School of Chemical and Process Engineering

FACULTY OF ENGINEERING

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Upgrading of oils from catalytic co-pyrolysis of waste plastics and biomass using ex-situ metal/zeolite catalysts

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Centre of Doctoral Training in Bioenergy (EPSRC)

UK Outlook

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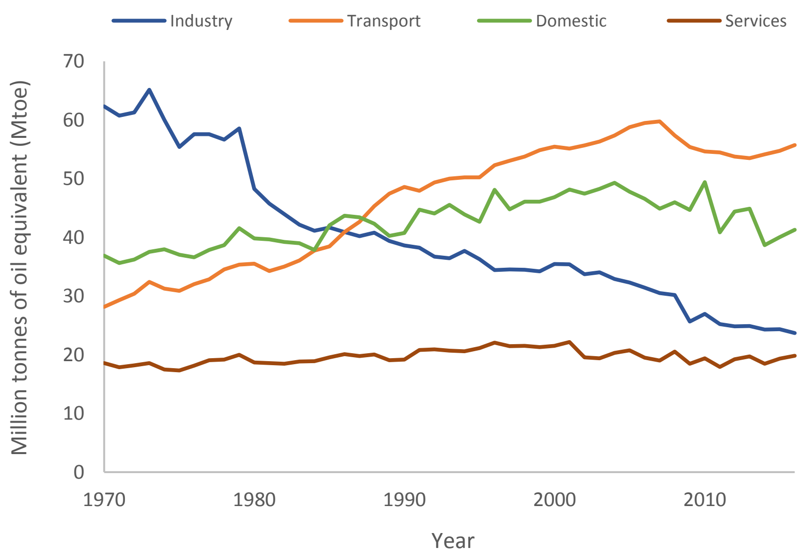
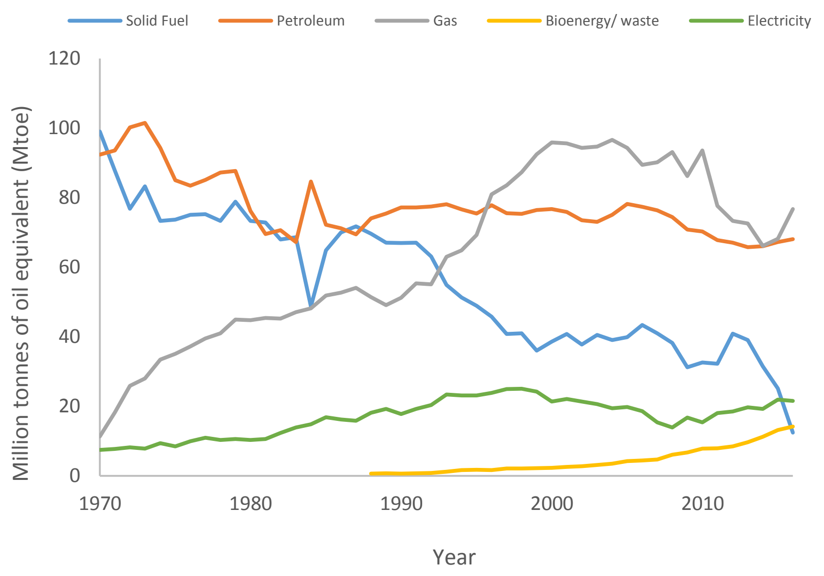
Transport in the UK makes up a significant proportion of all energy demand, of this a high proportion is sourced from petroleum.





Figures adapted from BEIS, Energy Consumption in the UK (ECUK) 2017

Catalytic pyrolysis

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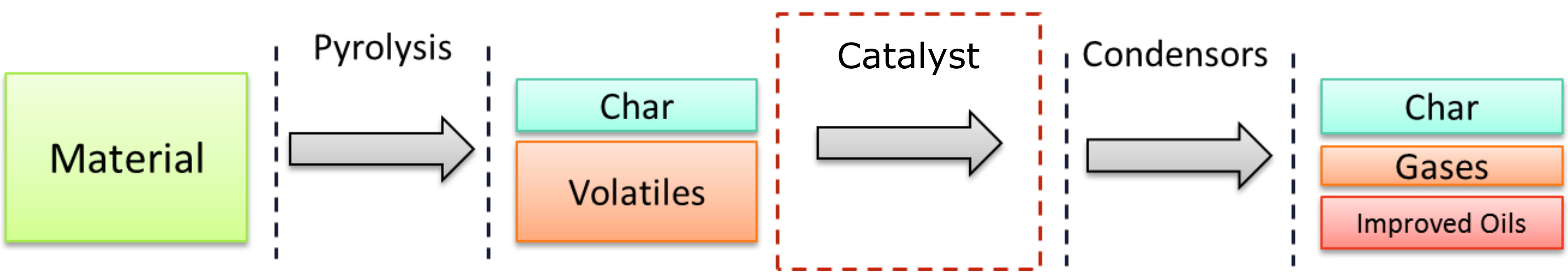
Problem:

1. High use of fossil fuels associated with environmental damage
2. Waste plastics and Biomass waste (380Mt Plastics made in 2015)
3. Need to find replacements fuels and chemical feedstock

Solution:

Can waste materials and biomass be used to produce fuels and chemical feedstock?

