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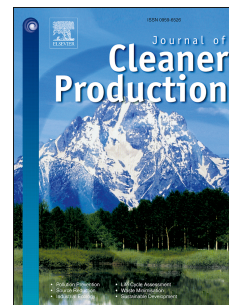
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CRediT author statement

Francesca Di Gruttola: Conceptualization, Methodology, Validation, Investigation, Roles/Writing - original draft, Writing - Review & Editing, Visualization, **Hessam Jahangiri:** Conceptualization, Validation, Writing - review & editing **Marcin Sajdak** Writing - review & editing, **Artur Majewski** Methodology, Resources**,** Writing - review & editing, **Domenico Borello** Conceptualization, Methodology, Investigation, Writing - Review & Editing, Supervision **Andreas Hornung** Conceptualization, Methodology, Supervision **Miloud Ouadi** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Review & Editing, Supervision, Project administration.

The Thermo-catalytic reforming (TCR©) of waste solid grade laminate

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Highlights

- Thermo-catalytic reforming (TCR) represents a promising technology for solid grade laminate waste valorisation and biofuel production;

- 50 wt% of the initial feedstock was converted to syngas, 28 wt% to char and 22 wt% to a liquid fraction containing both water (17 wt%) and organics (5 wt%);

- The syngas deriving from solid grade laminate contained almost 50 vol% of hydrogen.

Abstract

Thermo-catalytic reforming (TCR) is defined as intermediate pyrolysis at moderate temperatures and heating rates with subsequent reforming at elevated temperatures using biochar as a catalyst. TCR experiments were carried out to pyrolyze and subsequently reform Solid Grade Laminate (SGL) waste. SGL is a Kraft paper-derived product and as it is widely used in many applications, high volumes of waste laminate must be disposed of at end of life. To assess TCR for SGL waste treatment, the characterisation of the initial feedstock was accomplished, and it concluded that SGL is suitable to be processed via TCR. The main energy carrier products (char, oil and syngas) were generated by TCR in a 2 kg/h pilot-scale reactor under a pyrolysis temperature of 500°C and reforming temperature of 650°C, respectively. The mass balance analysis demonstrated that 50 wt% of the initial feedstock was comprehensively converted to syngas, 28 wt% to char and 22 wt% to a liquid fraction containing both water (17 wt%) and organics (5 wt%). The oil showed good properties as its HHV reached a value of 32.72 MJ/kg, with low oxygen and sulphur contents. However further processing is required for the fuels to be within suitable limits for use as drop-in fuels for vehicles. The syngas was found to be rich in hydrogen especially when pyrolysis temperature reaches its maximum. Lastly, char revealed a calorific value of 25.94 MJ/kg and was of a stable form of carbon, exhibiting potential as a feedstock for gasification or as a carbon capture and

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storage medium. TCR of SGL represents novelty as this feedstock has not been tested before in a pyrolysis/reforming system and it is a promising route in an optic of circularity. In waste valorisation, TCR oil has a great opportunity to be used as a fuel or blended with other conventional fuels, thus supporting the shift towards more sustainable mobility.

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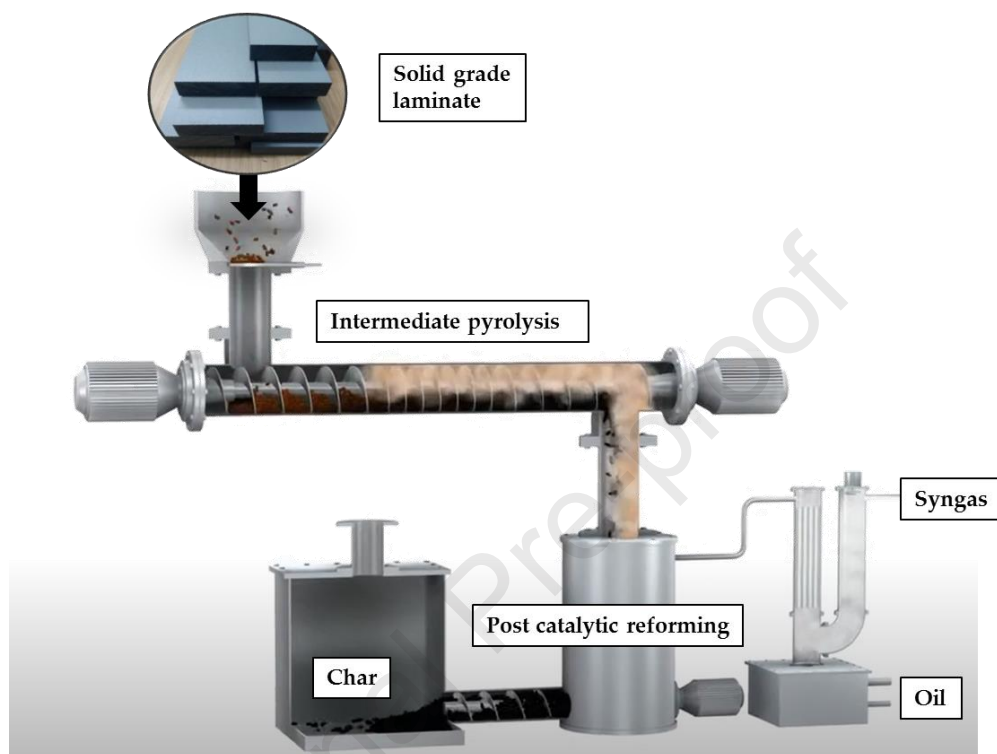
Keywords: thermo-catalytic reforming, syngas, char, oil, alternative fuels, hydrogen, waste valorisation.

Abbreviations

TCR	Thermo-catalytic reforming
SGL	Solid Grade Laminate
CHNSO	Carbon Hydrogen Nitrogen Sulphur Oxygen
GC-MS	Gas Chromatography-Mass Spectrometry
H/C	Hydrogen/Carbon
O/C	Oxygen/Carbon
HHV	Higher Heating Value
TGA	Thermo-Gravimetric Analysis
BEIC	Birmingham Energy Innovation Centre
UK	United Kingdom

1. Introduction

Since the industrial revolution, the world has been consuming ever-increasing amounts of energy from fossil fuels, thus emitting large amounts of non-neutral CO_2 from their combustion. This is widely believed to be the principal cause of climate change [1]. Several actions are currently employed to contrast it and to achieve the net zero target through the decarbonization of all energy sectors by 2050 [2].

Furthermore, we are witnessing increasing concerns over the price and security of the supply of petroleum and natural gas, since energy consumption has been increasing even faster with population growth and industrial development. Therefore, any attempt to decrease the demand for fossil fuels is considered environmentally beneficial [3].

In this regard, wastes (including second-generation biomass) represent abundant and cheap resources for the bioenergy sector and biofuels production. Compared to first-generation biomass, wastes do not compete with food production or any other industrial use [4] and do not affect biodiversity and water use. Their availability is analysed in [5] by considering all different end-use and competing applications. A further study also demonstrated their future and consistent availability in 2025 [6]. In fact, second-generation biomass is characterised by residues, wastes and co-products and they have the potential to change and decarbonise many industrial sectors with the lowest economic and environmental impact.

In recent years, many regulations and directives have been introduced aiming at discussing and supporting the most relevant aspects related to energy and the environment sector. One example is the Renewable Energy Directive (RED II), which proposed binding targets to limit first-generation biofuels and redirected public subsidies to advanced biofuels that are produced from second-generation biomass [7].

In this regard, Solid Grade Laminate (SGL) can be considered a full-fledged second-generation biomass or a waste at the end of its life.

The material is mainly composed of Kraft paper compressed with melamine and phenolic resins for the surface layer and core layers, respectively under simultaneous application of heat and pressure. Kraft paper is also characterised by 76.2wt% of cellulose, 16.2wt% of hemicellulose and 7.6wt% of lignin [8]. The low content of lignin is due to the Kraft process, which consists of a delignification process aiming at breaking the bonds that link lignin, hemicellulose, and cellulose in wood chips under pressure and high temperatures [9][10].

