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## Thermo-catalytic reforming of co-form<sup>®</sup> rejects (waste cleansing wipes)

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### Abstract

Co-form<sup>®</sup> products are typically used for personal hygiene care (cleansing wipes), household cleaning (pads and mops) and absorbent applications. Co-form<sup>®</sup> is a thermo-bonded multilayer nonwoven composite and Kimberly-Clark patented its process in 2008. Co-form<sup>®</sup> rejects are composed of 30% plastic polypropylene and 70% wood pulp fibre. It is difficult to recycle and to-date no research articles explore pyrolytic valorisation for its energy recovery. This paper investigated pyrolytic valorisation of co-form<sup>®</sup> rejects into energy vectors. Pelletised co-form<sup>®</sup> rejects obtained from a secondary fibre paper mill were processed using a laboratory scale 2 kg/h Thermo-Catalytic Reforming (TCR<sup>®</sup>) reactor. The TCR<sup>®</sup> process combines intermediate pyrolysis, using an auger reactor to heat the material under moderate temperatures (350–450 °C) and moderate solid residence times (minutes) in the complete absence of Oxygen, with post catalytic reforming in a fixed bed reactor at 700 °C. Pelletised co-form<sup>®</sup> rejects were successfully converted into 12 wt% bio-oil, 9 wt% aqueous phase liquid, 8 wt% char and 71 wt% syngas products. The bio-oil higher heating value was found to be 39.36 MJ/kg, comparable to biodiesel. Naphthalene was found to be the most abundant aromatic compound within the oil, with a relative abundance of 15.22% measured by GC-MS. Oleic acid methyl ester (15.86%) was the most abundant long chain hydrocarbon detected. The higher heating value of produced gas was 11.02 MJ Nm<sup>3</sup> and char 30.79 MJ/kg. TCR<sup>®</sup> conversion of co-form<sup>®</sup> rejects proved to be a feasible route for the valorisation of this waste stream into sustainable energy vectors. In previous works, gasification processes could not successfully convert organic waste streams with a high plastic content, without implications attributed to agglomeration and melting of plastics. The TCR<sup>®</sup> process overcome these issues with no evidence of agglomeration or melting of plastics present within the reactor. The success was believed to be through applying moderate heating rates (°C/min) and temperatures (max 700 °C), as well as the mechanical effect of continuous mixing of material within the reactor via the internal auger screw. Overall, TCR<sup>®</sup> is a promising future route for the valorisation of co-form<sup>®</sup> rejects to produce energy vectors.

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**Keywords:** Organic waste; Thermal conversion; Energy vectors; Pyrolysis; Synthesis gas

## 1 Introduction

The European paper industry produced around 91 million tonnes of paper and board in 2016 [1]. Waste generated is between 10 and 15% of total paper and board production [2]. Paper utilised for recycling in 2016 is estimated

at 47 million tonnes [1]. In Europe, legislation (Directive 94/62/EC on packaging and packaging waste and 2008/98/EC on waste) is in place to reduce paper and board waste [3]. The Paper Packaging Coordination Group (PPCG) represents the European paper industry and in 2014, the average paper and board packaging recycle rate reached 81.1% [1]. Landfill disposal of paper and board waste is becoming increasingly costly and in many countries, such as Germany and Netherlands, this disposal route is already prohibited. Regulations globally are also becoming more stringent towards recycling and recovery of organic waste and plastics from composites. The composite market is expected to grow by 40%, reaching a global value of \$95bn between 2014–2020 [4]. At present, waste from carbon fibre reinforced polymer (CFRP) commonly used for production of composites (co-form<sup>®</sup> rejects) exceeds end-of-life waste. Waste associated with production is typically between 30–50% of production volume, and several companies across the globe are now beginning to recycle these wastes.

Composites are difficult to recycle because they are generally non-homogeneous with excellent structural and durability characteristics. Job et al. [4] reported several recycling and recovery processes to valorise composite and end-of-life waste; these include mechanical, thermal (several pyrolysis variants), chemical/thermochemical (solvolysis) and cement kilns. Recycled composites recovered mechanically, are commonly used for products such as fillers and retainers. The high-energy demand associated with grinding and competition from other low cost fillers and retainers, such as calcium carbonate and silica, limits utilisation of composites recovered mechanically. Structural properties may also be impaired (e.g. fibre damage and poor bonding) between new materials and recyclates. Energy recovery, of composites recovered mechanically, by combustion is a possible recovery route if gaseous emissions, such as PAH's, nitrogenous aromatics and phenolics, meet environmental regulations. Pyrolysis, chemical/thermochemical (solvolysis) and gasification offer alternative valorisation routes for energy and chemical recovery.