Catalytic pyrolysis:



Biomass – Structure

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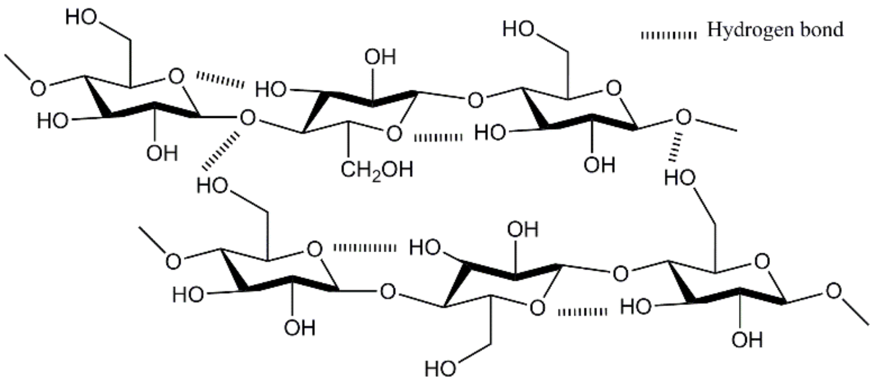
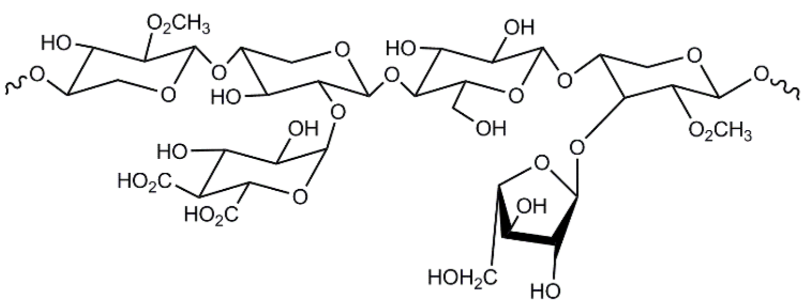
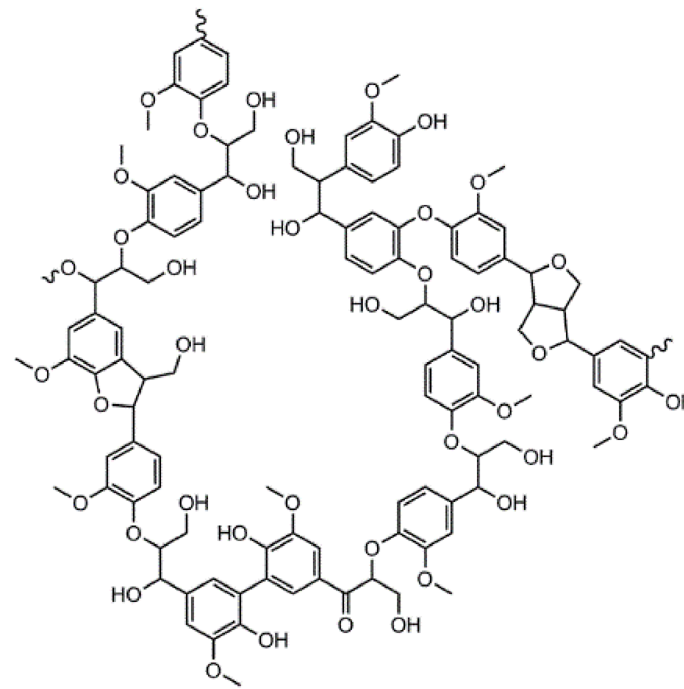
Cellulose



Hemi-cellulose



Lignin



A lot of structural oxygen!

Plastic

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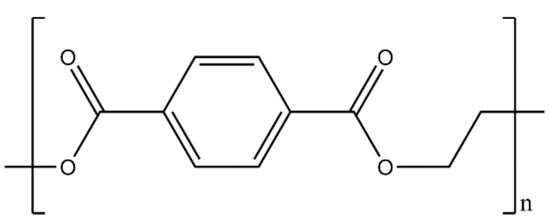
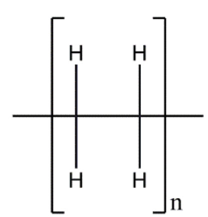
5 Different plastics used

- PET – Polyethylene Terephthalate
- HDPE – High Density Polyethylene
- LDPE – Low Density Polyethylene
- PP – Polypropylene
- PS – Polystyrene

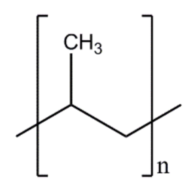
PET



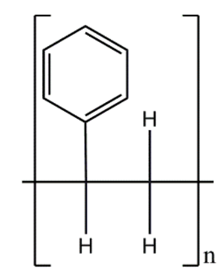
HDPE



PP



PS



Effects of Oxygen in Fuel

Oxygen in the pyrolysis material will likely be reflected in the pyrolysis oils leading to unhelpful properties in fuels.

- Acidic
- Unstable
- Low energy density
- High water content
- High viscosity
- Low vapour pressure
- Corrosive

Composition

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Content	Basis	Units	Biomass	HDPE	LDPE	PET	PP	PS
Moisture	a.r.	wt%	7.8	0.0	0.0	0.0	0.0	0.0
Ash	dry	wt%	0.3	4.1	0.3	42.7	0.8	1.6
Volatile	daf	wt%	93.3	98.1	100.0	94.6	100.0	100.0
Fixed Carbon	daf	wt%	6.7	1.9	0.0	5.4	0.0	0.0
GCV	dry	MJkg-1	19.6	47.5	51.2	16.4	46.2	47.5
Elemental								
C	daf	wt%	50.1	82.5	83.3	69.0	81.0	87.8
H	daf	wt%	5.4	13.1	12.6	5.0	11.4	9.5
O	daf	wt%	48.6	1.8	0.7	32.7	0.6	0.0
N	daf	wt%	0.1	0.1	0.1	0.0	0.1	0.0