SGL blocks are used in different applications as a construction material [11][12], furniture [13][14] and electronics [15]. Hence, it would not be surprising to find high volumes in the waste streams of manufacturing companies. Globally, it has been estimated that about 130 million tons of Kraft paper are annually produced via the Kraft process [16], even though it is not reported the actual quantity destined for solid grade laminate production. In the UK, the annual sale of laminate destined to the flooring market is approximately 30 million m² [17] and it could represent a sustainable choice of feedstock if reused in large-scale biomass plants. Generally, SGL waste undergoes a collection process (with and without other mixed construction wastes). Afterwards, a recovery system for SGL can include reuse or recycling, disposal as incineration in waste-to-energy applications or storage in landfill [8].

The recovery of waste SGL blocks through the thermochemical process is still an unexplored field. No current research exists in this area as demonstrated by the lack of specific information in the literature and so it represents novelty to significantly reduce the environmental impact in waste management.

Kraft paper is characterized by cellulose, hemicellulose and lignin whose values are compared with wood and other lignocellulosic residues in **Table 1**. As Kraft paper is produced from wood pulp in a dedicated process, the composition of Kraft and pure papers are quite comparable. However, Kraft fibres have higher content of cellulose and lower content of both lignin and hemicellulose than wood, since they are subjected to the delignification treatment. The low lignin content in Kraft paper constitutes a benefit in terms of biofuel production derived from lignocellulose. Indeed, although lignin showed a great potential in producing fuels, value-added chemicals, and functional materials thanks to its high-energy density and intrinsic aromatic-based structure [10], [18], it is also a recalcitrant molecule that impedes accessibility to polysaccharide and then their transformation into commercially significant products. That is why the upstream removal of lignin is often mandatory in the pre-treatment of feedstocks to produce biofuels [19].

Table 1 Chemical composition of Kraft fibres

	Unit	Lignin	Cellulose	Hemicellulose
Kraft fibres [8]	wt.%	7.6	76.2	16.2
Paper [6]	wt.%	0-15	85–99	0
Newspaper [6]	wt.%	18-30	40-55	25-40
Wastepaper from chemical pulps [6]	wt.%	5-10	60-70	10-20
Wood [6]	wt.%	18-32	40-44	15-35

Pyrolysis and gasification are usually employed for the thermochemical conversion of lignocellulosic material. However, pyrolysis and gasification differ among themselves in terms of operating conditions like the different conversion stages, temperatures, reactor design and gasifying agent which is absent in the pyrolysis. Different products are obtained from them: a solid (char and ash), a liquid/condensed fraction (tars and oil) and a non-condensable gas (syngas), whose yields differ according to the process as illustrated in **Table 2**.

Table 2 Mass balance and conditions for pyrolysis and gasification of woody biomass

Type	Operating Conditions	Char wt%	Oil wt%	Syngas wt%	Ref.s
Slow pyrolysis	~300 ºC, long solid residence time (hrs.-days)	35	30	35	[20]
Intermediate pyrolysis	~400 ºC, moderate solid residence time (min)	25	50	25	[20]
Fast pyrolysis	~500 ºC, short solid residence time (< 2s)	12	75	13	[20]
Flash pyrolysis	~600 ºC, short solid residence time (< 1s)	7	83	10	[20]
Gasification	800-900°C	53.8*	3.5* (tar)	82.92*	[21]

*data are indicated as mean values

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Thermocatalytic reforming (TCR) represents another potential solution to convert such lignocellulosic material into valuable products as it combines the intermediate pyrolysis with the catalytic reforming. According to Table 2, intermediate pyrolysis obtains high yields in oil but also syngas and char, whilst, it was proved that the extra catalytic reforming step is essential for high product quality. Similar studies on TCR valorisation of other waste biomass are well demonstrated and are presented elsewhere [22], [23]. Depending on reforming conditions specific targeted pyrolysis products can be formed and reforming using biochar derived from pyrolysis has been shown to deoxygenate volatiles leading to bio-oils with improved physical and chemical properties [23].

The char also acts either as heat carrier for the upgrading pyrolysis oil or as a promoter for hydrogen formation. In this way, larger amounts of H_2, CH_4, and CO are also produced and less tar is generated at lower reforming temperatures. This is advantageous as typical state of art implements steam gasification, which can cause high tar content, and further more energy intensive tar removal steps [22].

Finally, the reforming temperature affects not only the quality of bio-oil but also the yield of both gas and liquid products. The higher reforming temperatures, the higher gas yield and the lower liquid yield [22], [24].

Combination of reactor configurations is possible by designing the plant with a multi-zone auger reactor for the pyrolysis phase and a fixed bed post-reformer. This configuration allows separate operating conditions for both the pyrolysis and reforming, thus allowing high feedstock flexibility, high scalability, and high fuel quality in the TCR. The process can convert a wide range of second-generation biomass into hydrogen-rich syngas, high-quality oil and char without volatiles with yields based on the type of biomass and operating conditions.

According to the mass balances of several feedstocks (i.e. digestate, sewage sludge, sugarcane bagasse and oat hulls) tested in the TCR reactor in previous studies [3], [24], [25], the ranges of products mass yields are illustrated in the following **Table 3**:

Table 3 Typical mass yield ranges of TCR products

	Char	Aqueous phase	Bio-oil	Syngas
Product yield wt%	20 - 50	19 - 34	2 - 15	25 - 50

Due to the high-pressure manufacturing process, SGL has high density (1350 kg/m³) and low moisture content (1.5 wt%) [11][20]. The former characteristic ensures a lower volume during both the transport and the storage phase and it influences how easily biomass can be ground for processing. The latter minimizes the weight during transport as well as avoids the drying process [26]. These properties facilitate the whole supply-chain of the thermo-catalytic reforming. Solid Grade laminate (SGL) also represents a new feedstock in the TCR process. Consequently, the goal of this research was to thermo-chemically process SGL using a lab-scale TCR reactor aiming at analysing its suitability as a new feedstock and its conversion into high-quality fuels. Hence, the characterisation of both the initial feedstock and the products was carried out. Results suggest that TCR could potentially be preferred to other pathways, such as fast pyrolysis, which does not produce hydrogen, and gasification, which does not produce liquids. Firstly, TCR is a well-thought-out technology as it combines in-situ two well-known thermochemical processes (i.e. pyrolysis and reforming) in a single reactor configuration. Secondly, all final products are valuable and can commercially be used. Finally,

the plant has the capability to optimise separately the operating conditions for both pyrolysis and reforming, thus allowing high feedstock flexibility, high scalability, and high fuel quality in the TCR.

2. Materials and Methods

2.1 Feedstock pre-treatment

For the present analysis, we used approximately 10 kg of dry SGL blocks. The feedstock was composed of more than 60 wt% of compressed Kraft paper layers and the remaining 30-40 wt% of phenolic resin for the core layers and melamine resin for the surface layer. Before TCR thermal conversion, it was first necessary to pre-treat the laminate. Hence, the material was shredded down by the HECHT 6420 device and further sieved with a VWR test sieve, having a mesh size of 5.6 mm and a sieve diameter of 200 mm (according to ISO 3310-1).

2.2 Feedstock characterisation

2.2.1 Proximate analysis

A small sample size of approximately 20 mg was subjected to pyrolysis via Thermo-Gravimetric Analysis (TGA) under a N_2 atmosphere to determine its proximate composition in terms of moisture, volatiles and fixed carbon content. The sample was also tested under TGA combustion to determine its total ash content. The instrument used for TGA was a NETZSCH TG 209 F1 device heating up to a maximum temperature of 900 °C, with a heating rate of 10 K/min and a total flowrate of purge gas of 50 ml/min (according to BS EN 15148:2009).

