Catering wastes conversion to bio-crude oil via hydrothermal liquefaction

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BIOMASS IN SPOTLIGHT FOR BIOFUELS PRODUCTION

Global energy demands increase – European regulations

Residual Biomass: Largely available - eco-friendly source for fuels

Application of two main thermochemical processes

PYROLYSIS

HYDROTHERMAL LIQUEFACTION

HYDROTHERMAL LIQUEFACTION

Thermochemical conversion of biomass into liquid fuels

Processing in hot, pressurized water environment for sufficient time

Break down solid biopolymeric structure to mainly liquid components

HTL benefits over pyrolysis:

- No feedstock drying – Utilization of wet biomass
- Solvents act as catalysts due to their high temp. favorable properties
- HTL bio-crude oil is enhanced in terms of yield and fuel properties

OBJECTIVES OF STUDY

2nd Generation biofuels production from catering wastes via HTL

HTL main parameters study in quantitative and qualitative terms

Comparative study between the different biomass types

MATERIALS

Spent coffee grounds

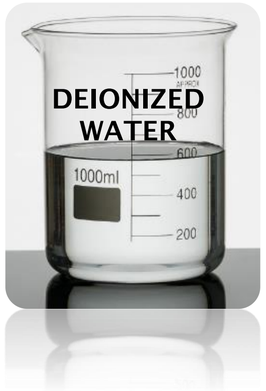
Properties	Spent coffee grounds	Orange peels
Moisture (wt%)	11.3	6.0
Ash (wt%)	1.12	3.8
Cellulose (wt%)	12.1	40.0
Hemicellulose (wt%)	33.5	24.0
Lignin (wt%)	22.2	5.2

Orange Peels

HYDROTHERMAL LIQUEFACTION PROCESS

BIOMASS

SOLVENT



- Temperature: 280º – 350 ºC
- Reaction Time: 5 – 60 min
- Solid – Liquid Ratio: 1 / 10
- Compression gas: N_2 30 bar

HTL

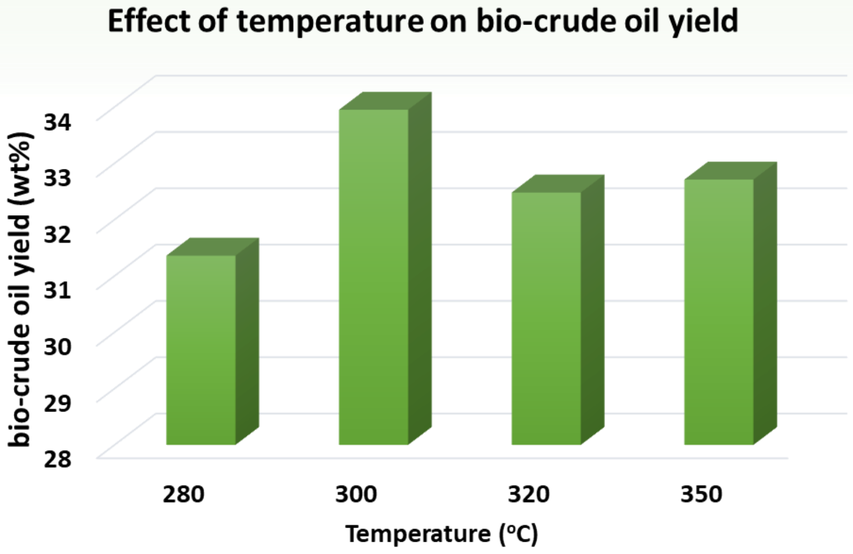

Batch autoclave reactor

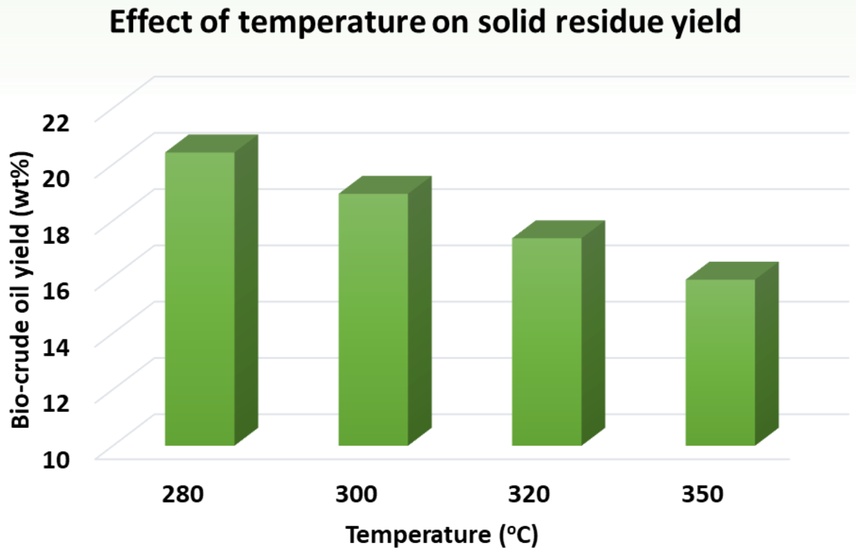
1. Gas sampling
2. Filtration of products
3. Aqueous phase removal
4. Acetone extraction
5. Acetone evaporation
6. Solid residue drying