Reactor set-up

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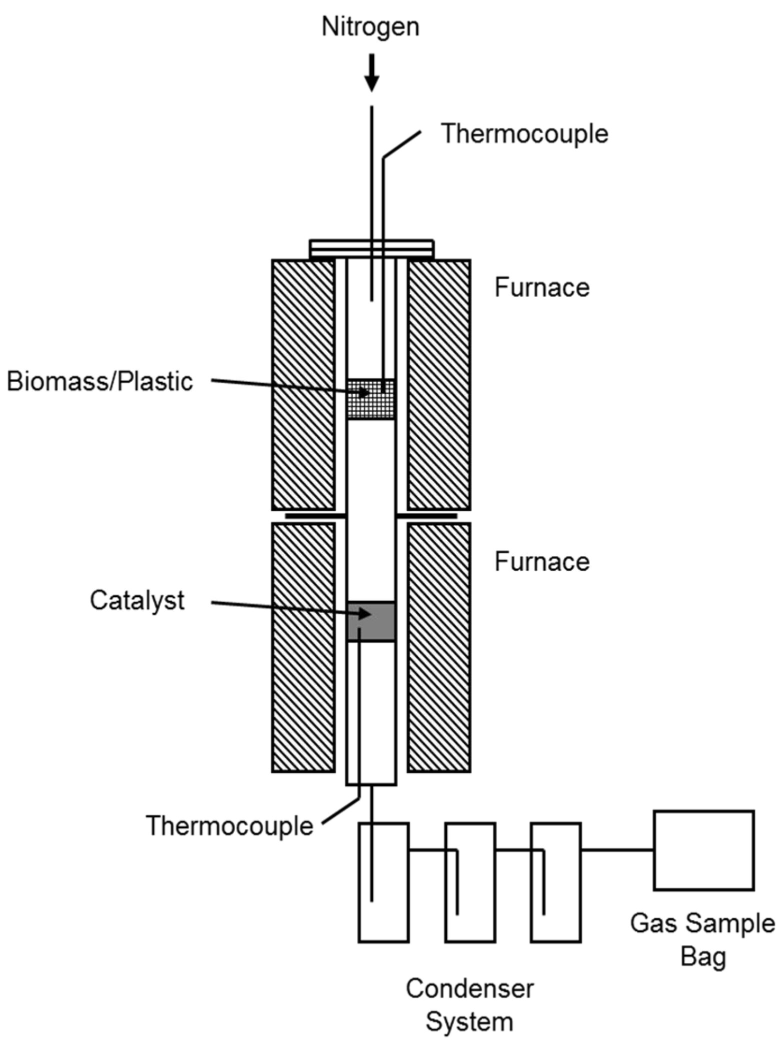

Sample: Biomass / plastic

Heat rate: 10°C/min

Temp of Reactor: 500°C

Runtime: 80-90 mins

Catalyst: ZSM-5

Analysis

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Gas analysis:
3 GC units
- Carbon dioxide
- Hydrocarbons (Methane, Ethane, Propane etc)
- Permanent gases (N_2, H_2, O_2, CO)

Oil analysis:
Water analysis
- Karl-Fischer titration

Oil analysis
- GC-MS

Analysis

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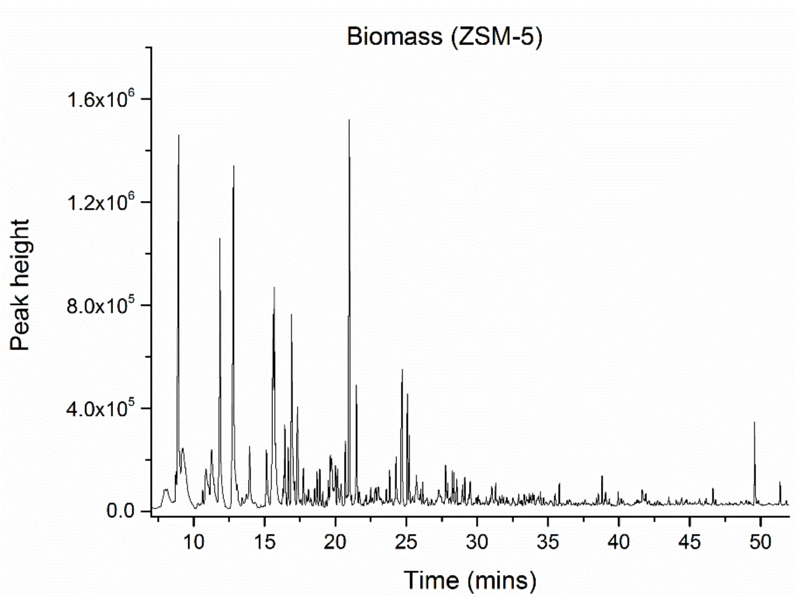
Use GC-MS to analyse the oils collected