2.2.2 Ultimate analysis

The SGL was sent to an external accredited laboratory, Medac Ltd, where the elemental content was quantified. Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen (CHNSO) content was analysed using the CHN and Eltra Helios (S) analysers following the ISO 16948:2015 and ISO 16994:2016 standards. Then, the oxygen was determined by difference, taking into account the ash content determined by TGA.

2.2.3 HHV

The HHV was calculated by using the unified correlation for fuels (**1**), namely the Channiwala equation, starting from carbon, hydrogen, sulphur, oxygen, nitrogen and ash weight fraction, respectively. The Channiwala equation shows a good correlation to compute the HHV in the absence of the bomb oxygen calorimeter [27].

$$HHV\ [MJ/kg] = 0.341\ (C) + 1.1783\ (H) + 0.1005\ (S) - 0.1034\ (O) - 0.0151\ (N) - 0.0211\ (A) \qquad (1)$$

2.3 The TCR experimental procedure

2.3.1　The TCR setup

The TCR-2 bench scale reactor (**Figure 1**) is located at the University of Birmingham and has the capacity to process up to 2 kg/h of feedstock. The plant works in an oxygen-free environment by applying a nitrogen purge at around 100 mbar inside both the feed hopper (1) and the pyrolysis auger reactor (2). The temperature in the reactor can be set between 500-700°C. The biomass is manually fed in the auger reactor. The auger reactor represents a very reliable and affordable solution for pyrolysis thanks to its simplicity of construction and operation, among different possible configurations [28]. The reactor comprises two co-axial rotating screws powered by two different electrical engines, thus allowing easy regulation and control of solid residence times through the reactor. This represents an advantage in terms of modularity and avoiding blockage risk, always possible in case there was a single screw. The inner screw conveys the biomass through 1 m in length of the reactor, while the outer screw connects the reactor with the fixed-bed post-reformer (3). In the post-reformer, the catalytic cracking of vapours and reforming reactions occur at higher temperatures (650-800 °C) between char and pyrolysis vapours to form condensable organic vapours and synthesis gas (or syngas). Both volatile vapours and permanent gases pass through a gas cleaning system which consists of a cyclone (4) for the removal of fly ash, followed by a shell and tube water-cooled heat exchanger (5) to quench the gases and condense out the volatile components. The scrubber (6) removes other contaminants such as solid particulate in the gas flow. Hence, the condensable gas is collected in the external oil vessel (7), while the non-condensable gas goes through the filtration unit for the removal of the remaining aerosols, fine particles and other contaminants. The filtration system consists of a series of gas wash bottles containing ice (8), biodiesel (9), isopropanol (10), acetone (11) and wool (12). Biodiesel, isopropanol and acetone act as solvents to clean pre-contaminants in the syngas produced during the intermediate pyrolysis and the catalytic reforming such as dust, tars, corrosive compounds (sulphur, chlorine and nitrogen), alkali and heavy metals delivered by wastes or second-generation biomass [29]. In particular, biodiesel is usually used as a trap for heavy hydrocarbons and tars [30], while isopropanol and acetone easily dissolve tars [31]. In addition, the wool bottle captures further solid particles like particulate and tars. Finally, a gas analyser detects the clean gas before permanent gases are flared with propane (13). The gas analyser was fitted with an upstream carbon bag filter to protect the device from harmful contaminants and particulates. To heat the TCR system, external electrical heating tapes are used. The operating temperature is measured and controlled through several K-type thermocouples installed all along the unit. The process control is performed using a Siemens SIMATIC WinCC software developed by Fraunhofer UMSICHT, where the analysed parameters can be changed in a wide range of options.
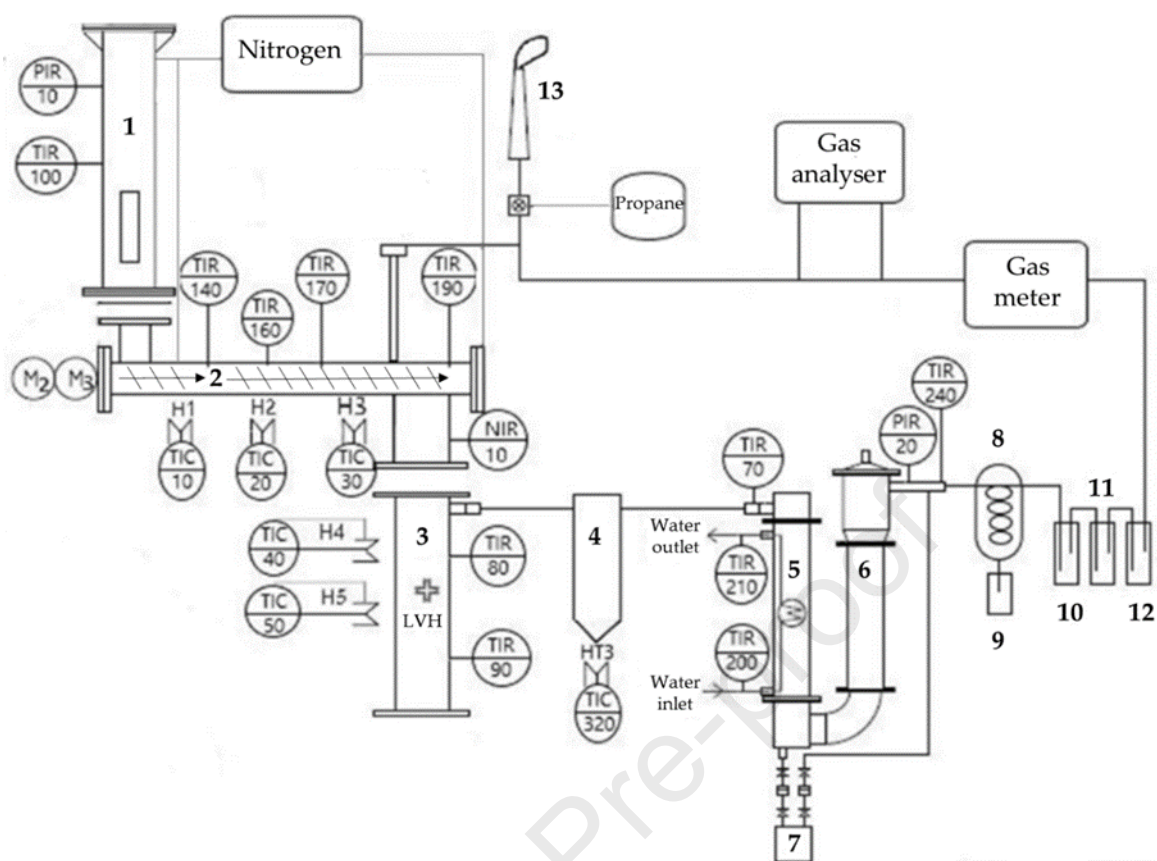
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Figure 1 The Process schematic diagram of the TCR-2 (2 kg/h): (1) Feed hopper; (2) Auger reactor; (3) Post reformer; (4) Cyclone, (5) Shell and tube heat exchanger; (6) Scrubber; (7) Oil collection vessel; (8) Ice bath; (9) biodiesel wash bottle; (10) Iso-propanol wash bottle; (11) Acetone wash bottle; (12) wool bottle; (13) Flare [32]

2.3.2   The TCR methodology

Before running the experiment, the TCR-2 plant was cleaned, closed and flushed with N_2 at 80-100 mbar to remove the oxygen from the pyrolysis reactor and to test if there was any leakage from the system. Once the gas analyser detected an oxygen content below 0.5 vol% in the plant, the N_2 flow was stopped. During the experiment, the temperature in the auger screw reactor was gradually increased up to 500°C until it reached the intermediate pyrolysis conditions before the introduction of SGL. In the post-reformer stage, the temperature was set to 650 °C. The setting of both the pyrolysis and the reforming temperatures was decided beforehand according to the TGA analysis of the specific feedstock. During the heating process, the rotating screws were turned on and the speeds of the inner and outer screws were calibrated to have a residence time of about 40 minutes corresponding to the intermediate pyrolysis condition. Once the TCR reached steady temperatures, the screw in the auger reactor was stopped and the sealed hopper was opened to feed the plant with 4.6 kg of SGL. Afterwards, the feed hopper was closed, and the unit was flushed with N_2 again to decrease the oxygen below 0.5 vol%. When the N_2 flow was stopped, the first screw in the auger reactor was turned on to push the biomass along the TCR-2. The formation of the carbonised biomass