Co-form<sup>®</sup> is a thermo-bonded multilayer nonwoven composite. Its production process was patented by Kimberly-Clark in 2008. The process combines fiberized wood pulp with synthetic fibres (e.g. polypropylene) and other additives such as pigments and antibacterial agents [5]. Co-form<sup>®</sup> products are typically used for personal hygiene care (cleansing wipes), cleaning (household) and absorbent applications. Product properties can be tailored by different processes, synthetic fibres and additives, e.g. non-elastic or elastic properties. Ouadi et al. [6] investigated the gasification of co-form<sup>®</sup> rejects. Co-form<sup>®</sup> rejects tested were non-woven wipes commonly known as cleansing wipes (baby wipes). The authors investigated two types of co-form<sup>®</sup> rejects, dry and wet co-form<sup>®</sup> rejects. Dry co-form<sup>®</sup> rejects are composed of 30% polypropylene and 70% wood pulp fibres without additional additives, such as water or antibacterial reagents, whereas wet co-form<sup>®</sup> rejects contains water (up to 70 wt% before drying) and additional plastics and antibacterial reagents. The dry and wet co-form<sup>®</sup> rejects were sorted, dried, pelletised and characterised. The authors attempted to co-gasify wood and co-form<sup>®</sup> but were unsuccessful. This was due to major agglomeration issues caused by rapid gasifier heating rates and high temperatures experienced by the plastics within the pelletised feedstock. Alternative thermal conversion technologies with lower initial heating rates are more suited to materials with high levels of plastics, e.g. intermediate pyrolysis.

Chattopadhyay et al. [7] investigated catalytic co-pyrolysis of paper and plastic (mix of HDPE, PP and PET) using a fixed bed reactor. HDPE, PP and PET were firstly mixed, at a ratio of 1:1:1, before mixing with paper (cellulose 76.5 wt%, hemicellulose 15.2 wt% and lignin 3.3 wt%) at different weight ratios. Pyrolysis tests were carried out in batch (argon flow rate of 50 ml/min, heated from ambient temperature to 800 °C at 10 °C/min and maintained at 800 °C for 15 min) with samples sizes of 1.5 g. Small differences in pyrolysis yields were found when comparing paper and plastic and paper mixed with plastic at different weight ratios (without catalyst). Bio-oil yields are higher for plastics without paper (21 wt% for plastic and 15 wt% for paper) and yields of gas and char are higher for paper without plastic. Pyrolysis of plastic with paper (without catalyst addition, plastic to paper weight ratio of 1:3) at weight ratios comparable (but not used in this study) to that found in co-form<sup>®</sup>, 3:7 polypropylene to wood pulp fibres, yields a bio-oil yield of ~16 wt% and char and gas yield of ~30 and ~54 wt% respectively. A clear increasing trend can be seen with bio-oil yield and higher plastic weight ratios. The catalytic impact of cobalt based alumina, ceria and ceria-alumina (40%Co/30%CeO<sub>2</sub>/30%Al<sub>2</sub>O<sub>3</sub>) on pyrolysis product yields, bio-oil chemical content and gaseous products were investigated on a plastic to paper weight ratio of 1:3. In comparison to the same weight ratio without catalyst, total overall yields of bio-oil and char were found to drop by ~5 wt% and ~14 wt% respectively and gas yields increased by ~19 wt%. The authors investigated the chemical content of the bio-oil produced (aromatics 20 wt%, C2-C4 olefins 16.8 wt%, petrochemicals 36.8 wt% and coke 13.9 wt%) but did not compare or report without catalysts findings. Pyrolysis gas evolution profiles are shown between 700 and 800 °C for ~1.5 g of sample using 40%Co/30%CeO<sub>2</sub>/30%Al<sub>2</sub>O<sub>3</sub> at paper to plastic weight ratios of 5:1 and 1:0 only. At a paper to plastic weight ratio of 5:1 Hydrogen gas production peaked at 37 vol%.

This paper investigates pyrolytic valorisation of pelletised co-form<sup>®</sup> rejects using a novel Thermo-Catalytic Reforming process (TCR<sup>®</sup>) developed by Fraunhofer UMSICHT [8]. The TCR<sup>®</sup> process combines intermediate pyrolysis using a screw (auger) reactor at moderate temperature (350–450 °C) with a solid residence time of several minutes, with post catalytic reforming at 700 °C. The TCR<sup>®</sup> process has been shown by Neumann et al. [9–11] to produce superior product properties. Other variants of pyrolysis technologies are unable to achieve similar product properties without additional upgrading steps. Experimental work has been carried out using a pilot scale 2 kg/h TCR<sup>®</sup> reactor. To-date there are no research articles exploring the valorisation of co-form<sup>®</sup> rejects by pyrolysis. The importance of reducing the global epidemic of plastic and organic wastes polluting land, air and water is the motivation for continued further research and efforts in this area.