	Compound	Peak Area	C	H	N	O	M_R	Cyclic	Aromatic
1	Toluene	222003	7	8	0	0	92	1	Y
2	Ethylbenzene	63051	8	10	0	0	106	1	Y
3	p-xylene	157428	8	10	0	0	106	1	Y
4	4-vinyltoluene (p-methylstyrene)	6049	9	10	0	0	118	1	Y
5	Naphthalene	80101	10	8	0	0	128	2	Y
6	2-methylnaphthalene	93268	11	10	0	0	142	2	Y
7	2-Ethylnaphthalene	9202	12	12	0	0	156	2	Y
8	2,6-dimethylnaphthalene	24258	12	12	0	0	156	2	Y
9	1,4 dimethylnaphthalene	5691	12	12	0	0	156	2	Y
10	phenanthrene	8506	14	10	0	0	178	3	Y
11	Pyrene	4175	16	10	0	0	202	4	Y
12	3-Methyl-1H-pyrazole	151814	4	6	2	0	82	1	N
13	o-xylene	423774	8	10	0	0	106	1	Y
14	m-xylene	180520	8	10	0	0	106	1	Y
15	3-Ethyltoluene (1-ethyl-3-methyl-benzene)	13674	9	12	0	0	120	1	Y
16	4-Ethyltoluene (1-ethyl-4-methyl-benzene)	40222	9	12	0	0	120	1	Y
17	Phenol	310979	6	6	0	1	94	1	Y
18	1,2,3-trimethyl-benzene	195316	9	12	0	0	120	1	Y
19	Indane	62475	9	10	0	0	118	2	Y
20	1-propynyl-benzene	74441	9	10	0	0	118	1	Y
21	3-Methylphenol (m-cresol)	134020	7	8	0	1	108	1	Y
22	4-Methylphenol (p-cresol)	351339	7	8	0	1	108	1	Y
23	4-Methylindane	43507	10	12	0	0	132	2	Y
24	1,2-dihydronaphthalene	18720	10	10	0	0	130	2	Y
25	1-methyl-4-(1-propynyl)-benzene	65425	10	10	0	0	130	1	Y
26	2,6-Xylenol	73396	8	10	0	1	122	1	Y
27	2,4-Xylenol	101794	8	10	0	1	122	1	Y
28	2,5-Xylenol	37627	8	10	0	1	122	1	Y
29	2,3-Xylenol	29848	8	10	0	1	122	1	Y
30	3,4-Xylenol	56225	8	10	0	1	122	1	Y
31	1-Methylnaphthalene	70179	11	10	0	0	142	2	Y
32	1,2-dimethylnaphthalene	82844	12	12	0	0	156	2	Y
33	2,3-dimethylnaphthalene	66503	12	12	0	0	156	2	Y
34	1,7-dimethylnaphthalene	37985	12	12	0	0	156	2	Y
35	2-Isopropylnaphthalene	27366	13	14	0	0	170	2	Y
36	1-Naphthol	19051	10	8	0	1	144	2	Y
37	1,6,7-trimethyl-naphthalene	19426	13	14	0	0	170	2	Y
38	2,3,6-trimethylnaphthalene	15727	13	14	0	0	170	2	Y
39	Triethyl citrate	24772	12	20	0	7	276	0	N
40	Anthracene	13973	14	10	0	0	178	3	Y
41	2-methyl-anthracene	26685	15	12	0	0	192	3	Y

Analysis

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1) Biomass
2) Metal catalysts
3) Polymers
4) Co-pyrolysis

Biomass

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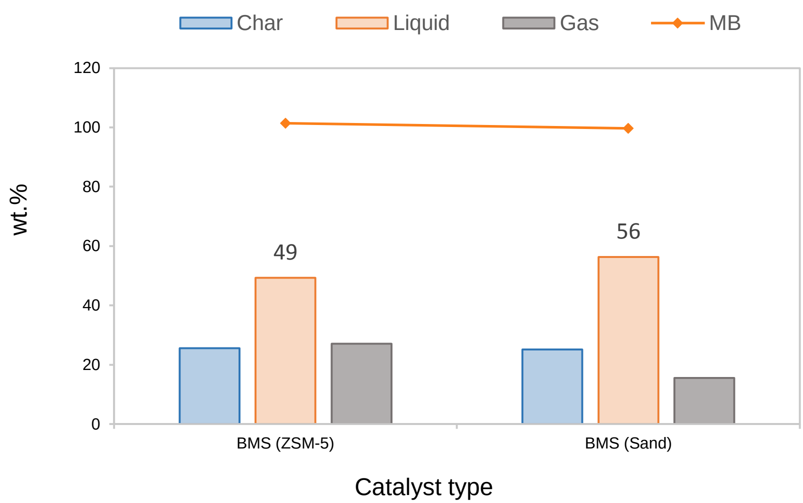