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produced as char in the auger screw reactor promoted an internal catalytic effect, thus improving the quality of the TCR-2 products and avoiding the exit of fine particles and dust from the post-reformer. The char and permanent gases formed in the auger reactor were then transported to the post-reformer by the screw. There, the residence time was regulated through the screws speed of the auger reactor. The post reformer had the double function of collecting the char produced from the previous step and converting the permanent gases into a syngas rich in H_2, due to the catalytic effect caused by the reactions between the char, acting as active carbon, and the pyrolysis vapours. During the reforming process, the condensable organic vapours were catalytically upgraded, thus enhancing their chemical and physical fuel properties and reducing tars. The char rich in carbon and with low hydrogen and oxygen contents remained in the post-reformer until the end of the experiment. Subsequently, the upgraded organic vapours were quenched at -5°C in the condensing unit to guarantee a complete separation between the pyrolysis liquid and the gas fraction. The pyrolysis oil was collected and stored in an external vessel. Then, the remaining non-condensable vapours passed through the filtration unit for the removal of aerosols, fine particles and other contaminants. The cleaned gas was directly measured and analysed via an online gas analyser.

TCR-2 experiments took around 4 h to be stabilised and completed. The plant worked in a semi-continuous mode with an overpressure of approximately 70-100 mbar controlled by a pressure indicator and the TCR software. The volume of synthetic gases was registered every 10-15 minutes. When no gas production was observed, the experiment was considered concluded and, consequently, the heaters and auger reactor screws were switched off. The plant was left to cool down for at least 24 hours. Afterwards, the auger pyrolysis reactor was cleaned from unconverted residues via a vacuum cleaner. The post-reformer was emptied by extracting the solid char produced from the bottom. The dust and fine particles, deriving from char, in the gas tube of the reforming unit were removed to prevent blockages in the following trials. Lastly, the condensing unit was cleaned to avoid contamination between different oils produced in different experiments with different operating conditions. All the products obtained from the cleaning were weighted and included in the mass balance. The washing bottle connected to the ice bath after the condensing unit was refilled with 600-700 ml of biodiesel, isopropanol and acetone. In the filtration unit, activated carbon, candle and glass wool filters were weighed, replaced and connected to the plant again. For the mass balance, all the liquids collection vessels, filters and wash bottles were weighed. Additionally, the char from the post-reformer was collected, separated and weighed, and a sample was sent for analysis to an external lab. Because of the different densities, the organics and the aqueous phase were separated after 24 h using a separating funnel. Afterwards, they were separately stored, measured and sent for their characterisation to an external lab. The permanent gas data were further analysed.

2.4 Products characterisation

2.4.1 Water content

The water content of the raw laminate oil was determined using a Mettler Toledo V20S compact volumetric Karl Fischer titration in accordance with ASTM E203.

2.4.2 Oil and Char ultimate and proximate analyses

Pyrolysis oil and char samples were analysed applying the same method already described in **(2.2.1)** and **(2.2.2)** for the determination of the elemental compositions (C, H, N, S and O). Regarding oil, the oxygen was determined by difference as described in the following **(2)**, assuming ash content approximately lower than 0.001 wt%:

$$O\ [wt\%] = 100 - \sum (CHNS + ash) - water \tag{2}$$

The water content is computed as illustrated in **(2.4.1)**.

Furthermore, a complete CHNSO analysis was made for char, while the ash content was computed by difference, by reversing **(2)** and neglecting the water content.

2.4.3 HHV

The HHV of the bio-oil and char was determined using the unified correlation for fuels as described in **(2.2.3)**.

2.4.4 Viscosity

The dynamic viscosity of oil was tested by IKA ROTAVISC (according to DIN 53019) at the temperature of 23.2°C and with a rotational speed of 100 rpm. The instrument measured the resistance of the oil to flow when an external (rotational) force was applied, without considering the fluid density (or the inertial force).

2.4.5 Density

The pyrolysis oil density was measured by Academy Glass Measuring Cylinder at 20 °C having a total volume of 100 ml and a tolerance of ±1.0 ml.

2.4.6 Gas Chromatography/Mass Spectrometry (GC-MS)

The chemical compounds of the oil were detected by a two-dimensional gas chromatography and mass spectrogram GC-MS Agilent 8890. The separation technique allowed counting the peak value due to the presence of organic compounds at a specific retention time by two detection columns and modulator. The gas used as a carrier was H_2 and the oil samples were dissolved in dichloromethane (DHM). The concentration of oil was 1%. Afterwards, the compounds were identified by library searches (NIST libraries).

2.4.7   Gas analysis

During TCR, the produced syngas was frequently measured and analysed using a Pollutek GAS 3000P Syngas Analyser. The measurement principle of the gas analyser is based on Non-Dispersive Infrared (NDIR) sensor (CO, CO_2, CH_4, C_nH_m), a thermal conductivity sensor TCD (H_2) and an electron capture (ECD) detector (O_2) [33].

2.4.8   Mass and energy balances

The mass and energy balances represent the statements on the conservation of mass and energy. The mass balance was computed by weighting the initial material and collecting and weighting char and liquid fraction (oil and water) after the TCR experiment. Consequently, the syngas yield was computed by difference. Any mass loss due to weight measurement errors, non-detectable gases by the gas analyser and the remained oil in the cleaning section were not considered.

The energy balance shows how the energy of the initial feedstock was distributed in time unit among its products during the TCR conversion process. It was computed through the following equation:

$$Q_i \ [MW] = \sum_i \dot{M}_i \left[\frac{kg}{s}\right] \cdot HHV_i \ \left[\frac{MJ}{kg}\right]$$

(3)

Where Q is the output energy power of each i-th final product (i.e. char, oil and syngas) according to its mass flow rate $\dot{M}_i$ and higher heating value (HHV).

3.   Results and Discussion

3.1 Feedstock characterisation

A small sample of 20 mg of SGL was subjected to TGA under both pyrolysis (N_2 as a purge gas) and combustion (air as a purge gas) conditions and their profiles are presented in **Figure 2** and **Figure 3**, respectively.

Under pyrolysis conditions (**Figure 2**), the weight loss of moisture and volatiles was evaluated, and the fixed carbon was obtained by the difference between the total mass and the moisture and volatiles fractions in percentage. Fixed carbon content gives information about the amount of char formation in the thermochemical process after the release of volatile matter. The value is equal to 31wt%, meaning that one-third of the initial feedstock can be used as char (and ash) in the post-reformer. The objective of using those carbonaceous substances is to exploit their influence in terms of catalytic action capacity.
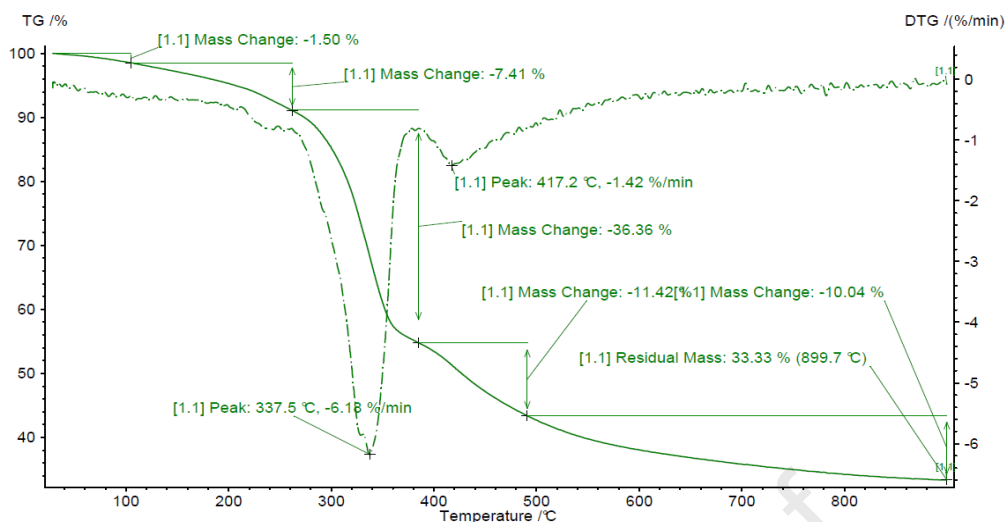
Figure 2 TGA/DTG Pyrolysis Profile Solid Grade Laminate