PRODUCTS

- Gas products 
- Aqueous phase 
- Bio-crude oil 
- Hydrochar 

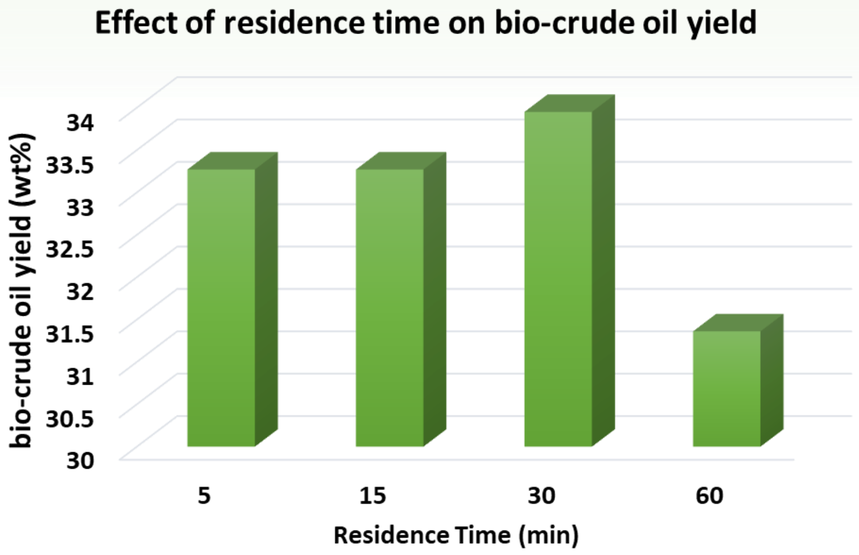
HYDROTHERMAL LIQUEFACTION OF SPENT COFFEE GROUNDS

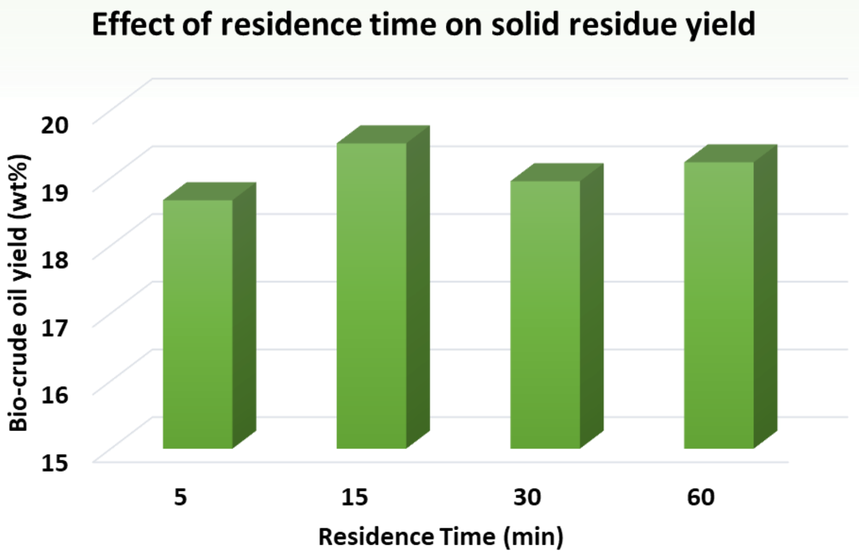




- High conversion rates of spent coffee grounds (over 80 wt%)
- Optimal Temperature was found at 300 °C
- Solid Residue yield was declining as temperature rose (from 20 to 17 wt%)
- Maximum bio-crude oil yield obtained was 33.5 wt%