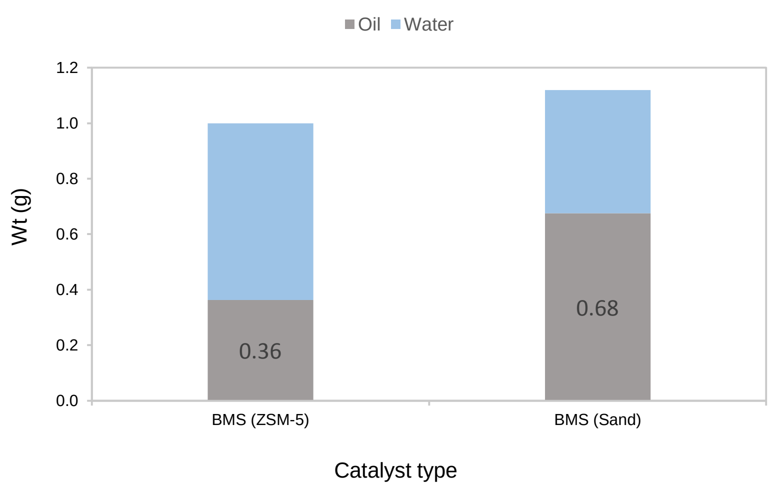

Biomass

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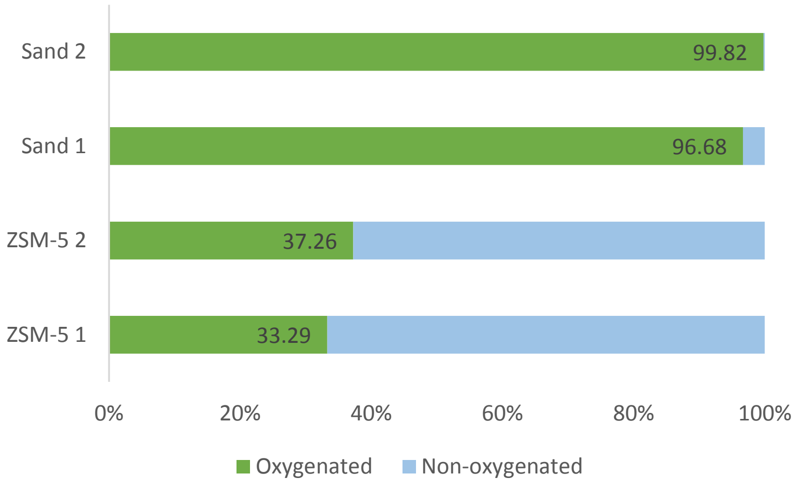
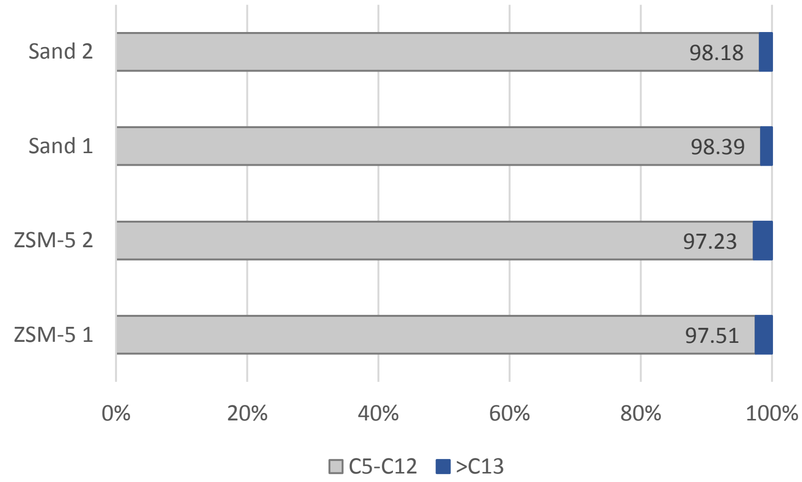
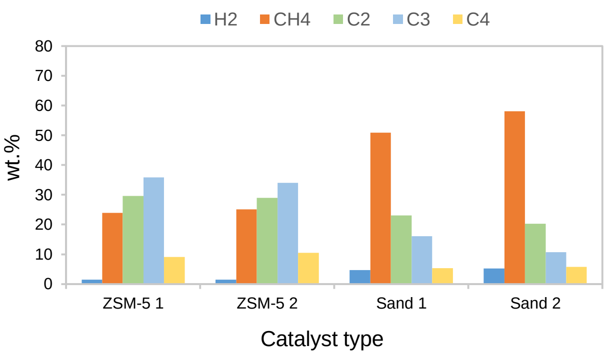
b) Low Oxygenates



c) High C_5-C_{12}





Analysis

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Metal Cat

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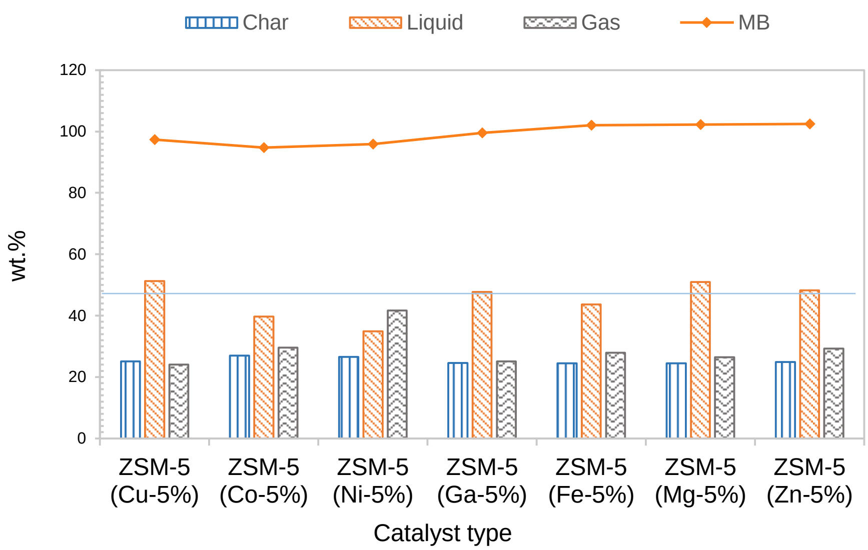

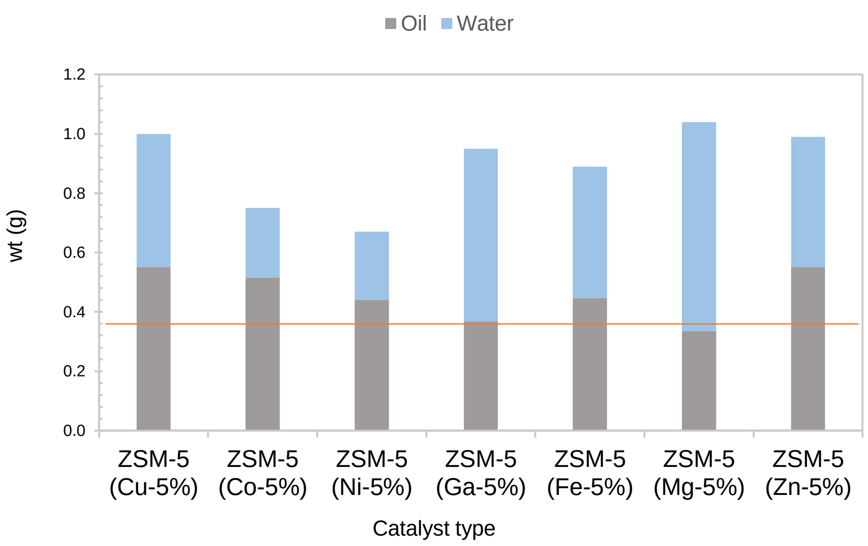

Metal Cat

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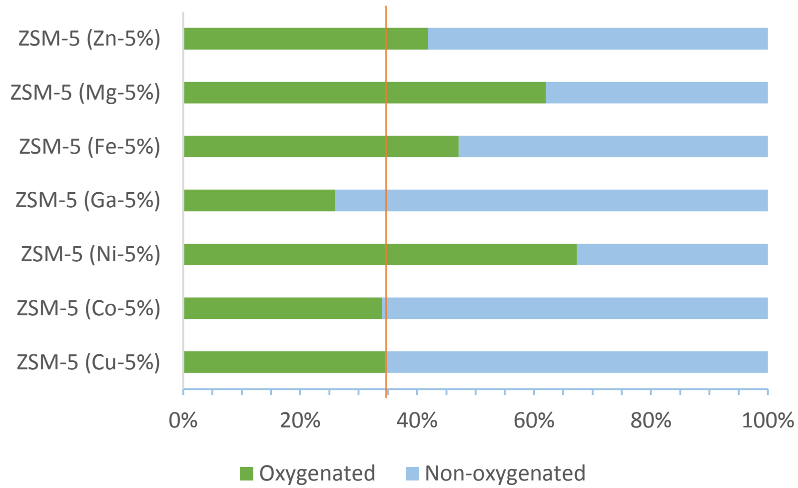