Figure 2 shows a weight loss of 1.5% in moisture from ambient temperature (25°C) to 105°C. In the range between 105°C and 260°C, there was another mass change of 7.41%, due to the volatilisation of Kraft paper. This behaviour fits well with other results available in the literature which suggest that Kraft paper releases volatiles starting from 150°C [34]. The majority of volatiles were then released between 240°C and 390°C, which contributed to approximately 36% weight loss. This result matches the degradation temperature of melamine resin, whose volatilisation values range between 250°C and 400°C [34]. The successive peak was noticed between 400°C and 470°C, indicating a release of phenol resin and cellulose, as reported previously in [35],[36].

Figure 3 TGA/DTG Combustion Profile Solid Grade Laminate
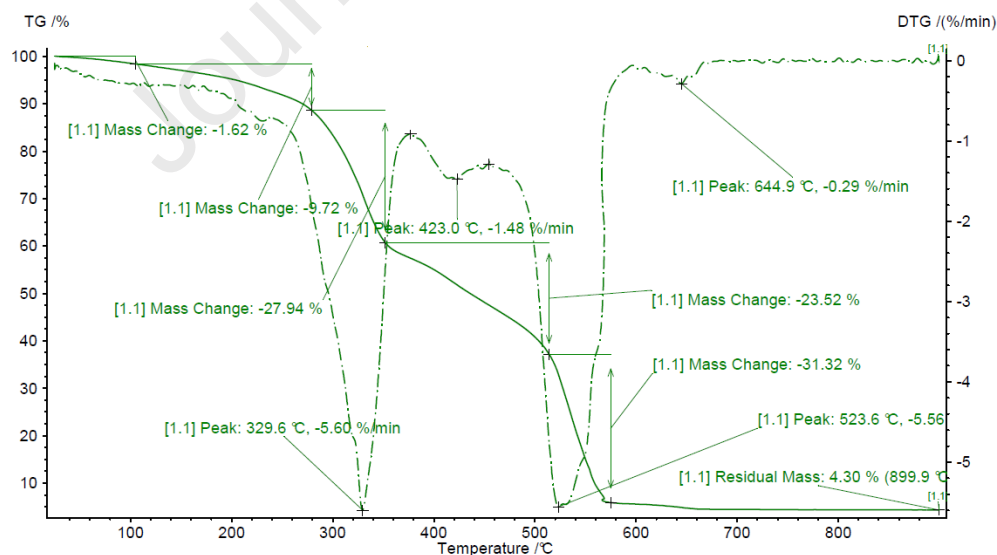
The combustion analysis **(Figure 3)** showed a weight loss of 1.62% from moisture release at temperature from 25°C to 105°C. In the range between 150°C and 250°C, there was a small mass decrease of 9.72%, which is attributed to the starting point of Kraft paper combustion [34]. Then, volatile products from cellulose combustion were combusted between 270°C and

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390°C and then again there was a peak between 400°C and 450°C due to the combustion of the resins content in the SGL [35]-[37] with an overall weight loss of about 51.5%. As soon as the laminate was burnt between 500°C and 600°C under air conditions, fixed carbon was released obtaining stable mass at lower temperature than that obtained from the pyrolysis trial in the same temperature range. The weight loss at that temperature accounted for 31.3%. The ash content was 4.3wt%, therefore, the stable solid carbon formed during pyrolysis at this temperature range was around 29%.

The proximate and ultimate analysis for the TGA of SGL are shown in **Table 4**.

Table 4 Proximate and Ultimate Analysis of Solid Grade Laminate

	Units	Result
Proximate Analysis		
Moisture	wt%	1.5
Volatiles	wt%	65.2
Fixed Carbon	wt%	29.0
Ash	wt%	4.3
HHV	MJ/kg	18.6
Ultimate Analysis		
C	wt%	44.4
H	wt%	5.9
N	wt%	7.8
S	wt%	0.48
O*	wt%	35.62

*calculated by the difference

The HHV was determined by using the unified correlation for fuels and the resulting value is equal to 18.6 MJ/kg similar to the value measured for woody materials. The ash content of SGL was evaluated as the residual mass after the combustion (as already illustrated in **Figure 3)**. The oxygen was determined by difference, considering the ash content equal to 4.3wt%.

Both the nitrogen and sulphur contents give information about the possible formation of SOx and NOx emissions during the thermochemical process (e.g. pyrolysis and gasification). Therefore, lower values correspond to lower emissions. Nitrogen is also an inert element, meaning that it does not react during the conversion process. However, NOx deriving from TCR was not expected, as temperatures were under the threshold required for the formation of thermal NOx. If compared with woody biomass, Nitrogen and Sulphur were found to be higher for SGL, with concentrations approximately 4 x higher for nitrogen and 5 x higher for sulphur content [38]. However, these heteroatoms can effectively be removed from the TCR syngas by utilising downstream scrubbers, this has been proven at larger TCR scales.

The initial atomic O/C and H/C ratios of solid grade laminates are 0.6 and 1.59, respectively. These values are comparable with lignocellulosic biomass ratios as reported in [39]. However, SGL's H/C ratio was higher than wood, thus suggesting a good initial HHV.

Finally, the optimal pyrolysis and reforming temperatures for TCR test were also found from TGA analysis. They turned out to be 500°C and 650 °C, respectively. The former was due to the release of the majority of volatiles from the feedstock, whilst the residual mass remained almost unchanged after 650°C as illustrated in **Figure 2** and **Figure 3**. Furthermore, from previous studies it is shown that TCR oil has more calorific values from 600 to 700 °C [24][40].

3.2 Mass balance and energy balance

After the TCR process, the mass balance and the energy balance for laminate were computed and shown in **Figure 4**. Regarding the mass balance, 50 wt% of the initial feedstock was converted to syngas, 28 wt% to char (and ashes) and 22 wt% to a liquid fraction containing both water and organics.

According to the energy balance the majority of the energy moves from feedstock to syngas and char with a percentage of 56% and 39% respectively. The remaining 5% is characterised by pyrolysis oil. The energy balance only considers the chemical energy transferred from the feedstock to the products. Approximately 20% of the total chemical energy from the feedstock is required as heat input to the process [41]. This energy could potentially derive from the downstream thermal conversion of the biochar or syngas. There is sufficient energy in these vectors to satisfy the heat demand of the plant.
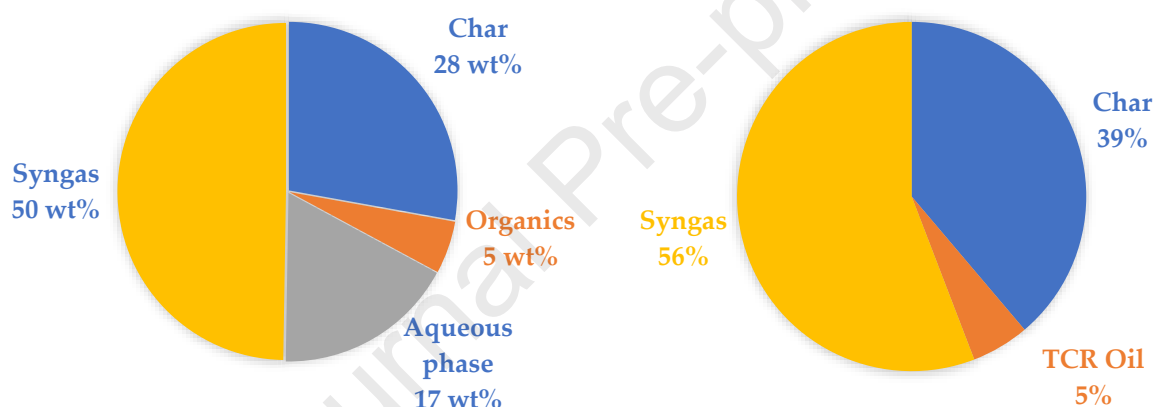

