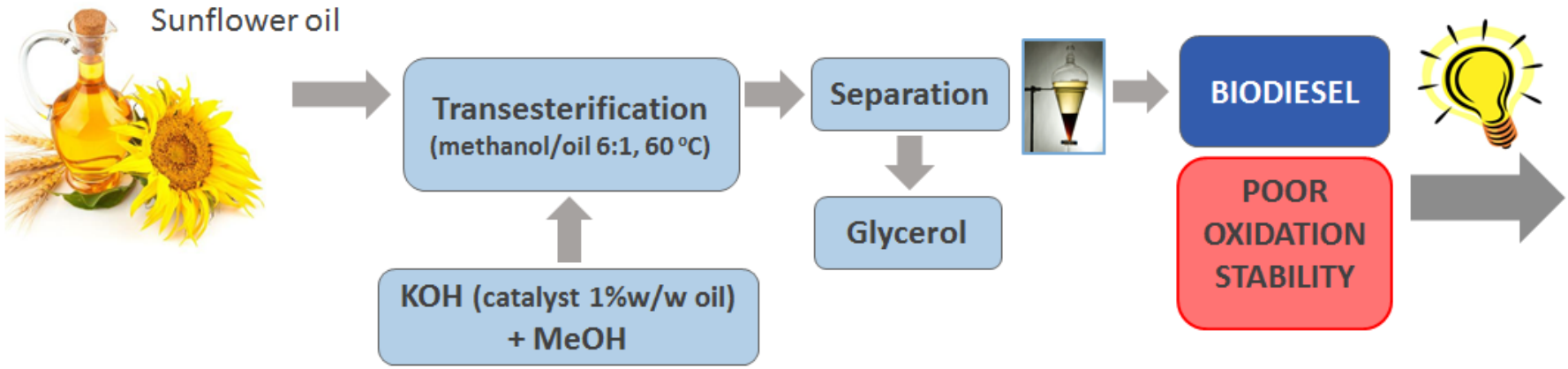
Bio-oil can contain up to 30 wt. % of high molecular weight compounds non-detectable by GC-MS, which can also be a source of smaller phenolic units

Hydrothermal treatment of bio-oil at high pressure and under different reaction media has been studied, aiming at promoting the depolymerization of the lignin remaining fraction in order to obtain an antioxidant additive for biodiesel

Biodiesel production



Biodiesel production

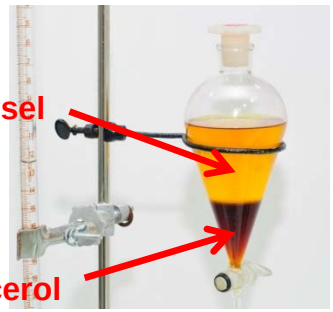


o <u>Raw materials</u>: Sunflower oil, MeOH, KOH (catalyst)

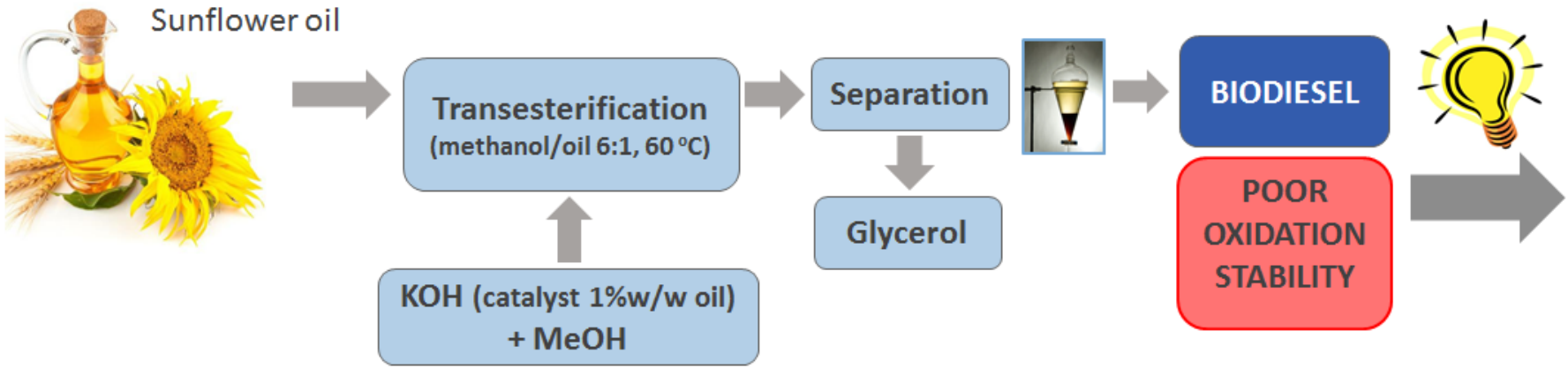
Oil / alcohol = 1:6 molar ratio.