## 2 Materials and methods

### 2.1 Feedstock

Co-form<sup>®</sup> rejects (Fig. 1) were obtained from a secondary fibre paper mill, which manufactures tissue and hygiene products. The feedstock was composed of approximately 30 wt% polypropylene and 70 wt% wood pulp fibres.

The dry co-form<sup>®</sup> rejects contained no additional additives, i.e. water, plastic packaging or antibacterial agents.



**Fig. 1** Co-form<sup>®</sup> rejects as received [12].

alt-text: Fig. 1

The moisture content of co-form<sup>®</sup> rejects (as received) was <6 wt%. Co-form<sup>®</sup> rejects were shredded using an industrial shredder and pelletised into 6 mm × 20 mm pellets with a roll and die pelletiser (Model: 9PK-200 7.5KWe). The pellets were characterised and the ultimate and proximate compositions of pelletised co-form<sup>®</sup> rejects is shown in [Table 1](#). Thermal conversion trials (TCR<sup>®</sup>) were carried out using pre-treated pelletised co-form<sup>®</sup> rejects.

**Table 1** Feedstock on dry basis, co-form<sup>®</sup> reject pellets.

alt-text: Table 1

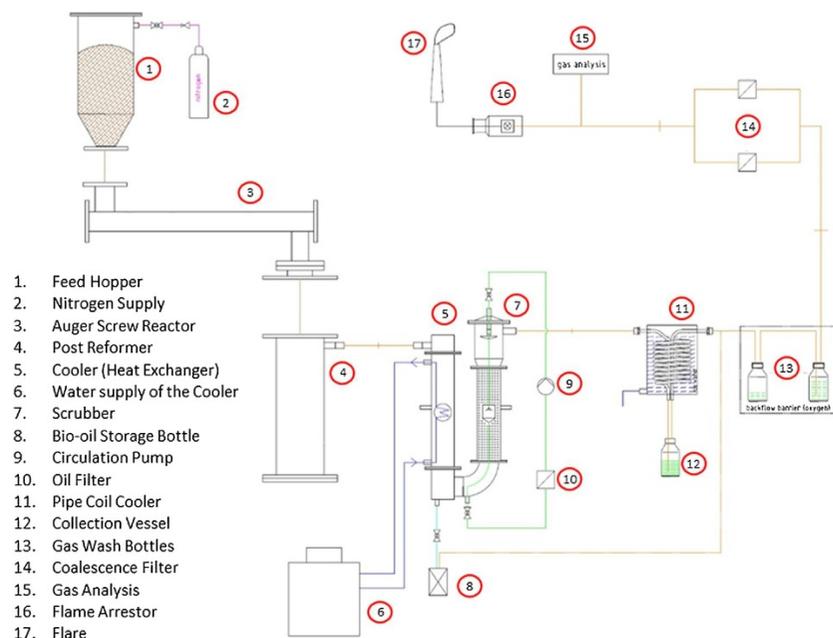
Ultimate Analysis (wt%) m.f	
C	58.9
H	6.1
N	0.4
O*	30.2
S	0.2
Proximate Analysis (wt%) d.b	
Moisture	5.5
Volatiles	82.7
Fixed Carbon	7.7
Ash	4.1
HHV (MJ/kg)	20.4
LHV (MJ/kg)	19.1

d.b Dry Basis

m.f Moisture Free Basis.

## 2.2 Experimental setup

Pelletised co-form<sup>®</sup> rejects were processed with a 2 kg/h Thermo-Catalytic Reforming bench scale reactor (TCR<sup>®</sup>) developed by Fraunhofer UMSICHT, Sulzbach-Rosenberg, Germany [8]. The setup consists of a batch feed hopper (5 kg capacity), TCR<sup>®</sup> reactors (intermediate pyrolysis auger reactor combined with a fixed bed reforming reactor), condensers, filtration and gas totaliser/analyser. The process flow diagram (PFD) is shown in Fig. 2. The two reactors are connected in series. The first intermediate pyrolysis (350–450 °C; feedstock heating rate 1 °C/s) reactor (approx. length 1000 mm) conveys feedstock by means of an auger (ID of screw 80 mm) with an average solid residence time of less than 10 min. The auger conveys pyrolysed material into a second stage post-reformer (fixed bed with internal temperature of 700 °C) both reactors operate in an atmosphere of Nitrogen to ensure the complete absence of Oxygen from the system. Pyrolysis vapours were catalytically cracked (reforming reactions occur between char and pyrolysis gases) into condensable organic vapours and synthesis gas rich in Hydrogen. Condensable vapours exiting the post-reformer were quenched by means of a shell and tube condenser (cooling medium water glycol mixture cooled to –5 °C) within a u-tube condenser. Condensable vapours exiting the condenser were further quenched by means of an ice bath cooler. The remaining vapours were then routed into two-gas wash bottles one filled with biodiesel and the other filled with water for aerosol capture. The gas analyser was fitted with an upstream carbon bag filter to protect against contaminants (dust and remaining aerosols). Permanent gases were routed to an online gas analyser/calorimeter for detection and gas totalisation before flaring.