Figure 4 Mass balance (on the left) and Energy balance (on the right) of Solid Grade Laminate

In **Figure 5**, the Van Krevelen diagram is shown to highlight the H/C and O/C ratios of laminate and its products obtained from TCR. The diagram represents the degree of stability of the initial feedstock in terms of char decomposition, showing similar properties to wood. Regarding TCR products, although, both laminate oil and char had approximately the same O/C ratio, meaning that they lost many oxygenated compounds in favour of major carbonisation, the oil shows a greater H/C ratio, due to the presence of a high amount of hydrogen, thus contributing to a good value of its HHV. The heating value of the oil was found to be 32.72 MJ/kg, which is almost double that of the original solid grade laminate. The increase in the calorific value was due to the catalytic reforming and cracking occurring in the post-reformer. As already shown in literature, the reforming process converts feedstocks in fuel with higher octane numbers, lower oxygen content and tar and more aromatics, thus contributing to get the best properties out of pyrolysis oil [42] [43]. As a matter of fact, a higher-octane number of fuel leads to a lower volatility and a major compression in the internal combustion engines [44] and the lower oxygen content increases the HHV [26].

Even though the laminate oil has a lower H/C ratio and a higher O/C ratio when compared with conventional heavy fuel oil and fossil fuels, it shows a closer agreement with their characterstics than typical oil from fast pyrolysis of wood as illustrated in **Figure 5** [3]. Heavy oil, gasoline and diesel fuel have higher HHV than laminate oil with their corresponding values of 41.8, 46.4 and 45.6 MJ/kg, respectively [45]. The presence of oxygen in the laminate oil, which is about zero in conventional fuels, negatively influenced its HHV. Therefore, a de-oxygenation process for pyrolysis oil is desirable in any pyrolysis process.
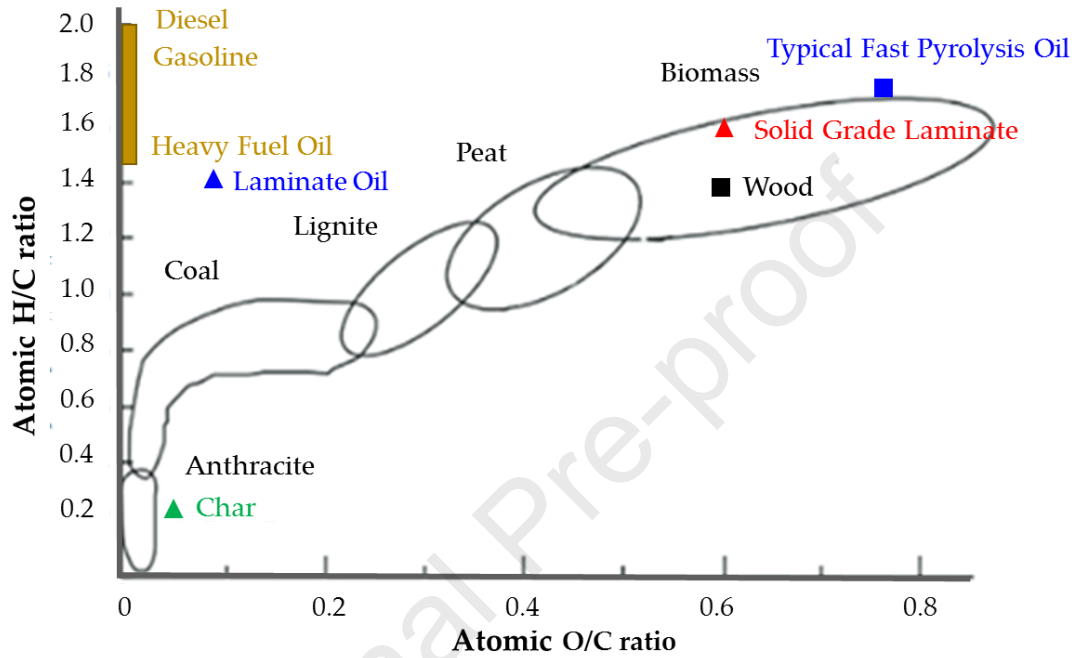
Figure 5 The Van Krevelen diagram [39] with the H/C and O/C ratios evaluated for conventional fuels, typical fast pyrolysis oil, wood, SGL and its products from TCR (char and laminate oil)

For the sake of clarity, the HHV values of the above-mentioned fuels are reported in **Table 5**.

Table 5 The calorific values of different fuels

Fuels	HHV [MJ/kg]	Ref.s
Solid Grade Laminate	18.6	Experimental values
Laminate oil	32.72	Experimental values
Heavy oil	41.8	[45]
Gasoline	46.4	[45]
Diesel	45.6	[45]
Typical fast pyrolysis oil	17.0 – 22.5	[46]

3.3 Pyrolysis oil analysis

The liquid products (oil and water) accounting for 22 wt% of the weight and deriving from TCR, were left to settle for 24 hours to separate water from the organics (**Figure 6**) and a clear phase separation was observed. Afterwards, both liquids were weighted, and the percentages of oil and aqueous phase were 5 wt% and 17 wt%, respectively (as previously shown in **Figure 4**). The oil yield from SGL resulted slightly lower than that obtained from other TCR trials with sugarcane bagasse, oat hulls, and sewage sludge at the same pyrolysis temperatures [3], [40]. However, the oil yield is expected to decrease when the reforming temperature increases, as also shown in [24] for sugarcane bagasse and oat hulls, since other volatiles are released during the reforming, thus enhancing the syngas yield. To obtain an increased oil yields against syngas production, the TCR process should be performed at a lower reforming temperature and considering the use of externally sourced catalysts such as steel slag [40][47] which has been found to lower reforming temperatures whilst retaining high yields of hydrogen production.

Figure 6 Aqueous phase (on the left) and pyrolysis oil (on the right) of Solid Grade Laminate

After the separation, the 5 wt% of pyrolysis oil was analysed. Its water content was equal to 7.21% on average, resulting about 2-4 times lower than common bio-oils [48]. This result confirmed the finding that the heating value of such oil is equal to 32,72 MJ/kg (**Table 5**), significantly higher than other bio-oils, even though it is still lower than the heavy fuel oil, whose water content is around 0.10% [48]. This difference suggests the presence of oxygenated compounds in the pyrolysis oil, which leads to reduced physical and chemical properties [48]. The sulphur content was found to be 0.65 wt%, slightly higher than that in the feedstock (0.48 wt%). This is partly due to the reproducibility of the experimental method which is related to the accuracy of the instrument [47] and partly to the major concentration of sulphur in the oil solution sample [40].

The dynamic viscosity of oil was 31 mPa·s at a temperature of 23.2°C, lower than heavy fuel oil, whose value is about 230 mPa·s at 30°C [48]. Viscosity represents an important property for fuels especially if used in unmodified internal combustion engines. As studied in [49], higher viscosity not only affects the mechanical characteristics of the engine, but also its performance and emissions. In fact, higher viscosity results in poor fuel atomization, carbon deposition on fuel filter, more energy demand from the fuel pump and thus more wear of pumps and injectors. Consequently, the slow-moving of oil causes the combustion of a lean

mixture and influences the start-up of the injection and its pressure. The overall properties of SGL oil are shown in the proximate and ultimate analysis reported in **Table 6**.