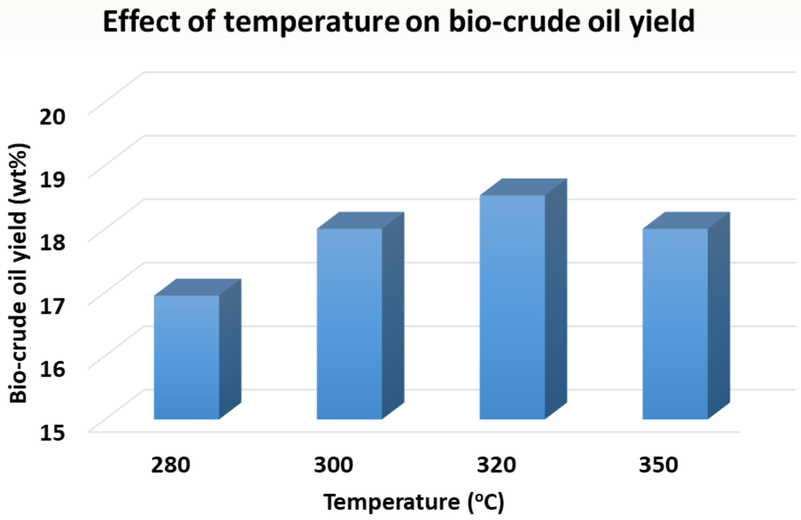
HYDROTHERMAL LIQUEFACTION OF SPENT COFFEE GROUNDS

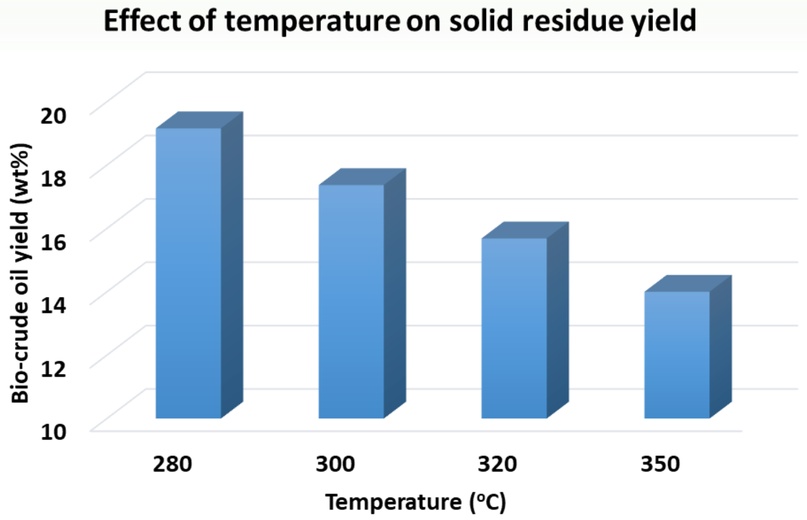




- Residence time has no significant effect in yield of bio-crude oil and solid residue
- Optimal residence time was found at 30 minutes
- At 60 min liquid molecules are gasified
- At lower temperatures there is small decline in oil yield

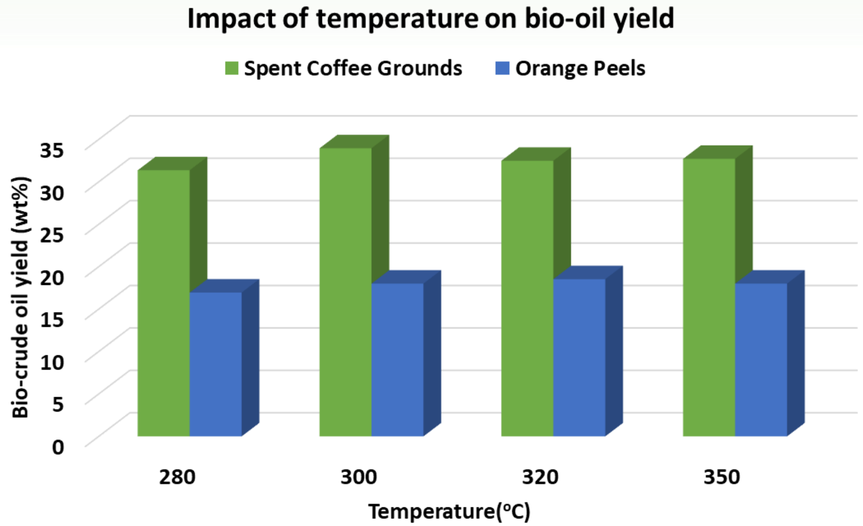
HYDROTHERMAL LIQUEFACTION OF ORANGE PEELS