Catalyst weight = 1 wt.% of oil mass.

o <u>Reaction conditions</u>: 60 ºC, 3h, stirring.



Biodiesel production



o Biodiesel upgrading:

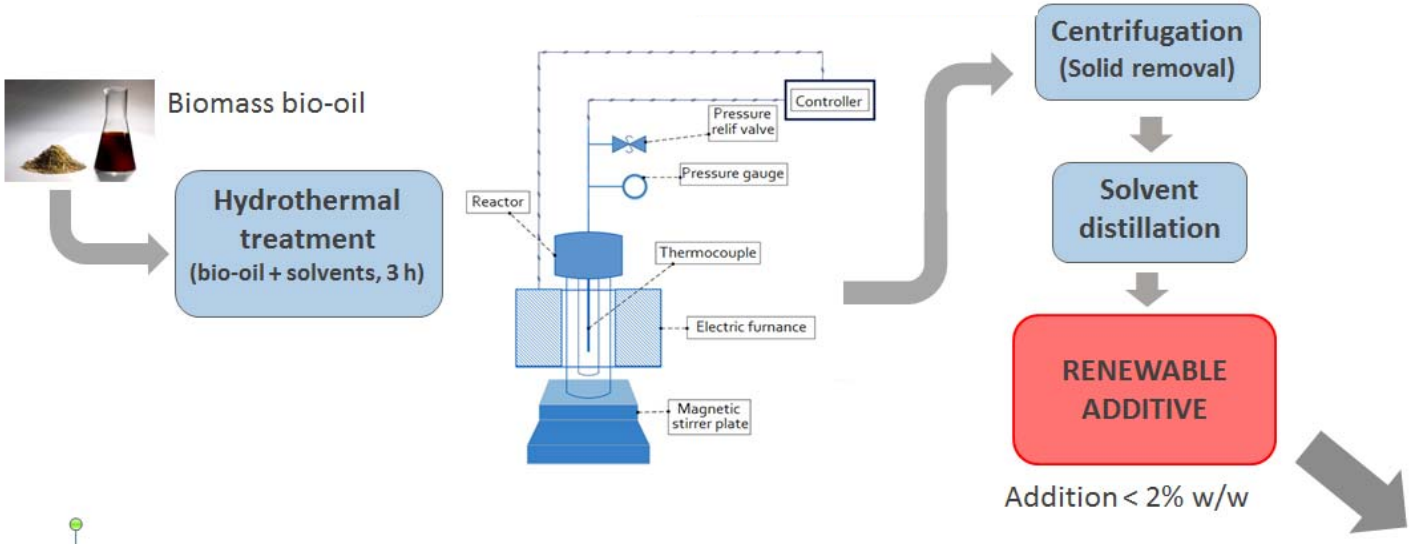
- ✓ excess methanol removal
- ✓ acid washing
- ✓ residual moisture removal

o Composition: Predominance of methyl linoleate (C18:2) followed by methyl oleate (C18:1).