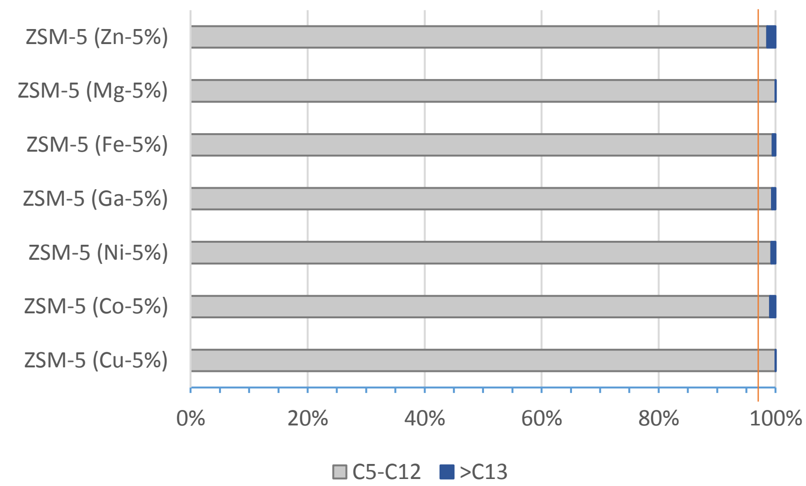

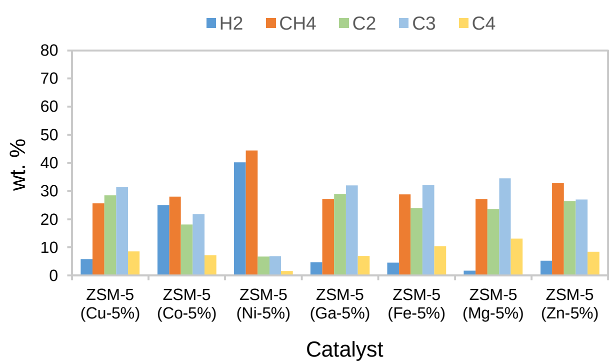

Analysis

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1) Biomass
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Polymer

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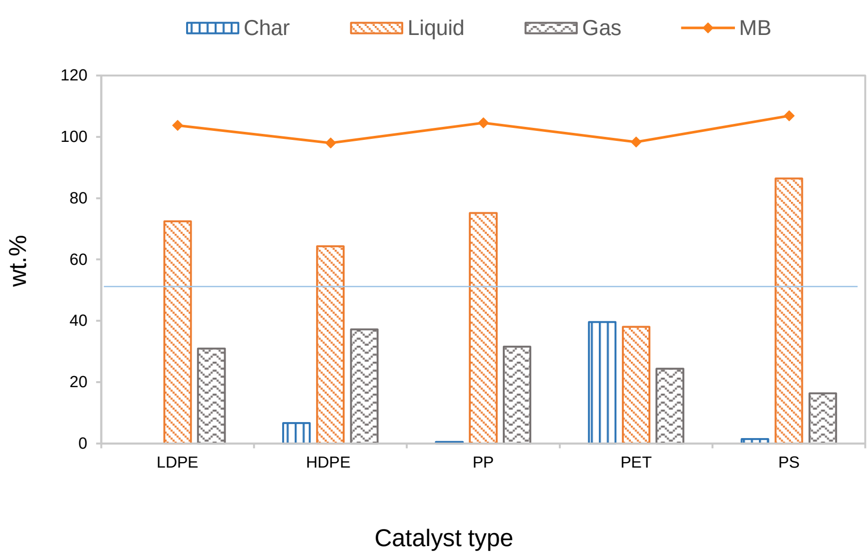