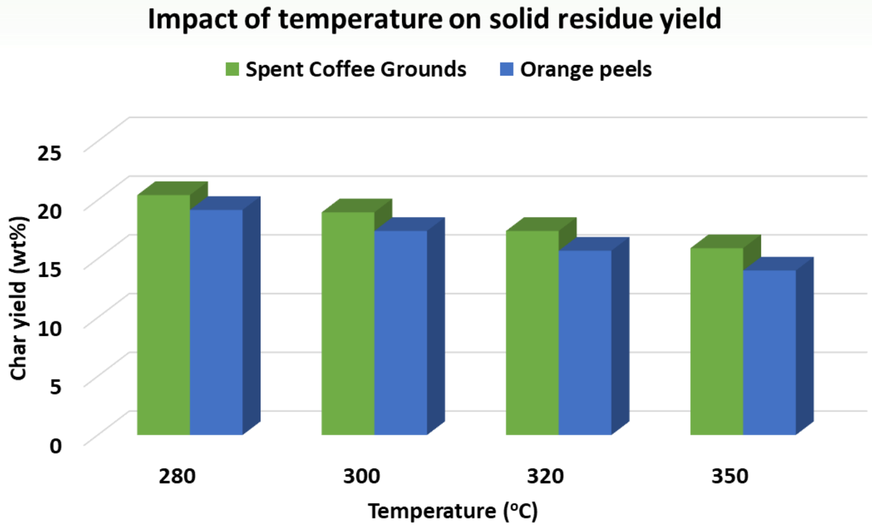




- Orange peels hydrothermal liquefaction renders poor bio-crude oil yield
- Bio-crude oil yield varied from 16.5 to 18.5 wt%
- Optimal temperature was 320 °C but with no significant difference
- Solid residue yield significantly declining as temperature rises

COMPARATIVE STUDY OF FEEDSTOCKS





- **Spent coffee grounds appear as more suitable feedstock for production of biofuel intermediates**

Spent coffee grounds: **Lignin: 22.2 wt%**

Orange peels: **Lignin: 5.2 wt%**

- **Solid residue yield has the same trend in both feedstocks and similar yields**

GAS PRODUCTS ANALYSIS

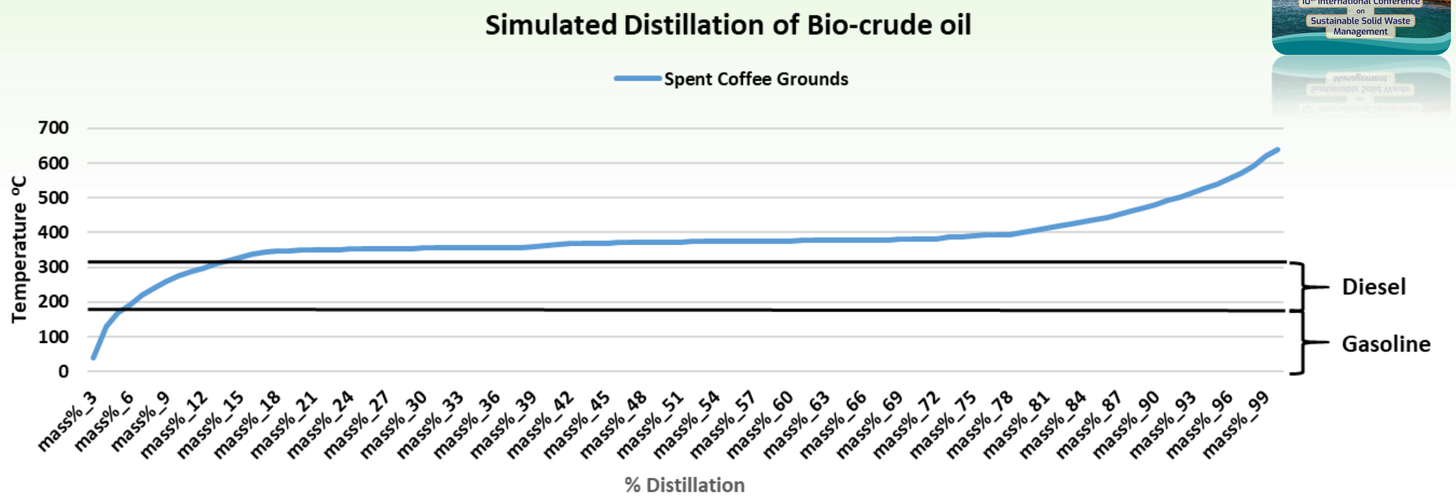
MOLECULE	SPENT COFFEE GROUNDS	ORANGE PEELS
Hydrogen	-	-
Methane	0 – 12	0.4 – 2.95
Ethane	-	0 – 0.5
Propane	0 – 0.5	0.04 – 0.22
Isobutane	0 – 0.2	0 – 0.03
N-butane	0.03 – 0.16	0 – 0.06
Isopentane	0 – 0.72	0 – 0.01
N-pentane	0.02 – 0.28	0 – 0.02
$C6^{+}$ (6 or more carbons)	0.15 – 1.27	0.14 – 0.21
Carbon dioxide	87 – 98.1	94.5 – 97.8
Carbon Monoxide	0 – 5.9	1.29 – 1.63