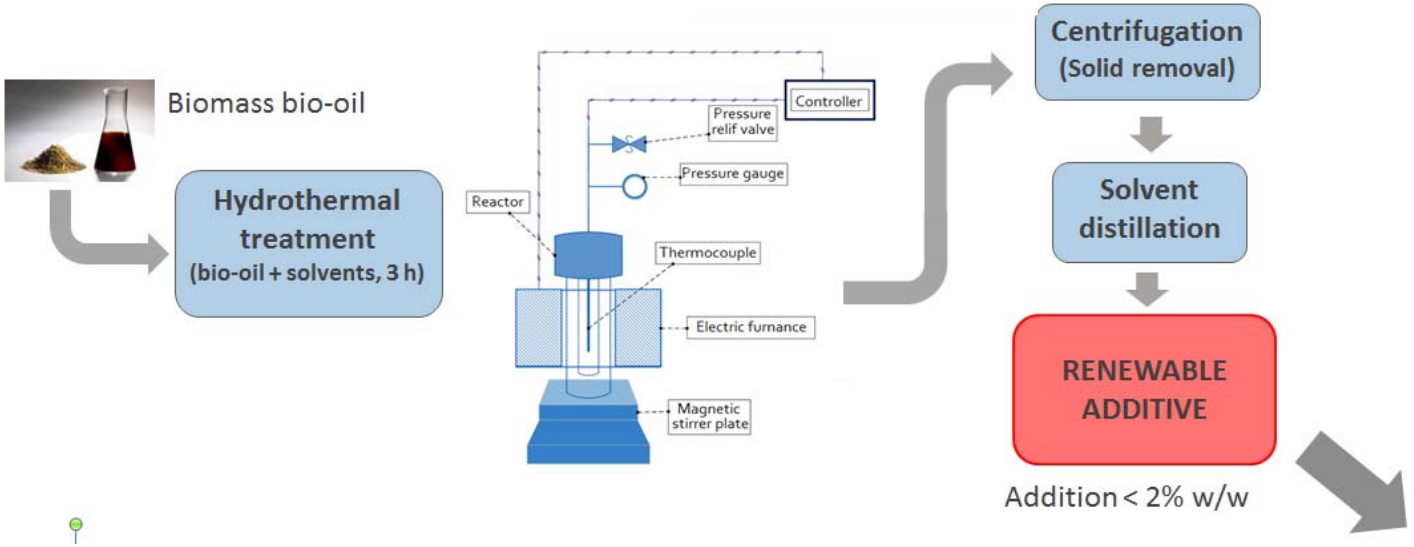
High polyunsaturated degree

Prone to oxidation

Additive production



Additive production



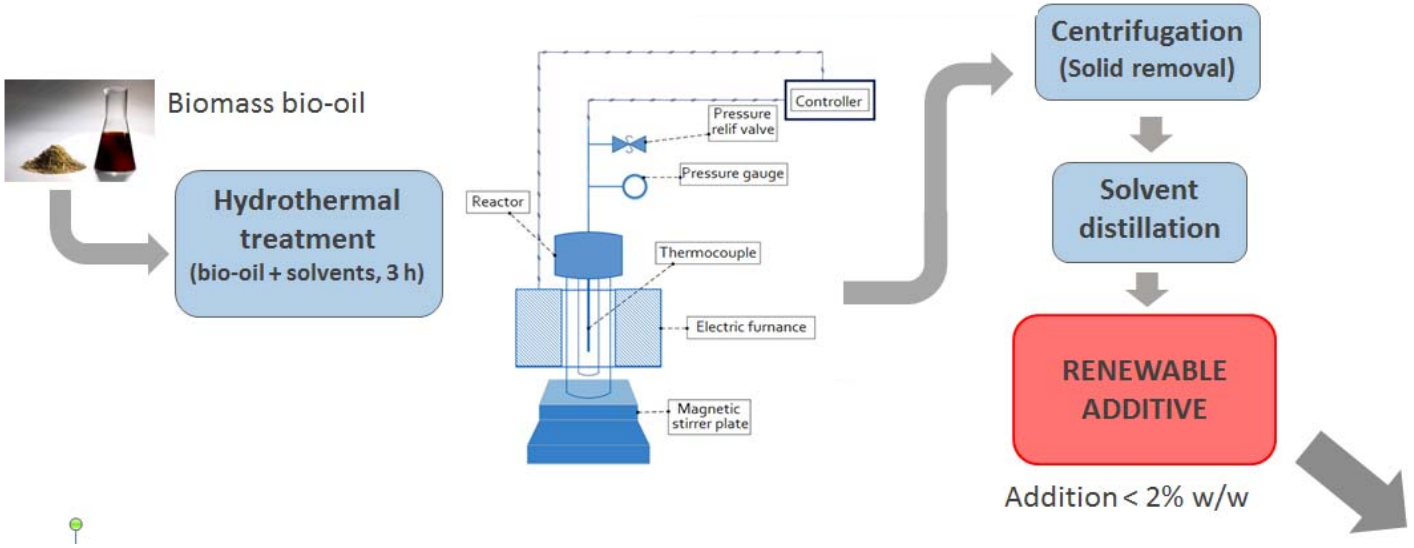
Fast pyrolysis of pinewood

Bio-oil

Some compounds identified in the bio-oil by GC-MS

Compound
2-hydroxy-3-methyl-2-cyclopenten-1-one
2-methoxyphenol
2-methoxy-4-methylphenol
1,2-benzenediol
4-ethyl-2-methoxyphenol
4-methyl-1,2-benzenediol
hydroxymethylfurfural
4-vinylguaiacol
2-methoxy-4-propylphenol
2-methoxy-3-(methoxymethyl)phenol
2,6-dimethylphenol
isoeugenol
vanillin
4-methoxy-3(methoxymethyl)phenol
2-methoxy-4-propylphenol
4-acetoguaiacol