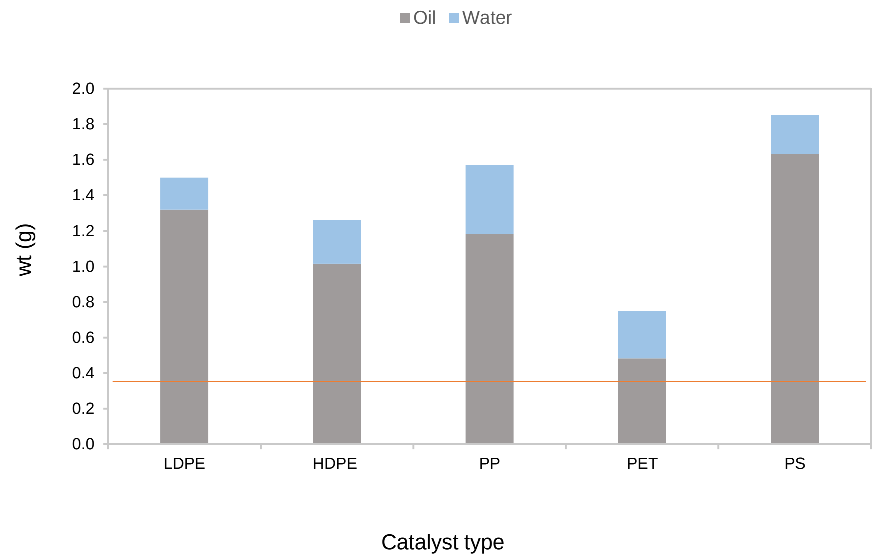

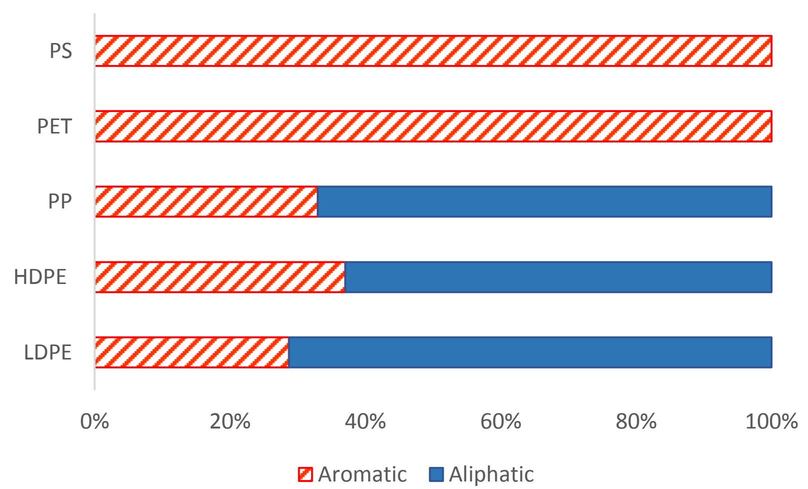

Polymer

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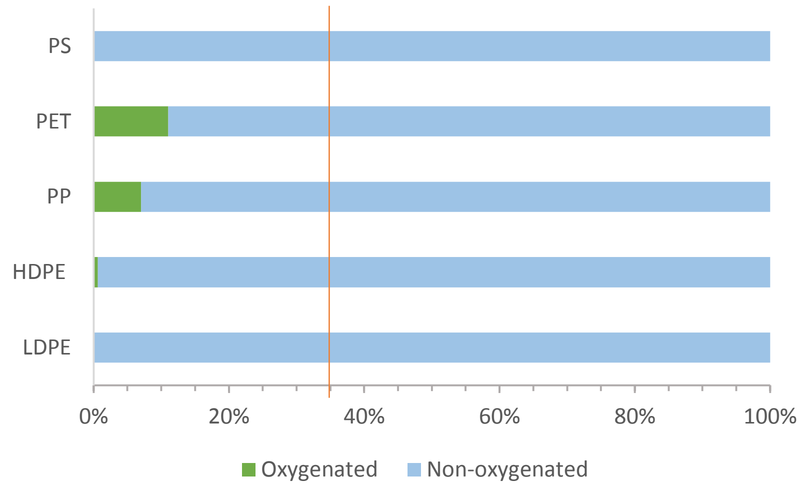

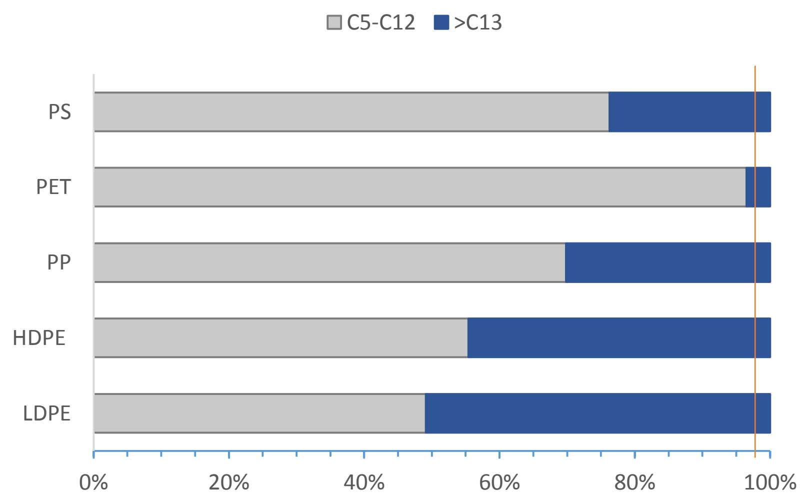

Analysis

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1) Biomass
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4) Co-pyrolysis

50:50 mix

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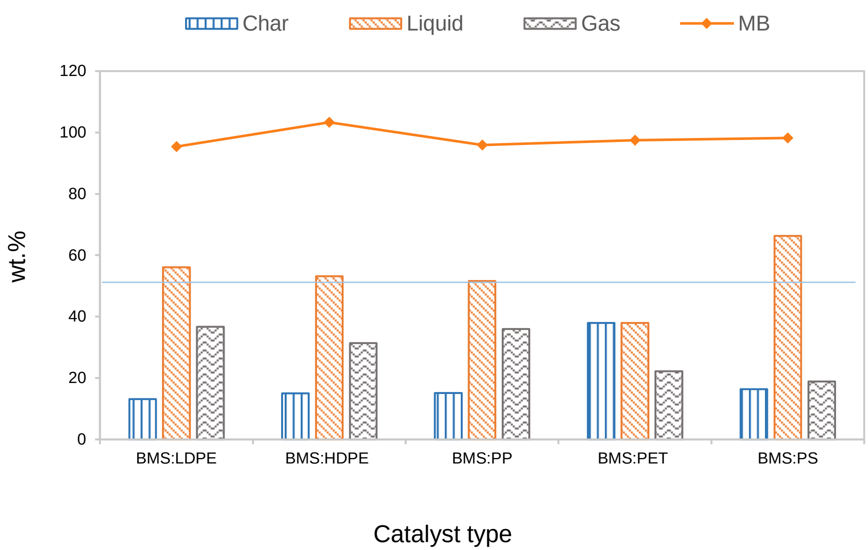