**Fig. 2** Process Flow Diagram PFD for TCR<sup>®</sup> (2 kg/h) Reactor.

alt-text: Fig. 2

## 2.3 Analytical methods and measurements

Ultimate analysis (CHNSO\*) of feedstock and products (bio-oil and biochar) were carried out on a moisture free basis using an elemental analyser (Vario Macro Cube Elementar). The Oxygen contents were calculated by difference ( $100\% - \sum(\text{CHNS} + \text{ash})$ ). Proximate analysis was performed using a Thermo-gravimetric (TGA) technique using a Pyris 1, Perkin Elmer, TGA device with auto sampler. TGA of the feedstock was performed in accordance with ASTM E1131-03. Ash contents were determined using the standard ASTM E1755 - 01(2015), as the mass percent of residue remaining after dry oxidation at  $575\text{ °C} \pm 25$  for 5 h using a muffle oven. Moisture content of the pre-treated raw materials and biochar were determined according to the standard ASTM E1756 - 08(2015), as mass percent lost after overnight oven drying at  $105\text{ °C} \pm 5$ . Heating values of the feedstock and products (MJ/kg) were determined using an Oxygen bomb calorimeter IKA 2000 Series. Water content of bio-oil samples were determined by Karl Fischer titration using a 915 Ti-touch KF titrator (Metrohm Toledo) in accordance with ASTM E203-01. In addition, TAN (total acid number) of bio-oil samples was determined by 916 Ti-touch (Metrohm Toledo) in accordance with ASTM D664-11a. Kinematic viscosity of the bio oil was determined in accordance with ASTM D445-06. For online gas measurement, a calibrated pyrolysis gas detection system (Gas analyser MGA 12, Dr. Födisch Umweltmesstechnik AG, Germany) was used. The measurement principle of the gas analyser is based on an infrared photometer (CO, CO<sub>2</sub> &

CH<sub>4</sub>), an electro chemical cell (O<sub>2</sub>) and a thermal conductivity detector (H<sub>2</sub>). The balance not detected was assumed to be hydrocarbons (above the detectable limits of the analyser). The calorific value of the gas was measured with an online gas-calorimeter from Union Instruments CWD 2005. The gas analyser was calibrated with a calibration gas prior to commencing experiments.

## 2.4 GC-MS analysis

Bio-oil samples dissolved in dichloromethane (10%w/w) were analysed using a gas chromatograph (HP 6850, Agilent) coupled to a mass spectrometer (Agilent HP 5975) equipped with a non-polar column HP-5MS (stationary phase poly [5% difenil/95% dimethyl] siloxane, 30 m × 0.25 mm i.d., 0.25 µm film thickness), using helium as a gas carrier (constant pressure 33 cm/s, linear velocity at 200 °C). The GC oven temperature program was 50 °C for 5 min, then 325 °C at 10 °C/min and hold for 7.5 min. Samples (1 µl) were injected in split-less conditions at an injector temperature of 280 °C. The mass spectrometer operates in electronic ionization (70 eV) in full-scan acquisition, range 36–450 *m/z*, with an elution time of between 3.6 and 44.0 min. Bio-oil samples were analysed in duplicate. The compounds were identified by library searches (NIST libraries) and mass spectra evaluation. Compounds were quantified in terms of relative abundance of peak area (% peak area to the total area).

## 3 Results and discussion

### 3.1 Co-form® rejects

Proximate and ultimate analysis of the pre-treated dried and pelletised feedstocks is shown in [Table 1](#), ash, moisture, fixed carbon, volatiles, elemental compositions and calorific values are presented. As mentioned previously, co-form® rejects are composed of 30% polypropylene, a thermoplastic linear hydrocarbon polymer, and 70% wood pulp fibre. The carbon content of pelletised co-form® rejects is considerably higher (58.9 wt%) than biomass such as straws, perennial grasses and hardwoods [13]. Chattopadhyay et al. [7] reported for pure polypropylene a carbon content of 84.70 wt% and ash content of 1.0 wt%. Careful consideration is always necessary for materials with high plastic contents because of the agglomeration issues caused by plastic softening as well as dioxin formation when dealing with other types of plastics such as PVC. However, no chlorinated plastics were present in co-form® rejects. Previous studies showed that the gasification of co-form® rejects were not successful because of agglomeration issues caused by the melting of plastics [12], [Fig. 3](#) shows an example of the agglomeration of this material in other work where gasification was used [6]. This highlights the advantage of TCR® technology for processing organic wastes with a high plastics content. The higher heating value (on dry basis) of pelletised co-form® reject was 20.4 MJ/kg and this is attributed to the high plastics content of the feedstock. The ash content was 4.1 wt% and moisture content was <6 wt% after drying.