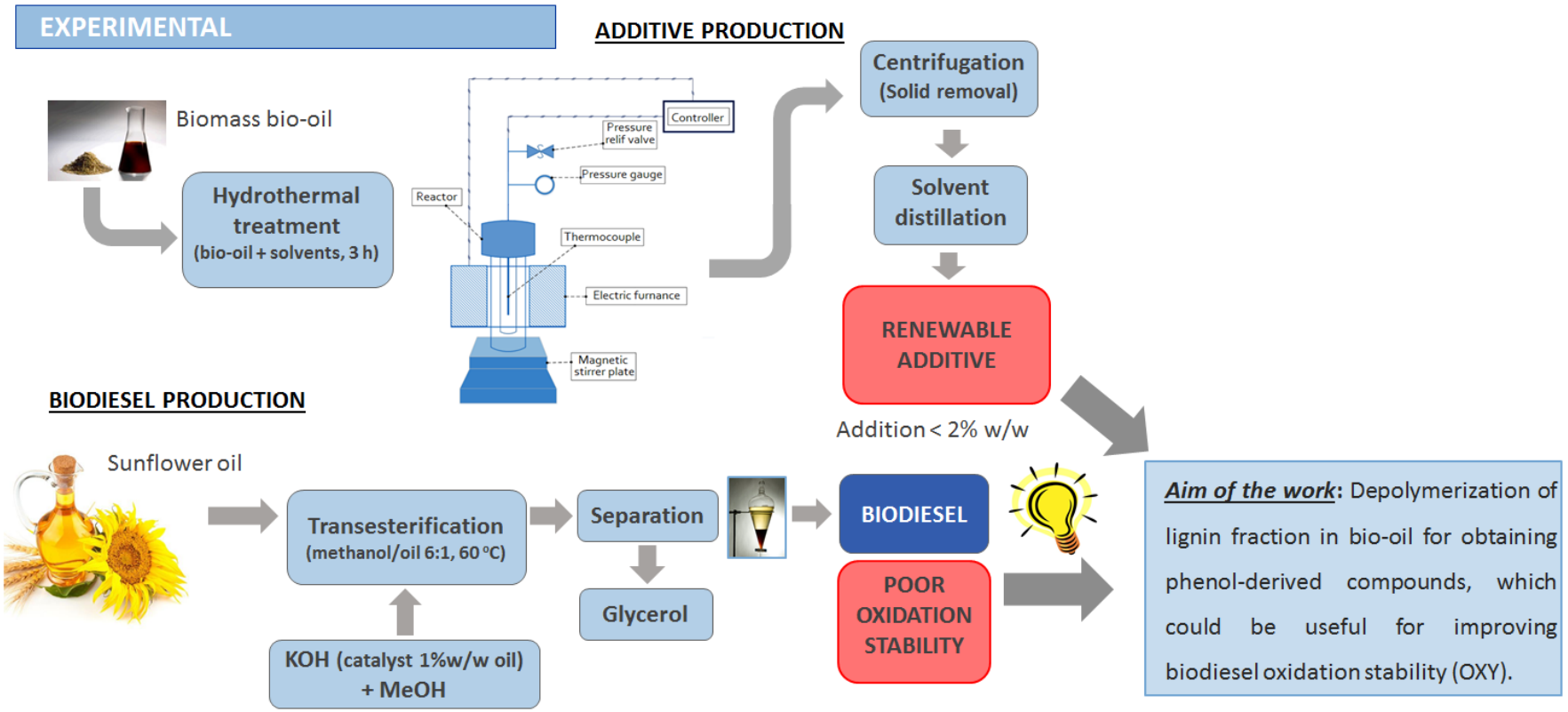
Additive production



Temperature (ºC)	Maximum pressure (bar g)	Solvent medium
300	87	Water
250	40	Water
300	108	Water / butanol
250	53	Water / butanol
300	102	Water / ethyl acetate
250	50	Water / ethyl acetate
290	115	Water / isopropyl acetate
250	52	Water / isopropyl acetate