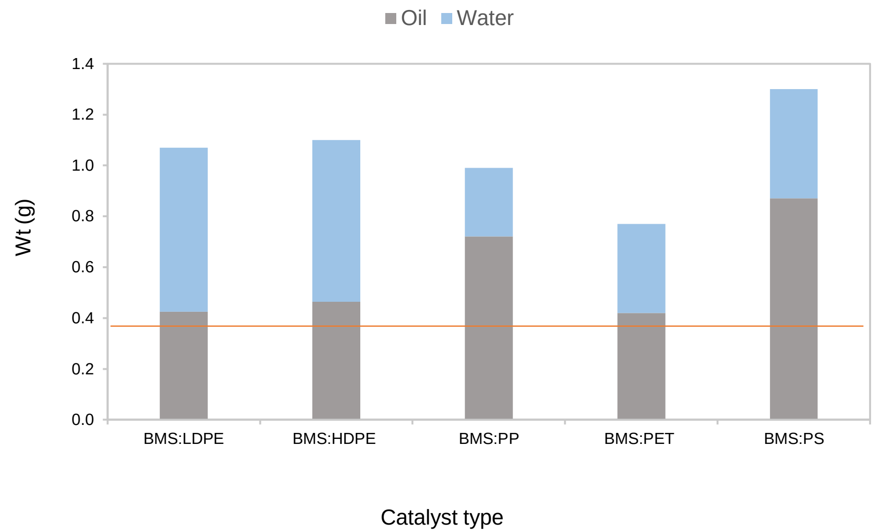

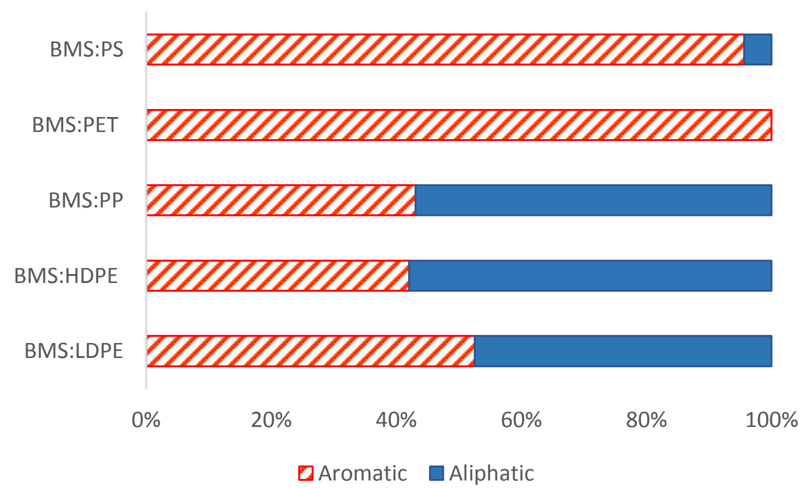

50:50 mix

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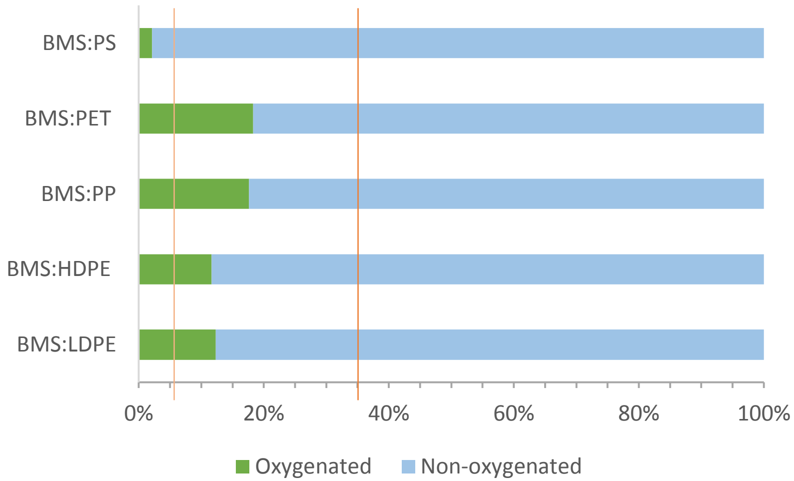

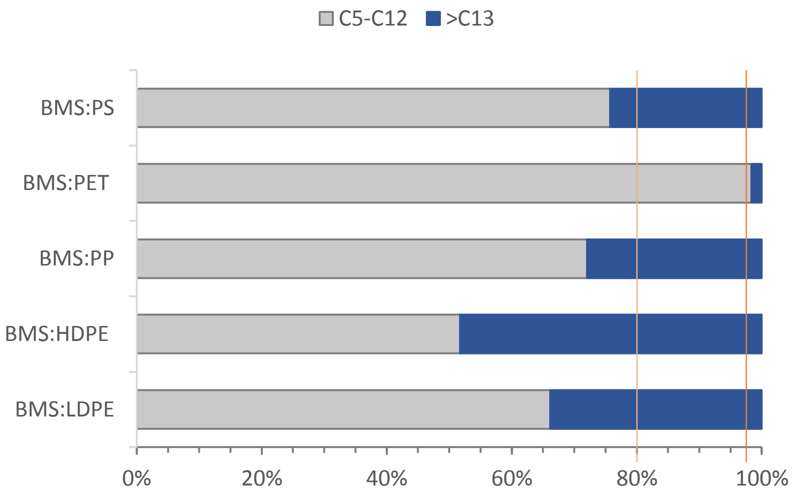

Conclusion

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1) Biomass
   - Oxygenated
   - ZSM-5 Catalysts improves oxygenation but not yield

2) Metal catalysts
   - Mostly better yields – Co, Cu, Ga, most promising catalysts

3) Polymers
   - High oil yield, low oxygenates but lower C_5-C_{12} proportion

4) Co-pyrolysis
   - PS improved yields to Biomass but less than PS. Much lower oxygenation than a mixture, but lower proportion of C_5-C_{12}

Thank you very much

- Any Questions?