**Fig. 3** Agglomerations formation of co-form® rejects in a gasifier [12].

alt-text: Fig. 3

### 3.2 Yield and composition of TCR® products

Pelletised co-form® rejects were processed using a pilot scale 2 kg/h TCR® reactor and product yields are shown in [Table 2](#). The mass balance was determined gravimetrically and gas yield determined via a gas meter. The TCR® process combines intermediate pyrolysis using a screw reactor, at moderate temperatures (350 °C–450 °C) with solid residence times of several minutes, with post catalytic reforming at 700 °C.

**Table 2** Mass balance.

alt-text: Table 2

TCR® Products	wt%
Bio-oil (organic)	12
Water Phase	9
Char	8
Gas	71

The total gas yield was 71 wt% and detected non-condensable gases, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>x</sub>H<sub>y</sub>, are reported in [Table 3](#). The volumetric percentages of Hydrogen was 13.04%. The Hydrogen content was not high, but the process could be more attractive with the optimisation of its production, by adjustment of reforming conditions to influence higher water gas shift reactions in the post reformer. Introducing additional steam into the post reformer, would be a way to achieve this [10]. The higher heating value of the produced gas was 11.02 MJ/Nm<sup>3</sup> which was still significant when compared with traditional air blown gasification of wood which achieves approximately 5.6 MJ/Nm<sup>3</sup> [14].

**Table 3** Gas properties.

alt-text: Table 3

H <sub>2</sub>	V%	13.04
CO	V%	12.25
CO <sub>2</sub>	V%	3.10
CH <sub>4</sub>	V%	13.00
C <sub>x</sub> H <sub>y</sub>	V%	5.00
Diff.	V%	53.61
HHV	MJ/Nm <sup>3</sup>	11.02

The total char yield was 8 wt% and property characteristics are reported in [Table 4](#). The carbon and ash content of the char was found to be 83.90 and 11.90 wt% respectively, with a higher heating value of 30.79 MJ/kg. Compared to pelletised co-form® rejects (feedstock), the ash content of the char is typically higher because non-volatile inorganics remain. The higher ratio of carbon in the char compared with the original feedstock corresponded to an increase in heating value relative to the original feedstock.

**Table 4** Char, on Moisture Free Basis.

alt-text: Table 4

C	wt%	83.90
H	wt%	1.66
N	wt%	0.49
O <sup>a</sup>	wt%	1.90
S	wt%	0.06
Ash	wt%	11.90

HHV	MJ/kg	30.79
LHV	MJ/kg	30.42

<sup>a</sup> Calculated by difference.

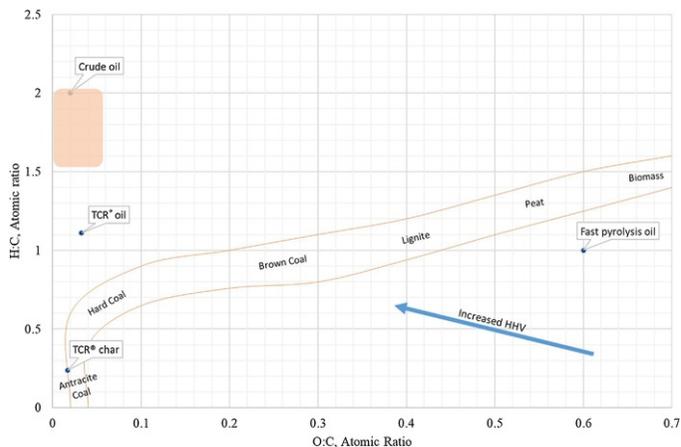
The liquid phase was separated with a total yield of 21 wt% (12 wt% bio-oil and 9 wt% water). The organic rich fraction, referred to as bio-oil, reported in Table 5 was separated and analysed and contained approximately 23% of the original energy from the feedstock. The bio-oil carbon content (87.60 wt%) was much higher when compared to findings for char (83.90 wt%) and starting material (70.50 wt%). The higher heating value of the bio-oil (39.36 MJ/kg) is comparable to biodiesel. The bio-oil Oxygen and water content are also very low (3.90 and 0.1 wt% respectively), which also contributed towards the high heating value. Low Oxygen content bio-oils are excellent fuels because not only do they lead to increased heating value but also a reduction in oil ageing effects and polymerisation of the oil over time. The bio-oil also contained a very low acidity and low viscosity (total acid number of 0.78 mg KOH/g and kinematic viscosity of 1.6 cSt at 40 °C) this is important when considering the use of bio oil as a fuel in engine applications. The total acid number measures concentration of acid constituents within the bio-oil and at low concentrations engine damage, corrosion to engine components, is limited or completely preventable. The kinematic viscosity gives an indication of fuel pumping and delivery properties. Other high viscosity bio-oils require special flow considerations, e.g. spray nozzle design and fuel line heating to prevent clogging.