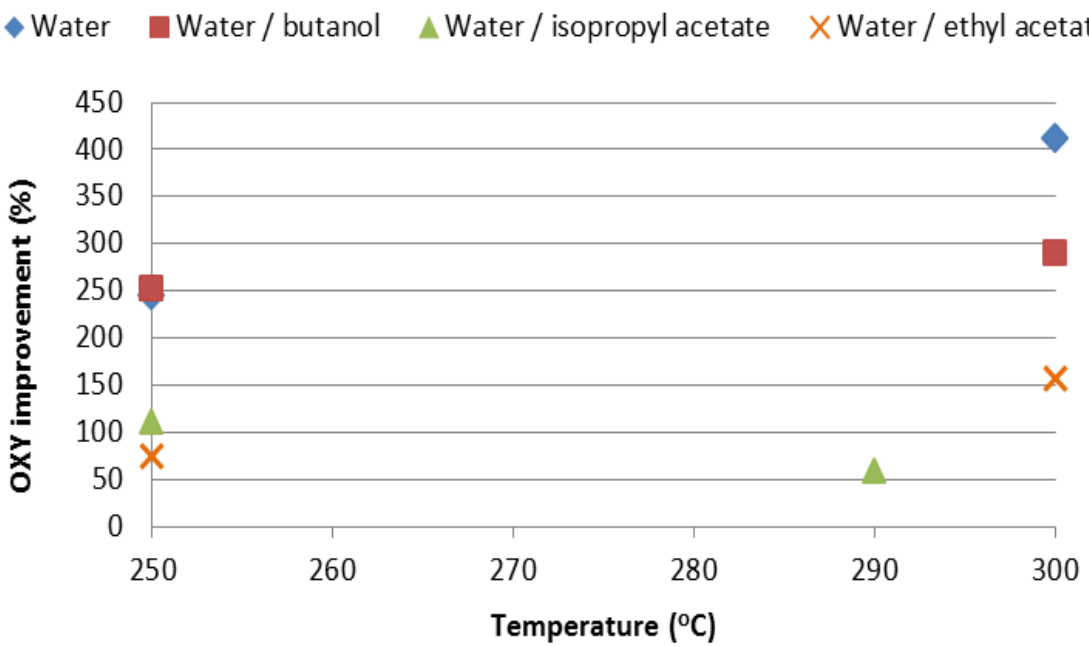
CONDITIONS TESTED IN THE HYDROTREATMENT OF BIO-OIL

Experimental



Results

Operational conditions during bio-oil hydrotreatment for the additive preparation		BIODIESEL PROPERTIES		
Solvent medium	**Temperature (ºC)**	**OXY (min)**	**Viscosity (cSt)**	**CFPP (ºC)**
Water	300	51.0 ± 0.5	4.23	-5.1
Water	250	33.3 ± 0.3	4.21	-6.2
Water / butanol	300	39.2 ± 0.4	4.23	-4.0
Water / butanol	250	35.6 ± 0.2	4.11	-3.9
Water / ethyl acetate	300	25.98 ± 0.02	4.25	-2.9
Water / ethyl acetate	250	17.66 ± 0.01	4.14	-2.9
Water / isopropyl acetate	290	13.71 ± 0.05	4.22	-1.8
Water / isopropyl acetate	250	19.72 ± 0.09	4.14	-4.0



$$\text{OXY improvement (\%)} = \frac{OXY_{\text{doped biodiesel}} - OXY_{\text{neat biodiesel}}}{OXY_{\text{neat biodiesel}}} \cdot 100$$