GC-FID ANALYSIS ON GAS PRODUCT

- **Main product is carbon dioxide**
- **Methane and carbon monoxide in lower concentration**
- **Small traces of:**
  - **Ethane**
  - **Propane**
  - **Butane**
  - **Pentane**
  - **6 or more carbon atoms**

QUALITATIVE ANALYSIS OF BIO-CRUDE OIL FROM COFFEE

Quantity	Chemical Compound
15.80	n-Hexadecanoic acid
8.61	9,12-Octadecadienoic acid (Z,Z)-
7.91	9,12-Octadecadienoic acid (Z,Z)-
3.94	Octadecanoic acid
2.79	Tetradecanamide
1.93	9,12-Octadecadienoic acid (Z,Z)-
1.89	n-Hexadecanoic acid
1.56	13-Tetradecen-1-ol acetate
1.55	n-Hexadecanoic acid
1.33	n-Hexadecanoic acid
1.33	1,19-Eicosadiene
1.10	9,12-Octadecadienoic acid (Z,Z)-
1.06	9,12-Octadecadienoic acid (Z,Z)-
0.95	9,12-Octadecadienoic acid (Z,Z)-
0.93	9,12-Octadecadienoic acid (Z,Z)-
0.92	9,12-Octadecadien-1-ol, (Z,Z)-
0.86	3-(3,4-Dimethyl-6-Phenylcyclohex-3-enyl)prop-2-enoic acid
0.83	n-Hexadecanoic acid
0.81	n-Hexadecanoic acid
0.77	9,12-Octadecadienoic acid (Z,Z)-
0.70	n-Hexadecanoic acid
0.69	9,12-Octadecadien-1-ol, (Z,Z)-
0.68	n-Hexadecanoic acid
0.65	n-Hexadecanoic acid
0.60	n-Hexadecanoic acid
0.58	9,12-Octadecadienoic acid (Z,Z)-
0.54	Octadecanoic acid
0.50	Linoleic acid ethyl ester



GC-MS ANALYSIS ON BIO-CRUDE OIL

- Oil contains significant quantities of diesel range carbon chains
- Most of these compounds contain heteroatoms (acids, esters, amides)

SIM-DIS ANALYSIS ON BIO-CRUDE OIL

- Oil is heavier than diesel and gasoline cuts
- Upgrading is necessary to remove heteroatoms and get the oil lighter

QUALITATIVE ANALYSIS OF BIO-CRUDE OIL FROM ORANGE PEELS

Quantity	Chemical Compound
6.68	Stigmastan-3,5-diene
4.54	Octadecanoic acid
3.67	Decanedioic acid, bis(2-ethylhexyl) ester
3.06	Heptadecane
2.80	9,12-Octadecadienoic acid (Z,Z)-
2.77	.gamma.-Sitosterol
2.67	1-Nonadecene
2.67	1-Chloroeicosane
1.85	n-Hexadecanoic acid
1.60	1H-Pyrazole-4-carbaldehyde, 3-(4-methoxyphenyl)-
1.53	Pyrene, 1-methyl-
1.46	1,2-Benzenedicarboxylic acid, diisooctyl ester
1.35	Benzene, 1,4-dichloro-2,3,5-triethyl-
0.91	1,3-Bis(trimethylsiloxy)benzene
0.84	Phenol, 4-ethyl-2-methoxy-
0.79	Cyclohexane, hexaethylidene-
0.66	4H-Thiazolo[5,4-b]indole, 2,5,7-trimethyl-
0.58	Tetradecane

GC-MS ANALYSIS ON BIO-CRUDE OIL

- Bio-crude oil from orange peels also contains diesel range carbon chains
- More complex molecules existence such as stigmastane
- Bio-crude oil needs also upgrading to remove heteroatoms and crack complex molecules
- Bio-crude oil not miscible in most solvents – no sim-dis analysis available

CONCLUSIONS

HTL appears as potential and sustainable process in bio-fuels production chain

Bio-crude oil yield and quality were with valorization of spent coffee grounds

Orange peels bio-crude oil was poor in terms of yield and properties

Produced bio-crude oil needs upgrading in order to be used as final liquid biofuels

Thank you !!

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