**Table 5** Bio-oil, organic fraction.

alt-text: Table 5		
C	wt%	87.60
H	wt%	8.11
N	wt%	0.27
O <sup>a</sup>	wt%	3.80
S	wt%	0.05
Ash	wt%	0.10
Moisture	wt%	0.10
Dynamic Viscosity	mPa/s	1.58
Kinematic Viscosity	cSt 40 °C	1.66
Total Acid Number (TAN)	mg KOH	0.78
HHV	MJ/kg	39.26
LHV	MJ/kg	37.54

<sup>a</sup> calculated by difference.

The Van Krevelen diagram in Fig. 4 compares H:C and O:C atomic ratios for char and bio-oil. Thermal conversion by TCR<sup>®</sup> produces a high carbonaceous bio-oil and char products with a O:C and H:C ratios of 0.03 and 1.1 for bio-oil and 0.02 and 0.25 for char respectively. The lower H:C and O:C ratios of char are suggestive of increased carbon-carbon bonds. The char has an order of magnitude comparable to anthracite coal [15]. The char is ideal for use as a fuel for gasification or combustion purposes to deliver a tar free synthesis gas. The high stability of the char is related to the low H:C content [16]. The bio-oil has characteristics closer to crude oil than fast pyrolysis oil [13]. This is due to the low O:C ratio, opposite from oils produced from fast pyrolysis (approximately 0.6) [13], the TCR<sup>®</sup> oil demonstrates unique blending properties with hydrocarbons and immiscibility with water again due to the low Oxygen content of the oil, bio oil samples from this work were blended with fossil diesel and visually checked for its miscibility. The bio oil was found to be completely miscible with fossil diesel when blended in ratios up to 50:50 v/v%.

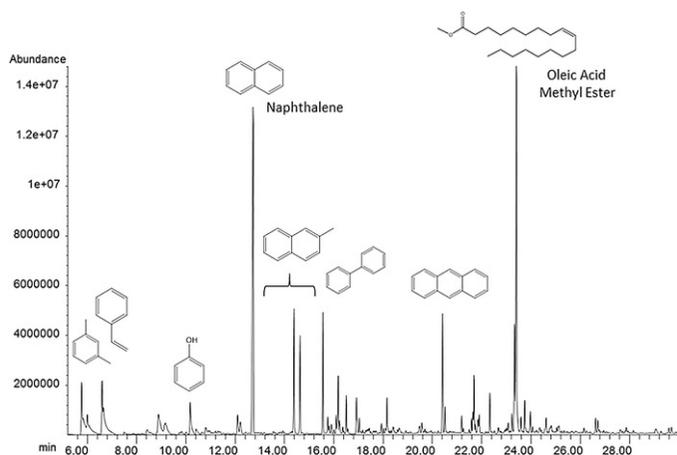


**Fig. 4** Van Krevelen diagram (H:C and O:C atomic ratios of TCR® char and oil).

alt-text: Fig. 4

### 3.3 GC-MS analysis of Co-form® rejects bio-oil

GC-MS was used to analyse the chemical content of the bio-oil (organic fraction). The bio-oil chromatogram can be seen in Fig. 5 and Table 6 lists detected and identified chemicals and their relative abundance. A good level of accountability can be seen for the chemical analysis of the bio-oil with most peaks identified. The most abundant compounds are oleic acid methyl ester (FAME), naphthalene, styrene, 2-methyl naphthalene and linoleic acid methyl ester. Naphthalene was the most abundant aromatic compound with a relative abundance of 15.22%. Selectivity to other aromatic compounds, such as styrene (6.38%), *p*-xylene (3.14%) and ethyl benzene (2.48%), was much lower. Oleic acid methyl ester (15.86%) was the most abundant long chain hydrocarbon. The abundance of other long chain hydrocarbons, such as linoleic acid methyl ester and palmitic acid methyl ester was much lower at 4.12 and 1.87% respectively.