Results

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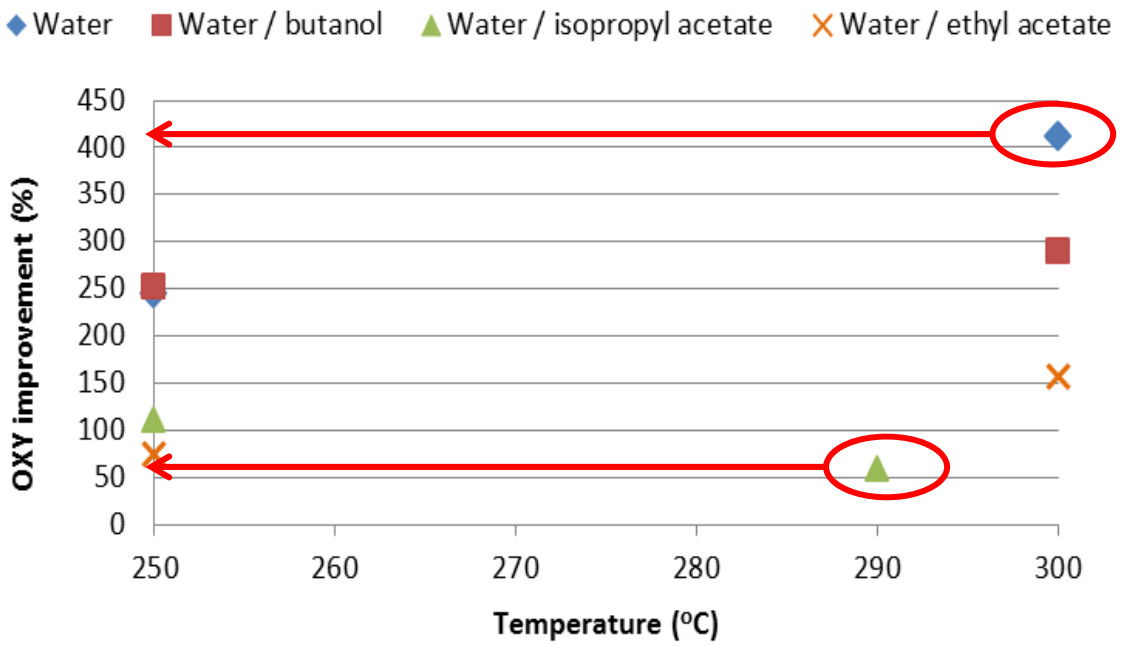

Improvement in oxydation stability between >50% and > 400%

Addition <2%

Results

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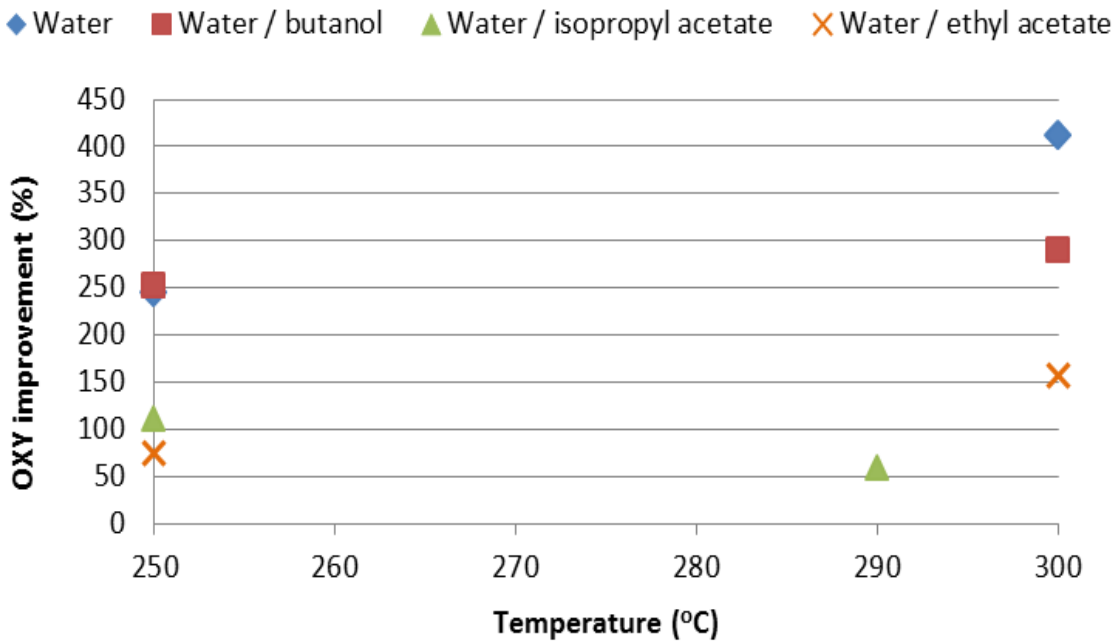

CFPP is hardly affected by the additive when using water as solvent

Conclusions

- Hydrothermal treatment of bio-oil appears as an interesting process to promote the depolymerization of the remaining fraction of lignin in bio-oil, thus obtaining a product rich in phenolic compounds.
- The oxidation stability of biodiesel was noticeably improved by incorporating these additives at low concentrations (< 2% w/w) with an improvement higher than 400% with respect to the neat biodiesel in the best case.
- Other important properties of biodiesel were hardly affected by the incorporation of the additives.

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