Table 6 Laminate oil characterization

	Units	Result
Proximate Analysis		
Water	wt%	7.21
Ash	wt%	<0.001
HHV	MJ/kg	32.72
Viscosity	mPa·s	31
Density	kg/m³	856
Ultimate Analysis		
C	wt%	69.12
H	wt%	8.27
N	wt%	3.46
S	wt%	0.65
O*	wt%	11.29

*calculated by the difference

3.3.1   GC-MS analysis

To detect and identify the organic compounds in the pyrolysis oil deriving from TCR, two-dimensional gas chromatography and mass spectrogram were computed.

In **Table 17**, the chemical compounds are reported with their molecular formula, group name, peak value and retention time deriving from the GC-MS analysis.

According to the peak values, the oil revealed a composition rich in aromatics, phenols and furans.

The aromatics and cycloaromatic hydrocarbons had the highest peak values in the oil as represented in **Figure 7**, thus suggesting promising oil properties, as these chemical compounds are present in most conventional fuels. The presence of phenols in the GC-MS results indicated that some of the resins were transferred to the oil. Further investigation would be required to understand in detail the influence of each component within the feedstock on the products and evaluate any co-pyrolysis effect occurring.

However, phenols and furans deriving from resins, hemicellulose and lignin present in the feedstocks and detected in the laminate oil were not abundant. However, they contain nitrogen and oxygenated compounds that reduce the calorific value (**equation 1**). It could be possible considering a successive hydrotreatment process to remove phenols and oxygenated substances thus further increasing the HHV of the resulting oil.

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Table 17 Chemical compounds detected and identified by GC-MS of the Solid Grade Laminate

| Chemical compound	Molecular Formula [50]	Group Name	Retention I (min)	Peak Value
1,3,5-Cycloheptatriene	C_7H_8	Aromatic	4.66	85663.73
p-Xylene	C_8H_{10}	Aromatic	6.34	68358.30
Benzene, 1-ethyl-2-methyl-	C_9H_{12}	Aromatic	8.25	24007.01
Benzene	C_6H_6	Aromatic	3.46	22506.99
Ethylbenzene	C_8H_{10}	Aromatic	6.18	16815.06
Benzofuran	C_8H_6O	Furan	8.85	13618.73
Chromium, tricarbonyl[(1,2,3,4,5,6-^{n})-1,3,5,7-cyclooctatetraene]-	-	Cycloalkenes (aromatic)	6.78	11139.36
1H-Pyrrolo[2,3-b] pyridine, 2-methyl-	$C_8H_8N_2$	Pyrrolopyridines (aromatic)	10.83	9764.16
Benzyl alcohol	C_7H_8O	Alcohol	10.08	9065.15
1H-Benzimidazole, 5,6-dimethyl-	$C_9H_{10}N_2$	Aromatic	13.07	8566.90
Phenol, 4-ethyl-	$C_8H_{10}O$	Phenol	11.04	7636.60
Cinnamaldehyde, (E)-	C_9H_8O	Aldehyde	10.99	7102.42
2,4,5-Trihydroxypyrimidine	$C_4H_4N_2O_3$	Pyrimidine (aromatic)	12.59	6083.76
2-Propenal, 2-methyl-3-phenyl-	$C_{10}H_{10}O$	-	12.88	5569.08
o-Xylene	C_8H_{10}	Aromatic	6.78	5331.62
1,3,5-Cycloheptatriene, 1-methoxy-	$C_8H_{10}O$	Aromatic	11.85	5157.36
p-Cresol	C_7H_8O	Phenol	10.54	5018.91
1,2-Dimethylindol-4-amine	$C_{10}H_{12}N_2$	-	14.71	4582.31
Cyclohexene, 1-(1-propynyl)-	C_9H_{12}	Aromatic	8.07	4546.32
1,5-Heptadien-3-yne	C_7H_8	Enynes	3.57	3779.06
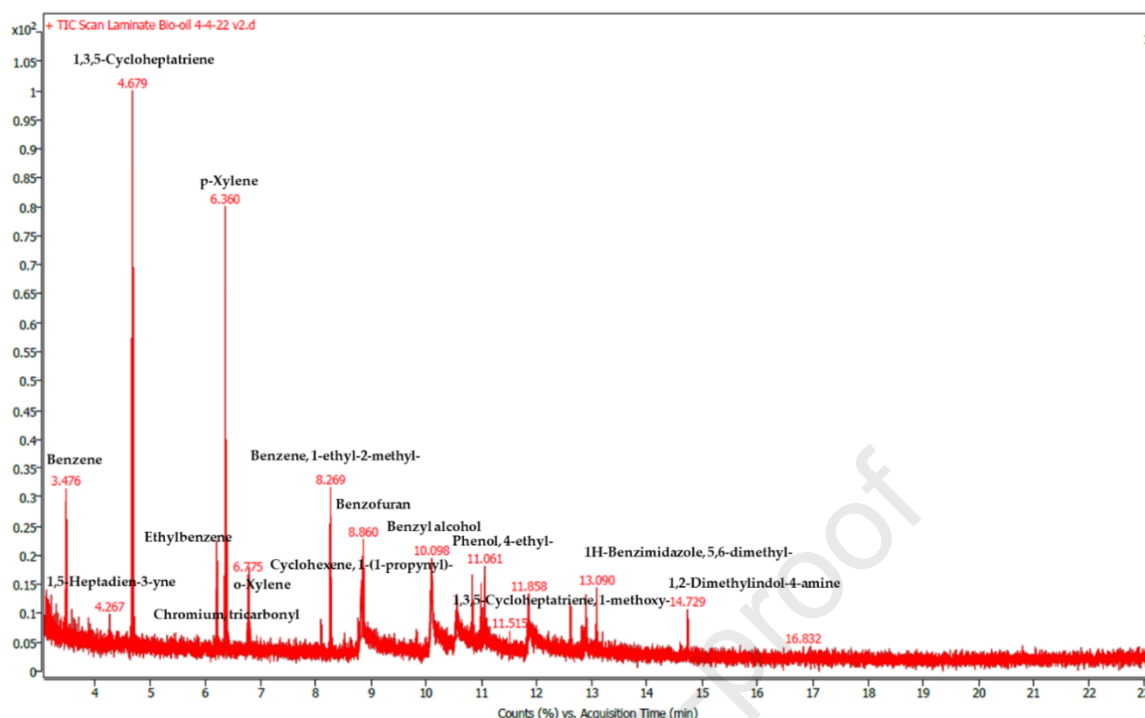
Figure 7 1D representation of GCxGC results of Laminate Oil

3.4 Gas Analysis

The syngas represents the gaseous fraction made of CO, CO_2, H_2, CH_4 and light hydrocarbons (typically consisting of C1-C4), whose values were recorded during the TCR process once the volume of oxygen reached values below 0.5 vol% and then normalized with respect to the volume of oxygen and nitrogen, as shown in **Figure 8**. Hydrogen represented almost 50 vol% of the syngas, while carbon monoxide, carbon dioxide and methane ranged between 15 and 25 vol% and the light hydrocarbons fraction were considered negligible. However, the syngas composition changed overtime. Indeed, there was a time interval where H_2 and CO reached the maximum, whilst CO_2 and CH_4 had a minimum. The reason for such a pattern might be related to the pyrolysis temperature. Although it was set at 500°C, the volatiles that were released during the pyrolysis, increased the temperature, leading to a decrease in the fraction of CO_2 and CH_4, thus allowing an increase of H_2 and CO. Additionally, the higher pyrolysis temperature inhibits the degradation of hemicellulose and cellulose thus reducing the formation of CO_2 that could be released by the cracking of carboxyl and carbonyl compounds. On the contrary, the lignin can be easily decomposed at a higher temperature, thus releasing much more hydrogen derived from its aromatic ring and methyl group [51], [52]. Finally, the increase of CO could be also related to all endothermic reactions occurring at higher temperatures and reported in the following **Table 8**.