**Fig. 5** GC-MS chromatogram of the TCR® bio-oil and its main compounds.

alt-text: Fig. 5

**Table 6** Detected and identified compounds by GC-MS of the bio-oil and their relative abundance.

alt-text: Table 6

Compound Name	Retention Time	Relative Abundance%
ethyl benzene	5.77	2.48
o-xylene	5.83	1.77
p-xylene	6.00	3.14
styrene	6.65	6.38
methyl styrene	8.89	2.73
2-propenyl benzene	9.17	1.94
indene	10.18	2.19
n.i.	10.42	0.51
n.i.	10.81	0.32
Benzene, 1-butynyl	12.10	1.04
Naphthalene, 1,2-dihydro	12.20	0.86
Naphthalene	12.72	15.22
2-methyl naphthalene	14.38	4.32
1-methyl naphthalene	14.63	3.15
Biphenyl	15.56	3.76
Naphthalene, 1-ethyl	15.75	0.68
n.i.	15.81	0.32
n.i.	15.90	0.41
Naphthalene, 2,6-dimethyl	16.10	0.61
Acenaphthene	16.22	0.65
n.i.	16.36	0.33
Acenaphthylene	16.51	1.12
3-methyl biphenyl	16.92	1.62
n.i.	17.03	0.54
n.i.	17.93	0.39
n.i.	18.02	0.20
n.i.	18.10	0.22
Fluorene	18.16	1.41
9H-Fluorene, 2-methyl	18.41	0.54
n.i.	19.49	0.54
n.i.	19.57	0.51

Phenanthrene	20.41	4.12
anthracene	20.51	0.94
Naphthalene, 1-phenyl	21.19	0.56
n.i.	21.58	0.51
n.i.	21.65	0.70
Palmitic acid methyl ester	21.69	1.87
Phenanthrene, 1-methyl	21.84	0.71
Phenanthrene, 1-methyl	21.90	0.66
2-Phenylnaphthalene	22.33	1.30
n.i.	22.68	0.34
n.i.	23.07	0.45
Fluoranthene	23.23	0.74
Linoleic acid methyl ester	23.33	4.12
Oleic acid methyl ester	23.41	15.86
Stearic acid methyl ester	23.59	0.82
Pyrene	23.74	1.45
m-Terphenyl	23.97	0.83
n.i.	24.06	0.35
Pyrene, 2-methyl	24.61	0.80
9-Ethyl-7H-benzo[de]anthracene	24.82	0.59
n.i.	25.13	0.44
Benz[a]anthracene	26.62	0.61
Naphthacene	26.72	0.59
n.i.	27.87	0.17
n.i.	29.60	0.25
n.i.	29.70	0.34

n.i. (not identified).

The high presence of FAME in the bio-oil makes its characteristics closer to fossil diesel and increases its blending properties. FAME and the others hydrocarbons are hydrophobic and its helps in the separation between oil and water [17]. Other abundant product was the naphthalene that can be used in the production of phthalic anhydride, surfactants and pesticides [18] it is also an excellent energy vector. Its presence can be explained by the high content of polypropylene (30 wt%) in the feedstock that is converted during the TCR<sup>®</sup> reaction. The other aromatics compounds in the oil also have direct industrial applications and can be used as a mixture analogue to conventional gasoline [19].

## 4 Conclusions

Co-form<sup>®</sup> rejects were successfully processed using a laboratory scale 2 kg/h Thermo-Catalytic Reforming (TCR<sup>®</sup>) reactor. Pyrolysis product yields for bio-oil, char and gas are 12, 8 and 71 wt% respectively. The bio-oil organic rich fraction accounts for ~60% of total liquid yield and its heating value (39.36 MJ/kg) is comparable to biodiesel. A good level of accountability can be seen for the chemical analysis of the bio-oil and most abundant compounds found are oleic acid methyl ester (most abundant long chain hydrocarbon, 15.86%), naphthalene (most abundant aromatic, 15.22%), styrene, 2-methyl naphthalene and linoleic acid methyl ester. The bio-oil produced also presents low viscosity and TAN values suitable for engine applications. Low Oxygen content bio-oils, such as the one produced, are excellent fuel oils because they are stable and do not suffer from polymerisation or ageing effects. Overall, the thermal chemical properties of the bio-oil produced are well suited for blending with fossil fuels. The higher heating value of the gas and char were 11.02 MJ/Nm<sup>3</sup> and 30.79 MJ/kg respectively. The volumetric percentages of Hydrogen was 13.04 vol% and its production could be further optimised by adjustment of reforming conditions, thus making the process more attractive for Hydrogen production. Combustion of char is a viable valorisation route considering the low levels of inorganics. This paper was able to demonstrate the advantage of the TCR<sup>®</sup> technology for processing organic wastes containing higher levels of plastic. The TCR<sup>®</sup> was able to tolerate high plastic content (polypropylene) in the feedstock (overcoming the agglomeration issue caused by the plastic melting) and can produce energy vectors with improved liquid fuel physical and chemical properties (analogue to the fossil fuels), therefore overall the TCR<sup>®</sup> showed to be a promising route for valorisation of co-form<sup>®</sup> rejects to energy vectors.

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## References

- [1] CEPI, Confederation of European paper industries. Preliminary Statistics (2016).
- [2] M.C. Monte, E. Fuente, A. Blanco and C. Negro, Waste management from pulp and paper production in the European Union, *Waste Manage.* **29**, 2009, 293-308.
- [3] PPCG, Paper Packaging Coordination Group, 2016, Position Paper.
- [4] S. Job, G. Leeke, P. Mativenga, G. Oliveux, S. Pickering and N. Shuaib, Composite Recycling: Where Are We Now?, 2016, Copyright Composites UK.
- [5] R.S. Rengasamy, 6 - composite nonwovens in wipes, Composite Non-Woven Materials, 2014, Woodhead Publishing, 89-119.
- [6] M. Ouadi, J.G. Brammer, M. Kay and A. Hornung, Fixed bed downdraft gasification of paper industry wastes, *Appl. Energy*. **103**, 2013, 692-699.
- [7] J. Chattopadhyay, T.S. Pathak, R. Srivastava and A.C. Singh, Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), (polypropylene) and PET (polyethylene terephthalate)) and product analysis, *Energy* **103**, 2016, 513-521.
- [8] A. Hornung, S. Binder, M. Jakuttis and A. Apfelbacher, Anlage und Verfahren zur thermokatalytischen Behandlung von Material und damit hergestelltes, *Pyrolyseol* 2014, DE201410105340.
- [9] J. Neumann, S. Binder, A. Apfelbacher, J.R. Gasson, P. Ramírez García and A. Hornung, Production and characterization of a new quality pyrolysis oil, char and syngas from digestate - introducing the thermo-catalytic reforming process, *J. Anal. Appl. Pyrolysis* **113**, 2015, 137-142.
- [10] J. Neumann, N. Jäger, A. Apfelbacher, R. Daschner, S. Binder and A. Hornung, Upgraded biofuel from residue biomass by Thermo-Catalytic reforming and hydrodeoxygenation, *Biomass Bioenergy* **89**, 2016, 91-97.
- [11] J. Neumann, J. Meyer, M. Ouadi, A. Apfelbacher, S. Binder and A. Hornung, The conversion of anaerobic digestion waste into biofuels via a novel Thermo-Catalytic Reforming process, *Waste Manage.* **47**, 2016, 141-148.
- [12] M. Ouadi, Sustainable Energy from Paper Industry Wastes, PhD Thesis, 2012, Aston University, Chemical Engineering, 242.
- [13] C.E. Greenhalf, D.J. Nowakowski, A.B. Harms, J.O. Titiloye and A.V. Bridgwater, A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products, *Fuel* **108**, 2013, 216-230.
- [14] A.V. Bridgwater and D. Boocock, *Developments in Thermochemical Biomass Conversion* vol. **1**, 2013, Springer Science & Business Media.
- [15] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresour. Technol.* **83**, 2002, 37-46.
- [16] E. Ahmad, N. Jäger, A. Apfelbacher, R. Daschner, A. Hornung and K.K. Pant, Integrated thermo-catalytic reforming of residual sugarcane bagasse in a laboratory scale reactor, *Fuel Process. Technol.* **171**, 2018, 277-286

**[17]** T. Yang, Y. Jie, B. Li, X. Kai, Z. Yan and R. Li, Catalytic hydrodeoxygenation of crude bio-oil over an unsupported bimetallic dispersed catalyst in supercritical ethanol, *Fuel Process. Technol.* **148**, 2016, 19-27.

**[18]** C. Jia and S. Batterman, A critical review of naphthalene sources and exposures relevant to indoor and outdoor air, *Int. J. Environ. Res. Public Health* **7**, 2010, 2903-2939.

**[19]** E.R. Umeki, C.F. de Oliveira, R.B. Torres and R.G.d. Santos, Physico-chemistry properties of fuel blends composed of diesel and tire pyrolysis oil, *Fuel* **185**, 2016, 236-242.

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### Highlights

- Co-form rejects were processed using Thermo-Catalytic Reforming reactor.
  - Pyrolysis product yields for bio-oil, char and gas are 12, 8 and 71 wt%.
  - The bio-oil has thermal chemical properties suited for blending with fossil fuels.
  - Char combustion is a viable valorisation route due to the low levels of inorganics.
  - The gas has 13.04 vol% hydrogen and this production could be further optimised.
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