Table 8 Reactions during pyrolysis

Reaction	Equation	$\Delta H°$ $[KJ\ mol^{-1}]$
Steam reforming: CH_4	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	206.2
Water gas (primary reaction)	$C + H_2O \leftrightarrow H_2 + CO$	131.3

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	$C + 2H_2O \leftrightarrow 2H_2 + CO_2$	90.1
Boudouard	$C + CO_2 \leftrightarrow 2CO$	172.5

Another possible explanation for such a behaviour of gases could be due to the stabilisation time of TCR reactor. In fact, the post-reformer needed time to collect char and reformate the gas during the whole process. Consequently, more oil and less syngas were expected at the beginning because of the low char content in the post-reformer. Later, the increase of char led to H_2 and CO formation resulting from reforming reactions. Once the char was stabilised in the post-reformer, catalytic reactions occurred, thus increasing CH_4 and CO_2 yields [47][53]. Afterwards, the behaviour reached a steady condition, with values constant until the end of the experiment.

Regarding the calorific value of syngas, it was calculated and based only on the combustible fraction (CO, H_2, and CH_4) of the gas, discounting N_2 and CO_2. Hence, the HHV of syngas was equal to 20.11 MJ/kg, which was greater than the initial feedstock.
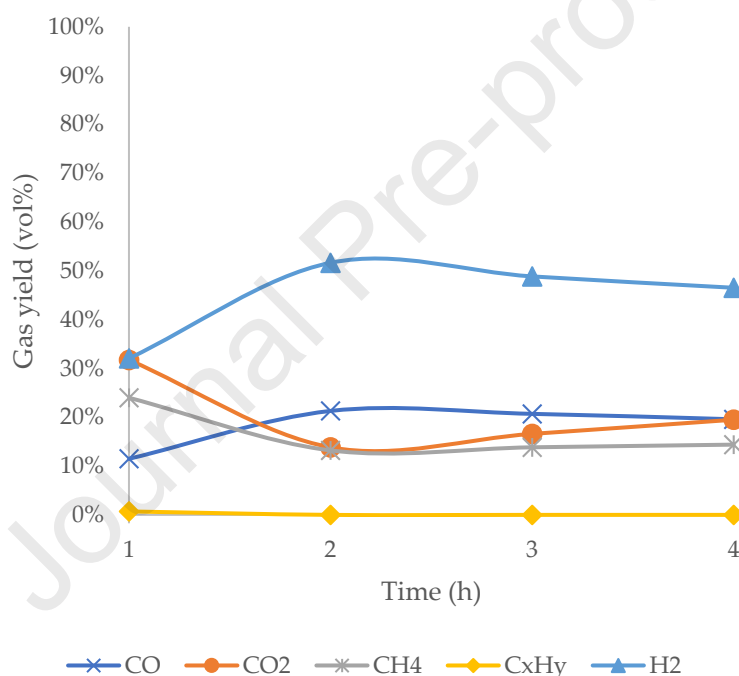

Figure 8 Gas analysis over time during the TCR experiment

3.5 Char analysis

The char (**Figure 9**) intended as a residual mass (ash included) represented 28 wt% of the initial feedstock. The amount of solid carbon formed during TCR process was lower than during pure pyrolysis as shown in **Figure 2**. This was due to both the longer residence time in TCR and the continuous contact with syngas and vapours where carbon was gasified, thus reacting with H_2O and CO_2 accordingly to reactions in **Table 8** [47][54]. Char is a carbonaceous high-molecular-weight residue with ash, inert material and metals and it can be used as a catalyst as it exhibits catalytic activity favouring higher yields of non-condensable gases [55]. The catalytic effect of char is used not only for tar cracking, but also to de-oxygenate volatile compounds. This is especially true when using high ash-containing feedstocks such as sewage

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sludge and de-inking sludge [53][56]. These results were investigated in a patented Pyroformer whose patents are reported in [57]-[59].

Figure 9 Char of Solid Grade Laminate

The char characteristics are reported in **Table 9**. As expected, only carbon and ash contents increased with respect to the initial feedstock (**Table 4**), by 1.6 and 4.7 respectively, while the remaining elements decreased. The presence of metals within the ash could certainly influence catalytic activity in TCR system [47]. Previous studies for example using sewage sludge showed a direct relationship between ash content and catalytic cracking in the TCR [40][54]. However, ICP assessment was not carried out to determine which metals were present within the ash. During post reforming, the char itself is active as a catalyst, no external catalysts are therefore necessary during the process. The extended vapour residence times, reforming temperatures, and char to vapour interactions with the post reformer is effective in promoting mono-cyclic aromatics in the bio-oil. The char also has an important function in promoting water gas shift reactions, steam methane reforming reactions and Boudouard reactions, for the production of CO and H_2. This can be seen from the decrease of CO_2, increase of CO and decrease of CH_4 with increase of H_2 (**Figure 8**). From the energy point of view, the calorific value of char was equal to 25.94 MJ/kg, which was higher than the initial HHV of laminate (18.6 MJ/kg). This result suggests its further potential use as a fuel in other thermal and thermochemical processes like combustion, co-combustion or gasification.

Other potential purposes are its application as a soil amendment or as an adsorbent material. Indeed, char can remain in the soil for years due to its high stability, thus improving the soil quality. However, its heavy metal composition must be analysed to avoid the release of toxic compounds or other negative impacts in terms of soil properties variations.

Finally, char can be used as an adsorbent to remove pollutants, heavy metals or contaminant gases [60].

Table 9 Laminate Char characterization

	Units	Result
Ultimate Analysis		
C	wt%	71.83
H	wt%	1.56
N	wt%	1.49
S	wt%	<0.10
O	wt%	5.09

Ash*	wt%	20.03
HHV	MJ/kg	25.94

*calculated by difference

4. Conclusions

In this research, the waste solid grade laminate (SGL) was subjected to TCR consisting of intermediate pyrolysis at 500°C and post-catalytic reforming at 650°C, both occurring at standard pressure.

The aim was to characterise a new material not yet investigated in literature as energy source in a pre-commercial technology such as TCR as well as its final products (char, oil and hydrogen-rich syngas) as alternative fuels. Such characterisation helped to determine the feasibility of SGL in the thermo-catalytic reformer according to its physiochemical properties and operating conditions and eventually to understand how the mass and the energy of SGL were distributed between its final products.

Based on the ultimate and proximate analyses, the solid grade laminate showed similar properties to wood in terms of oxygen, hydrogen and carbon content even if sulphur and nitrogen were found to be higher. The feedstock was already dried according to the low moisture content found in the TGA and its HHV was equal to 18.6 MJ/kg, thus showing a good quality to be used directly as a fuel in other processes (e.g. incineration, combustion and gasification).

In accordance with the mass and energy balances, TCR showed that half of SGL was converted to hydrogen-rich syngas with a high calorific value (20.11 MJ/kg), thus allowing it to be involved either in further conversion processes or to be stored as chemical (e.g. hydrogenation of oil) or energy carrier for other applications (e.g. hydrogen fuel cells).

Furthermore, high production of char (equal to 28 wt%) was obtained from TCR. It was found to be rich in carbon and exhibited good catalytic effects as suggested by the high percentage of syngas and its low hydrogen and oxygen contents. This result also suggests that char from TCR could be used for combustion due to its HHV (25.94 MJ/kg) being higher than the initial feedstock.

Despite the lowest mass yields, pyrolysis oil showed good potential as a fuel even without upgrading, if it would require further upgrading (hydrotreatment) would be implemented to completely remove nitrogen, oxygen, and sulphur content as well as convert phenols and furans compounds into hydrocarbons. In this way, it could be used either as a drop-in fuel or blended with other conventional fuels in case it met fossil fuel standards EN 228 and EN 590 for use in vehicle engines. Overall, TCR was shown to be a promising thermochemical process for the valorisation of such material, since it offered a novel method to produce high-quality products from SGL.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: