Full Length Article

Catalytic upgrading of intermediate pyrolysis bio-oil to hydrocarbon-rich liquid biofuel via a novel two-stage solvent-assisted process

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ABSTRACT

A novel two-stage solvent-assisted batch catalytic hydroprocessing method has been developed for upgrading intermediate pyrolysis bio-oil to produce blended liquid fuels with ≈23 wt% hydrocarbon-rich biofuel content. Stage I reactions (160 °C for 3 h, then 300 °C for 3 h) involving mixtures of dodecane and bio-oil (mass ratio = 3:2), hydrogen gas and 5 wt%-metal supported catalysts (Pd/C, Pt/Al$_2$O$_3$ Pd/Al$_2$O$_3$, Ru/Al$_2$O$_3$) suppressed char formation. Up to 80 wt% liquid organic products were obtained, with the biofuel component dominated by ketones and phenols. Significant amounts of water and gas (mainly CO$_2$) were also produced. Stage II reactions (300 °C for 3 h; 5 wt% Pt/Al$_2$O$_3$; hydrogen gas) with Stage I organic liquid products gave >90 wt% of blended liquid fuel. Overall, up to 96 wt% bio-oil deoxygenation and 53.4 wt% bio-carbon retention were achieved in the final organic liquid product via a combination of various reaction mechanisms. Pt/Al$_2$O$_3$ catalyst deactivated via hydrolysis of alumina and coking in stage I but remained stable during Stage II.

1. Introduction

Liquid fuels, produced from a variety of sustainable biomass feedstocks, are a promising alternative to diversify global energy resources and contribute to achieving Net Zero by 2050. While conventional liquid biofuels such as bioethanol and biodiesel, have made significant contributions to the global renewable energy mix, their production is limited to a narrow range of biomass feedstocks. Therefore, the production and deployment of advanced biofuels from non-food feedstocks, wastes and residues have become very important [1]. The technology pathways for advanced liquid biofuels production include thermochemical processes such as gasification-Fisher Tropsch, pyrolysis, hydrothermal liquefaction, are at various stages of research and commercial development [2,3]. There are also biochemical routes being developed for advanced biofuels [4], which are outside the scope of this present study.

Among the thermochemical processes, pyrolysis [5,6] and hydrothermal liquefaction (HTL) [7,8] can directly produce crude organic liquid products that can be used for various applications. During pyrolysis and HTL, organic materials are degraded into bio-oil, gas and char at moderate temperatures between 300 and 400 °C for HTL and around 400 – 600 °C for pyrolysis [9]. However, HTL requires hot-pressurised water at elevated pressures of up to 200 bar [8], which

makes it most suitable for wet organic wastes. For low moisture (around 10 wt%) biomass feedstocks, pyrolysis is the conversion technology of choice for bio-oil production. The process of pyrolysis can be tuned, in terms of reaction temperature, heating rate and vapour residence times, to favour the production of liquid (bio-oil), solid (char or biochar) or gas (syngas). Detailed descriptions of variants of pyrolysis (slow, intermediate, fast and flash) can be found in review articles on the subject [5,9].

Among the various pyrolysis technologies, intermediate pyrolysis (IP), which occurs at moderate heating rates (1 – 10 °C per second) and at a temperature range of 400 – 650 °C, gives a fair distribution of reaction products is obtained during IP, with 35 – 50 wt% of bio-oil, 25 – 40 wt% of biochar and 20 – 30 wt% of gas [5]. While still highly unstable compared to hydrocarbons, the bio-oils obtained from IP are relatively more stable than those obtained from fast pyrolysis [10]. In some cases, the IP bio-oils may be used directly in engines with little or no modifications [5,11]. Due to the moderate vapour residence times (up to 20 s) used during IP, the bio-oil has good physical and chemical properties, including good miscibility with fossil fuels, low moisture content, low oxygen content, intermediate to high acidity (pH = 3 – 4) and a wide range of high calorific value (22 – 40 MJ/kg) [9,12]. The low moisture content in IP bio-oil is due to the separation that occurs readily between the organic and aqueous phases in the liquid product. Therefore, IP bio-oils contain less polar compounds making it a potentially good feedstock

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for upgrading to cleaner liquid fuels, compared to fast pyrolysis (FP) bio-oils. FP produces higher yields of lower quality bio-oils, with high moisture ($\geq$30 wt%), high acidity and oxygen (up to 50 wt%) contents [5,9–11], which means nearly half of its mass would be lost in case of complete deoxygenation (oxygen removal). Using FP bio-oil for upgrading will involve high feedstock throughputs to obtain reasonable yields of deoxygenated biofuel, which has implications on equipment sizes and processing costs.

Irrespective of the variant of pyrolysis used, bio-oils are dark-coloured viscous acidic liquids, characterised by a complex mixture of a wide range of oxygenated compounds including sugars, esters, ethers, carboxylic acids, alcohols, aldehydes, ketones and phenols [5,13]. Small amounts of hydrocarbons may be present in some bio-oils. However, the relative contents of these groups of compounds are different depending on the type of pyrolysis (ad also on the type of biomass), which can influence the outcomes of bio-oil upgrading. The severity of the pyrolysis conditions, especially vapour residence times, heating rates and temperature, are the main factor that govern the compositions of pyrolysis bio-oils. With the relatively longer vapour residence times and slower heating rates, intermediate pyrolysis oils contain less sugars but more phenolic compounds than fast pyrolysis oils [9,12].

Upgrading fast and intermediate pyrolysis bio-oils is important to remove reactive oxygen species and enhance the hydrocarbon contents to produce a liquid biofuel that can be used a direct replacement for fossil-derived fuels or blended with hydrocarbon fuels [5,13,14].

Catalytic hydrotreatment (including hydrodeoxygenation (HDO)) is among the most attractive pathways to convert pyrolysis bio-oils to upgraded liquid products and typically requires high temperatures of up to 400 °C [15] and high hydrogen pressures ($\approx$ 100 bar) [15]. Successful one-pot catalytic bio-oil upgrading systems have been reported to give high yields of deoxygenated oil products [16–19], however, the formation of char (carbon) and water may rapidly deactivate the catalysts. Hence, some of the best results with longer catalytic activities during bio-oil upgrading to hydrocarbon-rich liquid fuels have come from two-step processes [20–22]. These involve initial mild treatment (150 – 300 °C) to stabilise the oil by eliminating significant amounts of thermally unstable oxygenated compounds (e.g., sugars, aldehydes, furans, carboxylic acids, esters and ethers), which are known are to form char by water elimination (dehydration) and condensation reactions. In the second stage, much severe reaction conditions (up to 400 °C) are used for HDO of the stabilised oil to produce hydrocarbon-rich liquids. However, some of the reported results showed significant carbon losses via char formation, while the final products remained highly oxygenated, with oxygen contents of up to 30 wt% in some cases [20–22].

Due to these limitations, some researchers have reported the use of organic solvents during the catalytic upgrading of bio-oils to minimise char formation and to enhance deoxygenation reactions [15,23]. The combinations of solvents and several supported noble metal catalysts (Pt, Pd, and Ru) have been successfully used to upgrade bio-oils to hydrocarbon-rich fuels [15,20,22,23,25,26]. In addition, co-processing of fossil-derived liquids with biomass-derived liquids can make significant contributions towards defossilisation of liquid fuels during the transition to Net Zero. For instance, Xu et al. [15] reported that the use of several organic solvents (decalin, tetralin, diesel and isopropanol) as upgrading media, led to lower char formation and increased deoxygenation, producing a blended hydrocarbon-rich fuel with less than 0.5 wt% oxygen content. However, the best deoxygenation rates were obtained with tetralin and diesel/isopropanol solvents, which left significant amount of soot-forming naphthalenes and other aromatics in the final product. In addition, the two-step process still required higher temperatures of up to 400 °C in the second stage and high hydrogen pressures of between 100 and 130 bar [15]. The requirement for such a large excess of expensive hydrogen is unattractive and unsafe for efficient process development. It would also require the use of large and expensive hydrogen recovery and purification equipment to recycle the mostly unreacted hydrogen. Therefore, a combination of lower

processing temperatures, lower hydrogen pressures and appropriate catalysts during solvent-assisted bio-oil upgrading, are important to achieve a potentially viable and sustainable process of transforming oxygen-rich bio-oils into upgraded ready-to-use hydrocarbon fuel blends.

In this present study, the development and application of a novel solvent-assisted two-stage process for the upgrading of intermediate pyrolysis bio-oil feedstock with low hydrogen pressure (10 bar) has been investigated in the presence of four supported noble metals (Pd, Pt and Ru) catalysts. These catalysts have been reported as effective for both bio-oil stabilisation [15] and HDO [25,26] but with uneconomically large hydrogen requirements. The rationale for the selection of catalyst support is provided in *Section 2.2*. A major innovation in this work was the use of a hydrocarbon solvent (dodecane) and low hydrogen pressure to promote gas–liquid reactions in a stirred batch reactor, minimising char formation. The rationale for selecting dodecane and the solvent/IP bio-oil mass ratio used in this work is provided in *Section 2.3*.

The Stage I reactions involved the catalytic hydrotreatment (stabilisation) of the IP pyrolysis bio-oil feedstock separately using all four catalysts in the presence of hydrogen gas. While some researchers have suggested the use of low temperature (175 °C – 250 °C) for the stabilisation of bio-oil during two-stage upgrading [22], some have used temperatures >300 °C in the presence of solvents [15]. The Stage I experiments were conducted in two steps due to practical observations. First, the Stage I experiments were run initially at 160 °C for 3 h to stabilise the IP bio-oil and then without opening the reactor, the temperature was raised to 300 °C for 3 h. This process was adopted following observations from preliminary experiments at 160 °C for up to 6 h in the presence of Pd/C and dodecane (solvent). These low-temperature experiments led to the formation of viscous liquids, which could only be recovered from the reactor with large amounts of solvent to allow its separation from the solids (catalyst and char). This two-step Stage I approach resolved this challenge, producing a much lighter organic liquid, which was easy to recover from the reaction mixture by simple vacuum filtration. In Stage II, the organic liquid products from Stage I were reacted in the presence of Pt/γ-Al$_2$O$_3$. Overall, the extensive and detailed work reported here has been carried out with the aim of producing a ready-to-use blended fuel (with high biofuel content) within the gasoline and, especially kerosene range. Using a careful selection of catalytic upgrading conditions (catalyst, solvent and hydrogen), dramatic char reduction could be achieved, corresponding to high yields of biofuel content, with low oxygen and high bio-carbon contents.

2. Materials and methods

2.1. IP bio-oil feedstock and its characterisation

The IP bio-oil used as feedstock in this study was produced in-house from pine wood sawdust pellets (6 mm diameter and <10 mm length) using an augur reactor operating at 500 °C, with a feeding rate of 2 g min^{-1}. The kiln of the reactor has a diameter of 2.6 cm and a length of 50 cm, which is heated using a Carbolite VST 12/400 2 kW electric furnace. The solid residence time inside the reactor was approximately 1.5 min. A water-cooled condenser, followed by two dry ice-cooled condensers were used to recover liquid products. All three sets of liquid products were combined, and the phase-separated water decanted to obtain the IP bio-oil for this study. Detailed description of the augur reactor has been published elsewhere [28]. The material balances from the intermediate pyrolysis of the sawdust pellets were >95 wt% with values of 43.4 $\pm$ 2 wt% oil, 26.8 $\pm$ 0.8 wt% char (biochar) and 25.1 $\pm$ 1.1 wt% gas.

Some physico-chemical properties of the sawdust pellets and obtained IP bio-oil are presented in Table 1. Elemental analysis was carried out to the determine the C, H, N, and S contents of the sawdust pellets and IP bio-oil using a Thermo Scientific brand (Model: Flash 2000)

Table 1
Some physico-chemical properties of sawdust pellets and IP bio-oil used in this study.

Elemental compositions			
Parameter	Method	Sawdust pellets	IP bio-oil
C (wt%)	ASTM D8322	45.61 ± 1.2	62.8 ± 1.74
H (wt%)	ASTM D8322	5.78 ± 0.86	11.0 ± 0.36
N (wt%)	ASTM D8322	0.24 ± 0.03	0.29 ± 0.03
O (wt%) *	ASTM D8322	48.37 ± 1.8	25.9 ± 2.08
H/C molar ratio	–	1.52	2.10
O/C molar ratio	–	0.80	0.31
Other properties			
Parameter	Method	Sawdust pellets	IP bio-oil
Ash (wt%)	ASTM-D 482–07	0.63 ± 0.3	1.52 ± 0.25
Volatile Matter	ASTM 1982	77.20 ± 1.5	–
Moisture content (wt%)	ASTM E203	9.82 ± 0.8	3.2 ± 0.8
Fixed Carbon	–	12.35 ± 1.6	–
HHV (MJ/Kg) [a]	–	16.05 ± 0.55	32.4 ± 0.25
Acid number (mgKOH/g)	ASTM D664	–	161.6 ± 1.2
pH value	–	–	2.4 ± 0.3
Density at 25 °C (g/cm³)	ASTM D 4052	–	1.3 ± 0.01

*Calculated by difference; [a] calculated based on equation from Channiwala and Parikh [29].
The elemental composition of dodecane was confirmed as: C = 84.6 wt% and H = 15.4 wt%).

organic elemental analyser. Approximately 3 mg of the samples were used, and oxygen content was calculated by difference after ash determination. To determine ash contents, about 1 g of each sample was placed into a pre-weighted silica crucible and combusted in a muffle furnace under a constant flow of oxygen gas at 575 °C for 4 h. Afterwards, sample was cooled in a desiccator and weighed to a constant weight.

The water content of the IP bio-oil sample was measured using a Karl Fischer titration following the standard method ASTM E203. The results of ash and water contents were used to evaluate the volatile matter content of the bio-oil. Additionally, a Karl Fischer titrator (Mettler Toledo model G20 compact titrator) was used to measure the total acid number (TAN) of the sample, using 0.1 M potassium hydroxide solution in isopropanol. The pH value was determined in a Fisher Scientific pH meter model Accumet AE150. Density was determined using a Mettler Toledo DM40 Density Meter at 20 °C. The heating value was estimated using the results from elemental analysis and ash content, according to Channiwala and Parikh [29]. All these analyses were carried out in triplicates and averages reported with standard deviations. The chemical composition, in terms of compounds present in the IP bio-oil feedstock was also characterised by gas chromatography – mass spectrometry (GC/MS) (*please see Section 2.2.6*).

2.2. Catalyst selection and characterisation

Three noble metal catalysts (Pt, Pd, and Ru) on different supports have been extensively used in literature to successfully upgrade pyrolysis bio-oils to hydrocarbon-rich fuels [15,20,22,23,25,26]. The type of catalyst support is important in terms of their stability during HDO and potential catalyst recoverability after the upgrading reactions. The water formed under the high-pressure HDO conditions can destroy some catalyst supports e.g., through hydrolysis [30] and pore structure collapse [31]. Hence, carbon and gamma-alumina (γ-Al$_2$O$_3$) supports are commonly used as they are known to be stable in the presence of hot-pressurised water [24]. However, carbon formation on the surface of solid catalysts is a major cause of their deactivation during the initial reactions of bio-oil upgrading [21]. Such carbon deposition may be prevented by using appropriate solvents [15,23]. Nonetheless, where coke deposition occurs, it may be removed during catalyst regeneration through calcination [32,33], which is not suitable for carbon-supported

metal catalysts, due to carbon loss of the support from burn-off. Generally, alumina supports have been reported to promote char formation when used for HDO in the absence of solvents [21,34], however this problem can be resolved by using suitable solvents [15].

Moreover, γ-Al$_2$O$_3$ may suffer hydrolysis under hot-compressed water (hydrothermal) conditions to form boehmite (AlO(OH)) with extensive use [27,30]. Calcination can be used to regenerate alumina, both in terms of removing carbon deposits and reversing its hydrolysis {2AlO(OH) → Al$_2$O$_3$ + H$_2$O}. Hence, using catalysts with γ-Al$_2$O$_3$ support for HDO of bio-oils has the potential for stable operations and catalyst reuse, which favour low processing costs. For these reasons, mainly γ-Al$_2$O$_3$-supported catalysts have been chosen for Stage I bio-oil upgrading in this present study, with Pd/C included for comparison. Therefore, four commercial noble metal catalysts supported on gamma-alumina or activated carbon have been used in this study. These included 5 wt% palladium on activated carbon powder (Pd/C) and 5 wt % Pd on alumina powder (Pd/γ-Al$_2$O$_3$), which were purchased from Sigma-Aldrich UK. In addition, 5 wt% Pt on alumina powder (Pt/γ-Al$_2$O$_3$) and 5 wt% ruthenium on alumina powder (Ru/γ-Al$_2$O$_3$) were obtained from Catal International Ltd, Sheffield, UK. Due to Pd/C being only in powdered form, the remaining three catalyst were also used as powders for comparison.

The noble metal catalysts were reduced with H$_2$ gas at a flow rate of 50 mL min^{-1} flow rate in a tubular oven for 4 h at 200 °C according to the procedure reported by Checa et al. [35]. Thereafter, a continuous flow of H$_2$ was used to cool down the reduced catalysts to room temperature, followed by N$_2$ purge for 20 min at a flow rate of 50 mL/min. After this, the solids were transferred into amber vials, sealed and wrapped with paraffin wax for characterisation and catalytic experiments. Table 2 shows some characteristics of the reduced catalysts. X-ray diffraction (XRD) analyses of were performed on a Bruker D8 Advance diffractometer using Cu Kα1,2 radiation (0.02 mm Ni Kβ filter and 2.5° Soller slits, scanning from 5 to 105°), operated at 40 mA and 40 kV.

The catalyst materials were top-loaded into PMMA specimen holders and the diffractograms were collected in the Bragg–Brentano geometry with a step scan of 0.02° (1 s per step). The catalysts surface area, the pore size and total pore volume were measured by N$_2$ porosimetry on a Quantachrome Nova 4000e analyser with a NovaWin software. Prior to the analysis, the catalysts were degassed under vacuum for 4 h at 120 °C. Surface areas were measured by the BET method (Brunauer, Emmett and Teller), and pore diameter and total pore volume was calculated by the BJH method (Barrett-Joyner-Halenda) [36].

2.3. Selection of dodecane as solvent and IP bio-oil/solvent ratio

The recovery of solvents used during solvent-assisted bio-oil upgrading experiments by distillation or evaporation is challenging as their boiling points are similar to those of the compounds in the upgraded bio-oil. Hence, these solvents are usually left as part of the upgraded oil, which can have significant implications on the subsequent properties and potential use of the upgraded liquid product. For example, hydrogen-donating tetralin transforms naphthalene-type compounds which are known to form soot during internal engine combustion [15]. For this present work, dodecane has been chosen for its thermal stability at temperatures below 327 °C [27] and because as a C$_{12}$ hydrocarbon, it falls within the carbon range of the target gasoline and, especially kerosene fuels.

Interestingly, some of the most successful solvent-assisted upgrading of pyrolysis bio-oils in literature used between 23 wt% [15] and 80 wt% [23] of hydrocarbon solvents. In this present study, preliminary Stage I experiments with various solvent/IP bio-oil mass ratios in the presence of Pd/C, showed that using lower than 60 wt% of dodecane led to the formation of a viscous organic liquid layer at the bottom of the reactor. The viscous liquid required large amounts of additional solvent to recover from the reactor, thereby significantly diluting the target liquid

Table 2
Some characteristics of the catalysts used in this present study.

	Bulk density (kg m^{-3})	BET surface area (m^2/g)	Pore diameter (nm)	Average Particle size (μm)	Pore volume (cm^3 g^{-1})	Metal (wt %)
Pd/C powder	397	897	3.81	18.1	0.37	5.01
Pd/Al$_2$O$_3$ powder	550	148	13.7	70.5	0.61	4.97
Pt/Al$_2$O$_3$ powder	720	182	9.00	30	0.70	5.07
Ru/Al$_2$O$_3$ powder	610	174	9.10	28.0	0.81	5.20

product, which was deemed counterproductive. Therefore, the solvent/ IP bio-oil mass ratio of 60 wt%:40 wt% used in experiments involving dodecane in this present work was informed by examples in literature and from preliminary tests, especially with respect to efficient recovery of liquid products. The n-dodecane (99.5%, Acros Organics) solvent used here was purchased from Fisher Scientific, UK and used as received.

2.4. Experimental methods

#### 2.4.1. Two-stage catalytic hydrotreatment and hydrodeoxygenation of IP bio-oil

The two-stage hydrotreatment (stabilisation) and hydro-deoxygenation of the IP bio-oil feedstock were studied in two sets of experiments in a 100 mL Parr reactor (Parr series 5500, Parr Instrument Company, USA) equipped with a magnetic drive stirrer, a water-cooled solenoid, a digital pressure readout and a standard pressure gauge. The loading of the reactor and all experimental procedures described below were carried out in a fume cupboard. In each case, the whole reactor system (vessel and head) was dried, assembled and weighed empty (W_0). The schematic of the main experimental procedures is shown in Fig. 1.

Several initial experiments were carried out during method development for determine the best conditions for the two stages (examples shown in *Supplementary Information Table SI1*). The Stage I stabilisation reactions were carried out in two steps: initial stabilisation at 160 °C for 3 h and final stabilisation at 300 °C for another 3 h. In the Stage I experiments, 6.4 g of IP bio-oil was mixed into 9.6 g of dodecane in the reactor to give a total liquid loading of 16 g per experiment. This amount of feedstock loading gave sufficient volume of liquid to ensure stirring was achieved. Therefore, the mass ratio of solvent and IP bio-oil was 3:2 in the first stage. Thereafter, 2 g of each of the prior reduced catalysts (Pd/C, Pd/Al$_2$O$_3$, Pt/Al$_2$O$_3$ or Ru/Al$_2$O$_3$) were separately added into the reactor for the hydrotreatment (stabilisation) experiments. As

mentioned earlier, these catalysts and their supports have been selected based on previously reported work in literature [15,25,26]. The reactor was then purged with N$_2$ for 10 min, followed by H$_2$ for 5 min and then pressurised with H$_2$ to 10 bar. The total weight (W_1) of feedstock, solvent, catalyst and hydrogen gas (10 bar) was measured before starting the reaction. The reaction was carried for 3 h at 160 °C, then increased to 300 °C and held for a further 3 h. All reactions were carried out at a stirring speed at 600 rpm. At the end of the first stage the reaction was stopped, and the reactor rapidly cooled down to room temperature under 30 min with a large laboratory fan. The cooled reactor was depressurised with some gas collected for analysis. Thereafter, the reactor was opened to sample the liquid (organic and aqueous) and solid contents. The solid residues (char and spent catalysts) were separated from the liquid phase by vacuum filtration. Then, the liquid product obtained from Stage I was centrifuged to separate into two aqueous and organic phases.

At the end of Stage I, it became clear that most char formation occurred during this two-step stabilisation stage. Therefore, recovering and regenerating carbon-supported catalysts would be challenging. Hence, it was decided to use the Pt/Al$_2$O$_3$ (which would be easier to regenerate by calcination than Pd/C) for the second stage HDO. Where applicable, each of the Stage I experiments was repeated up to 6 times to obtain sufficient organic liquid phase for 2 tests in Stage II.

Therefore, for Stage II, 16 g of the organic liquid product mixture (dodecane and upgraded biofuel in most cases) obtained from a set of Stage I experiments was loaded into the reactor along with 2 g of reduced Pt/Al$_2$O$_3$. In the procedure, again the reactor was sealed, purged in succession with N$_2$ and H$_2$, and then pressurised to 10 bar with H$_2$. This time the reaction was carried out at 300 °C for another 3 h, after which the reactor was cooled to room temperature to sample the products in the same way as the Stage I experiments.
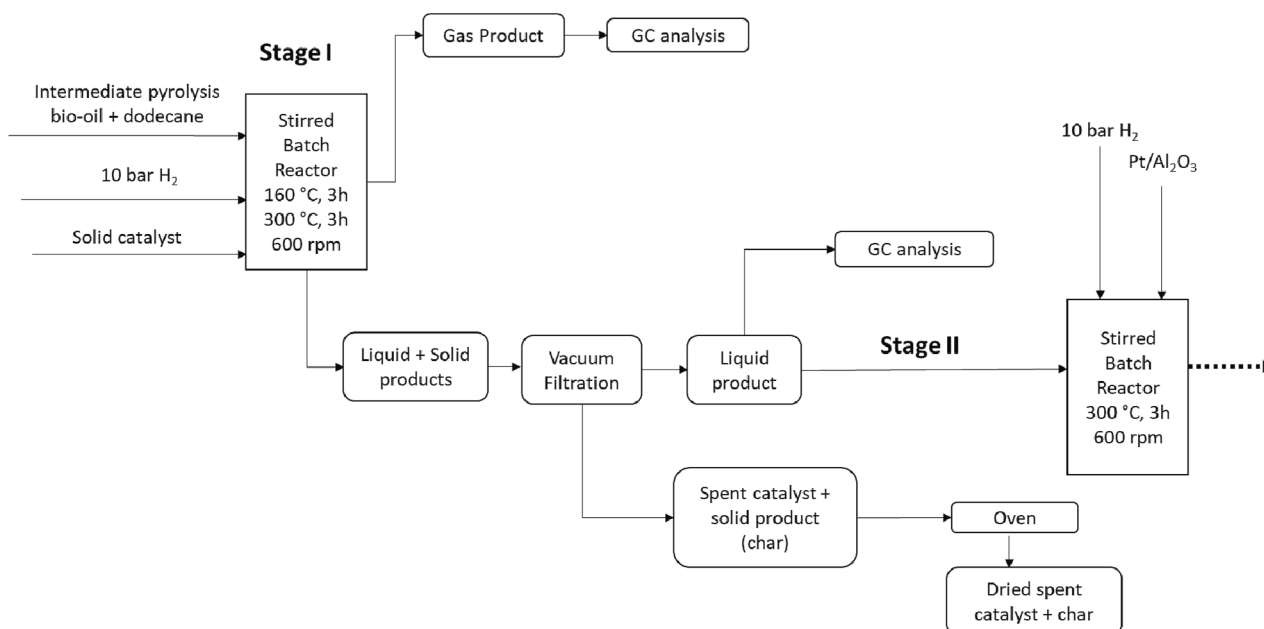
Fig. 1. Schematic of experimental programme adopted in this present study.

2.4.2. Sampling and analyses of reaction products

As mentioned earlier, at the end of each experiment (for both Stages I and II), the cooled reactor was weighed (same as W_1) with all its contents (gas, liquid and solid). The weighing of the reactor was carried out using a VWR weighing balance VWR1611-3472 Model LP-6292i, with 6200 g as its maximum load and the precision was 0.01 g. Thereafter, a sample of the gas was collected in a 1 L Tedlar bag for analysis, while the remaining gas was discharged inside the fume cupboard. After discharging the gas, the reactor was weighed again (W_2) with its remaining contents (solid and liquid). The difference between W_1 and W_2 was taken as the total weight of gas (W_{GAS}), including any unreacted hydrogen. The reactor was then opened to sample the liquid phase first and the solid phase afterwards. No additional solvent was used for the recovery of the liquid/tar products used for subsequent characterisation.

The liquid phase contained distinct aqueous and organic fractions after each stage but initially weighed together (W_{LIQUID}). However, for both stages, centrifugation was used to separate the aqueous and organic fractions into distinct layers and collected separately by careful decantation. The weights of the aqueous and organic liquid products were designated as W_{WATER} and W_{OIL}, respectively. The solid phase in the reactor, which comprised of the spent catalyst (where applicable) and any char formed during the reactions, was recovered from the reactor with a spatula. Once collected, the solid phase was washed with acetone on a filter paper until a clear liquid was obtained. The washed solid phase was then placed in an oven at 105 °C for 2 h, cooled in a desiccator and weighed. The initial mass of catalyst was assumed to be unchanged and so, the weight of char (W_{CHAR}) produced from the reaction was found as the difference the mass of the washed solid residue and initial mass of catalyst used [37]. The masses of all phases were used for mass balance calculations, according to the equation 1.

$$Overall\ Mass\ balance(wt\%) = \frac{W_{CHAR} + W_{LIQUID} + W_{GAS}}{W_1} \times 100 \tag{1}$$

2.4.3. Analysis of gas products

The gas phases from the two stages were collected with the 1 L Tedlar gas bags and analysed with Shimadzu GC-2014 gas chromatography (GC) fitted with a thermal conductivity detector (TCD) and flame ionisation detector (FID). Detailed description of the GC has been reported previously [28]. Briefly, it consisted of two injectors and two columns, with one connected to the FID for the analysis of hydrocarbon gases (C_1-C_4) and another column connected to the TCD for the analysis of permanent gases (H_2, O_2, N_2, CO and CO_2). The mass yield of each gas components was calculated based on the ideal gas equations using the volume percent of each gas obtained from GC analysis, the final reactor pressure and temperature after cooling, the headspace volume of the reactor [36].

2.4.4. Calculating the yields of upgraded fuel blend in liquid products

For experiments without dodecane solvent, the yields of products were easily calculated based on the amount of IP bio-oil and hydrogen gas used. However, for experiments involving dodecane, the organic liquid product obtained from the reactor after Stage I and Stage II reactions contained both dodecane and upgraded bio-oil i.e., biofuel. Therefore, the biofuel yields and contents in these upgraded fuel blends needed to be determined differently. The masses of these upgraded fuel blends W_{Oil1} and W_{Oil2} for Stage I and Stage II, respectively were gravimetrically obtained. Hence, by determining the mass of dodecane recovered from the control experiments, the mass fractions, x_{s1} and x_{s2} of dodecane in W_{Oil1} and W_{Oil2}, were respectively obtained. From these, the biofuel contents, $W_{Biofuel1}$ and $W_{Biofuel2}$ of the upgraded fuel blend were then calculated for Stage I and Stage II, according to the mass balance calculation Equations (2)–(6).

Feedstock mass balance

$$W_{Feed} = W_{s0} + W_{IPbio-oil} \tag{2}$$

Stage I Organic Liquid Product Yield

$$W_{Biofuel1} = W_{Oil1} - W_{s1} \tag{3}$$

Proportion of dodecane in Stage I Liquid Product (W_{s1})

$$W_{S1} = x_{s1} \times W_{S0} \tag{4}$$

Stage II Organic Liquid Product Yield

$$W_{Biofuel2} = W_{Oil2} - W_{s2} \tag{5}$$

Proportion of dodecane in in Stage II Liquid Product (W_{s2})

$$W_{S2} = x_{s2} \times W_{S1} = x_{s2} \times x_{s2} \times W_{S0} \tag{6}$$

where, W_{s0} = initial mass of dodecane solvent; $W_{IPbio-oil}$ = initial mass of IP bio-oil.

The percentage biofuel yields from each of the two catalytic upgrading stages were calculated, in relation to the initial IP bio-oil feed using Equation 7:

$$Biofuel_{i,j}Yield(wt\%) = \frac{W_{Biofuel_{i,j}}}{W_{IPbio-oil}} \times 100 \tag{7}$$

where i and j represent each of the upgrading Stage I and Stage II, respectively.

Lastly, the liquid biofuel contents in the upgraded fuel blends from Stage I and Stage II were calculated using Equation 8:

$$Biofuel_{i,j}Content(wt\%) = \frac{W_{Biofuel_{i,j}}}{W_{Oil_{i,j}}} \times 100 \tag{8}$$

where i and j represent each of the upgrading Stage I and Stage II, respectively.

2.4.5. Calculating the yields of char, aqueous phase, and gas products from IP bio-oil feed.

For experiments without solvent, the yields char, aqueous phase, and gas products were directly calculated from the amount IP bio-oil feed. However, for experiments involving the use of dodecane solvent, the yields of these products from the IP bio-oil were obtained after accounting for the solvent. Based on Table 3, it was valid to assume that all the other products (water, char and gas) originated from the reactions of the IP bio-oil component of the organic liquid in all experiments involving dodecane. Hence, yields of water, char and gas (products) were calculated using Equation 9;

$$X_{i,j}\ Yield(wt\%) = \frac{W_{X_{i,j}}}{W_{IPbio-oil}} \times 100 \tag{9}$$

where i and j represent each of the upgrading Stage I and Stage II, respectively. X represents char, aqueous phase, or gas products.

Stage II reactions depended on the biofuel components of the organic liquid product from Stage I, assuming the thermal and chemical stability of dodecane. Therefore, only the Stage II biofuel yield could be directly calculated on the initial IP bio-oil feed basis. The yields of remaining products (char, aqueous phase and gas) must be considered differently to be calculated accurately. In this present study, the yields of char, aqueous phase and gas obtained after Stage II would be based on the sum of their yields after the two upgrading stages. Hence, the cumulative yields of char, aqueous phase and gas products over the two stages were calculated from Equation 10.

$$X_{cumm.}Yield(wt\%) = X_i Yield(wt\%) + X_j Yield(wt\%) \tag{10}$$

where i and j represent each of the upgrading Stage I and Stage II, respectively. X represents char, aqueous phase, or gas.

In addition, the degree of deoxygenation (DOD) following the upgrading experiments was calculated as follows in Equations 11 and 12:

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Table 3
Results of thermal stability of dodecane solvent under the test conditions.

Products (wt%)	Stage I No catalyst	Stage II No catalyst	Stage I Pd/C	Stage II Pt/Al$_2$O$_3$	Stage I Pt/Al$_2$O$_3$	Stage II Pt/Al$_2$O$_3$	Stage I Pd/Al$_2$O$_3$	Stage II Pt/Al$_2$O$_3$	Stage I Ru/Al$_2$O$_3$	Stage II Pt/Al$_2$O$_3$
Liquid	99.3	99.1	99.6	98.7	99.1	98.9	98.7	98.7	98.7	98.9
Gas	nd	nd	nd	<0.1	nd	<0.01	nd	<0.1	1.20	0.06
Solid	nd	nd	nd	nd	nd	nd	nd	nd	Nd	nd

Experiments without solvent

$$DOD, wt\% = 1 - \frac{Wt\% \ oxygen \ in \ upgraded \ oil/tar}{Wt\% \ oxygen \ in \ IP \ bio - oil} \times 100 \qquad (11)$$

Experiments with solvent

$$DOD, wt\% = 1 - \frac{Wt\% \ oxygen \ in \ organic \ liquid \ product}{Wt\% \ oxygen \ in \ Feed(IP \ bio - oil + dodecane)} \times 100 \qquad (12)$$

The degree of deoxygenation is a commonly used parameter to represent the extent of bio-oil upgrading towards the formation of hydrocarbon-rich liquid fuels [15,23]. However, this parameter can give counter-intuitive results since it does not account for the yield of upgraded biofuel in the liquid products. Hence, using the amount of biomass-derived carbon remaining in the organic liquid products may give a better indication of the success of bio-oil upgrading. The experimental data from the thermal stability tests of dodecane (Table 3) and the quantification of the organic liquid products, were used to calculate the % bio-carbon retention (wt% BCR) were calculated for the two stages according to Equations 13 and 14.

Stage I:

$$wt\%BCR_I = \left(\frac{Mass \ of \ C_{OLP1} - Mass \ of \ C_{Dodecane1}}{Mass \ of \ C_{IPbio-oil}} \right) \times 100 \qquad (13)$$

Where:

$Mass \ of \ C_{OLP1} = C \ wt\% \ in \ Stage \ I \ organic \ liquid \ product \ (OLP1)$
$\qquad \times mass \ of \ Stage \ I \ OLP1$

$Mass \ of \ C_{Dodecane1} = Mass \ of \ C_{OLP1}$
$\qquad \times mass \ fraction \ of \ dodecane \ in \ OLP1$

$Mass \ of \ C_{IPbio-oil} = C \ wt\% \ in \ IP \ biooil$
$\qquad \times mass \ of \ IP \ biooil \ used \ in \ Stage \ I$

Stage II:

$$wt\%BCR_{II} = \left(\frac{Mass \ of \ C_{OLP2} - Mass \ of \ C_{Dodecane2}}{Mass \ of \ C_{StageIbio-carbon}} \right) \times 100 \qquad (14)$$

where:

$Mass \ of \ C_{OLP2} = C \ wt\% \ of \ Stage \ II \ organic \ liquid \ product \ (OLP2)$
$\qquad \times mass \ of \ Stage \ II \ OLP2$

$Mass \ of \ C_{Dodecane2} = Mass \ of \ C_{OLP2}$
$\qquad \times mass \ fraction \ of \ dodecane \ in \ OLP2$

$Mass \ of \ C_{StageIbio-carbon} = Mass \ of \ C_{OLP1} \ used \ in \ Stage \ II \times mass \ fraction \ of \ upgraded \ biooil \ obtained \ in \ OLP1$

Thereafter, the overall % BCR was calculated from Equation 15

$$Overall \ wt\%BCR = Fractional \ BCR_I \times Fractional \ BCR_{II} \times 100 \qquad (15)$$

2.4.6. Characterisation of IP bio-oil and organic liquid products by GC/MS

Gas chromatography coupled to a mass spectrometer (GC–MS) was used to identify key chemical compounds in the IP bio-oil feed and upgraded fuel blends. The GC/MS used was a Shimadzu model GC-2010 Plus gas chromatograph, fitted with a Shimadzu mass spectrometer (model QP2010 SE). The mass selective detector was operated in the electronic impact ionisation mode (70 eV). A 30 m length 0.25 mm i.d. SH-Rtx-5MS, supplied by Thames Restek, UK was used. Oven temperature was maintained at 45 °C for 2.5 min, followed by a first ramp at 2° min^{-1} to 140 °C and held 2 min, and a second ramp at 8 °C min^{-1} to 280 °C and held for 2.5 min. The injector and transfer line were both held at 280 °C, while a helium carrier gas flow of flow rate of 1 mL min^{-1} was maintained. For the analyses of the IP bio-oil or upgraded fuel blends, 0.5 mL of each sample was diluted with 9.5 mL of acetone (99+%, Fisher Scientific, UK) to make a 5 vol% solution. A sample injection size of 1 μL was used for each analysis.

Bio-oils contain a large proportion of non-volatile components such that quantitative analysis often account for less than 60 wt% of GC detectable components, e.g., considering their inherent high moisture contents. Hence, in this study, semi-quantitative analysis was carried out on the IP bio-oil based on peak area % [15,23] (Equation 15)

$$Peak \ area\% = \frac{Peak \ area \ of \ compound}{Total \ peak \ area \ of \ compounds \ in \ sample} \times 100 \qquad (15)$$

However, for organic liquids containing semi-volatile and volatile components, detailed quantification can be carried out using standard methods. Hence, the organic liquid compounds obtained from both stages of the IP bio-oil upgrading were quantified using a combination of external and internal standard methods. First, an external standard method was developed to create a calibration curve for dodecane. This method was used to quantify the amount of dodecane present in the upgraded oils obtained from the solvent-assisted experiments. In the second method, the same dodecane was used as internal standard to quantify the other compounds in the upgraded bio-oils. For the organic liquid products obtained without the use of solvents, a known amount of dodecane was added as internal standard when preparing their solutions for quantification by this method. In the quantification procedure, a selection of compounds identified from qualitive GC/MS analyses, was used to represent the different classes of compounds found in the upgraded liquid products over the two stages to obtain their relative response factors. These compounds included: octane, toluene, tetradecane and hexadecane for hydrocarbons; 2-methylphenol and 2,4-dimethylphenol for phenols; acetic acid for carboxylic acids; hexanol for alcohols, hexanone for ketones; hexanal and furfural for aldehydes; 2-methylfuran for furans and ethers and levoglucosan for sugars. In addition, the peak area compositions of the upgraded liquid products have been presented in the *Supplementary Information (Tables SI2 and SI3)* for easy comparison with similar published work.
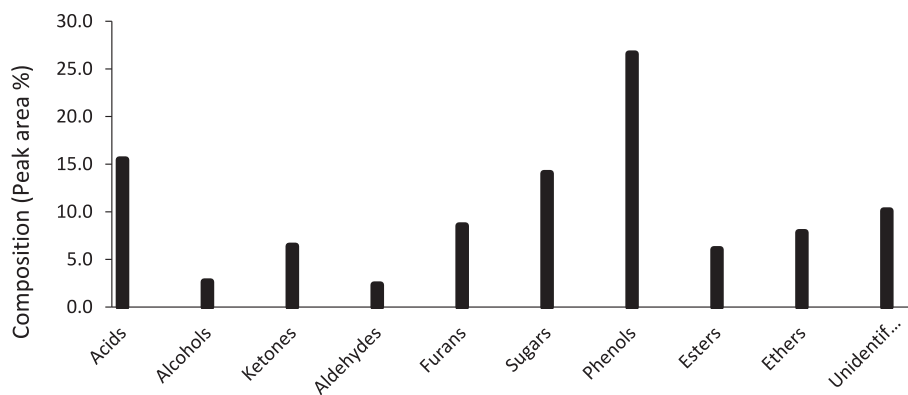
Fig. 2. Composition of compound groups in the IP bio-oil used in this study.

3. Results and discussion

3.1. Composition of IP bio-oil feedstock

Fig. 2 shows the main components (in peak area percent) of the IP bio-oil according to functional group categories, as identified by the NIST Library™. The compounds were classed into carboxylic acids, aldehydes, ketones, esters, ethers, alcohols, phenols and unidentified compounds. From the identified compounds, the most abundant classes were phenols, carboxylic acids and sugars. The dominance of phenolic compounds in IP bio-oils is well reported in literature [38]. The main carboxylic acids included lactic acid and acetic acid (*Supplementary Information Figure SI1*), considered to be responsible for the high acidity of bio-oil (pH = 2.4).

In terms of composition, β-D-1,6-anhydro-glucopyranose (levoglucosan) was the main sugar compound in IP bio-oil sample, while the main aldehydes were propanal, furfural and coniferyl aldehyde. The main ketones in the IP bio-oil were 2(5H)-furanone, 1-oxirananyl ethanone, and alkylated cyclopentanones and cyclopentenones. Phenolic compounds were the most dominant compounds and the main compounds in this class included creosol, guaiacol, ethylguaiacol and catechol were the major phenolic components of IP bio-oil, and the principal furanic compounds were furan and alkylated furans.

3.2. Control experiments with dodecane (stability tests)

To account for dodecane solvent used during the two-stage upgrading process, control experiments were carried out by reacting dodecane alone in the two stages using the four catalysts like in actual upgrading experiments. These tests were carried out with 16 g of dodecane, 2 g of each catalyst in relation to reaction stage and 10 bar of hydrogen, using the same experimental procedure used for the IP bio-oil upgrading tests. The results are presented in Table 3, which shows that virtually no solid products were formed from dodecane during the two-stage reactions. No change in liquid colour also occurred and the collected amounts of

liquids ranged from 98.7 wt% to 99.3 wt% in Stage I and from 98.7 % to 99.1 wt% in Stage II.

No significant differences were observed in the amount of dodecane recovered between the catalytic and non-catalytic tests. Analyses of the gas phase after the reaction of dodecane alone, showed that hydrogen gas (where added) was the only gas present in Stage I, while hydrogen and tiny peaks of methane (<0.1 wt%) were found in some cases in Stage II (especially with Ru/Al_2O_3). Therefore, it was concluded that the dodecane solvent was assumed to be thermally stable [27] under both test conditions used in this present work.

3.3. Stage I catalytic hydrotreatment (stabilisation) results

3.3.1. Stage I product distribution and mass balances

The distribution of reaction products as organic phase, aqueous phase, solid residue, and gas phase from the experiments carried out in this present study are presented in this section. Hence, the performances of the noble metal catalysts and solvents (dodecane) in Stage I (hydrotreatment) and Stage II (HDO) of the upgrading process are evaluated in detail. Using Equations 1 – 10 and data from Table 3, the dodecane contents of the organic phase product was eliminated and the percentage yields of the remaining products were calculated based on the IP bio-oil used in each experiment.

Table 4 shows the results from Stage I experiments involving the stabilisation of the IP bio-oil, with and without dodecane solvent and catalysts. These results were used to determine the yield of the reaction products, compositions of gas products, compositions of organic liquid products on IP bio-oil basis, and degree of deoxygenation of organic liquid product and its bio-carbon retention, which are presented in Fig. 3a – 3d. The results in both Table 4 and Fig. 3a indicate very good mass balance closures, respectively and corroborate the assumption that the dodecane solvent was virtually thermally stable and that water, char and gas products originated mostly from the IP bio-oil.

Fig. 3a shows that Exp. 01 and Exp. 02 produced the highest yields of char and the lowest yields of organic liquid products during Stage I.

Table 4
Product yields from Stage I upgrading experiments.

| Exp. # | Feedstock | *Catalyst | Tar | Product yields (wt%) | | | | |
				[a] Organic liquid	Aqueous liquid	Solid	Gas	Total
01	IP bio-oil	–	11.0 ± 1.21	–	16.2 ± 0.85	51.2 ± 0.18	21.4 ± 0.67	99.8
02	IP bio-oil + solvent	–	–	67.8 ± 0.65	7.52 ± 0.24	18.8 ± 0.07	6.13 ± 0.02	99.7
03	IP bio-oil	Pd/C	54.4 ± 0.66	–	13.9 ± 1.01	2.04 ± 0.01	29.5 ± 0.53	99.8
04	IP bio-oil	Pt/ Al₂O₃	40.1 ± 1.56	–	30.9 ± 1.07	9.13 ± 0.12	19.8 ± 0.10	99.9
05	IP bio-oil + solvent	Pd/C	–	80.6 ± 0.54	4.03 ± 1.2	6.30 ± 0.22	8.41 ± 0.09	99.3
06	IP bio-oil + solvent	Pt/Al₂O₃	–	78.3 ± 1.16	6.34 ± 0.18	1.83 ± 0.09	13.1 ± 0.95	99.6
07	IP bio-oil + solvent	Pd/Al₂O₃	–	68.4 ± 0.51	5.23 ± 0.04	5.10 ± 0.07	21.1 ± 0.95	99.7
08	IP bio-oil + solvent	Ru/Al₂O₃	–	78.0 ± 0.68	0.00 ± 0.01	6.20 ± 1.00	15.1 ± 0.75	99.3

*All catalysts in powdered form; a = monophasic liquid containing dodecane and biofuel (upgraded bio-oil) after Stage I.
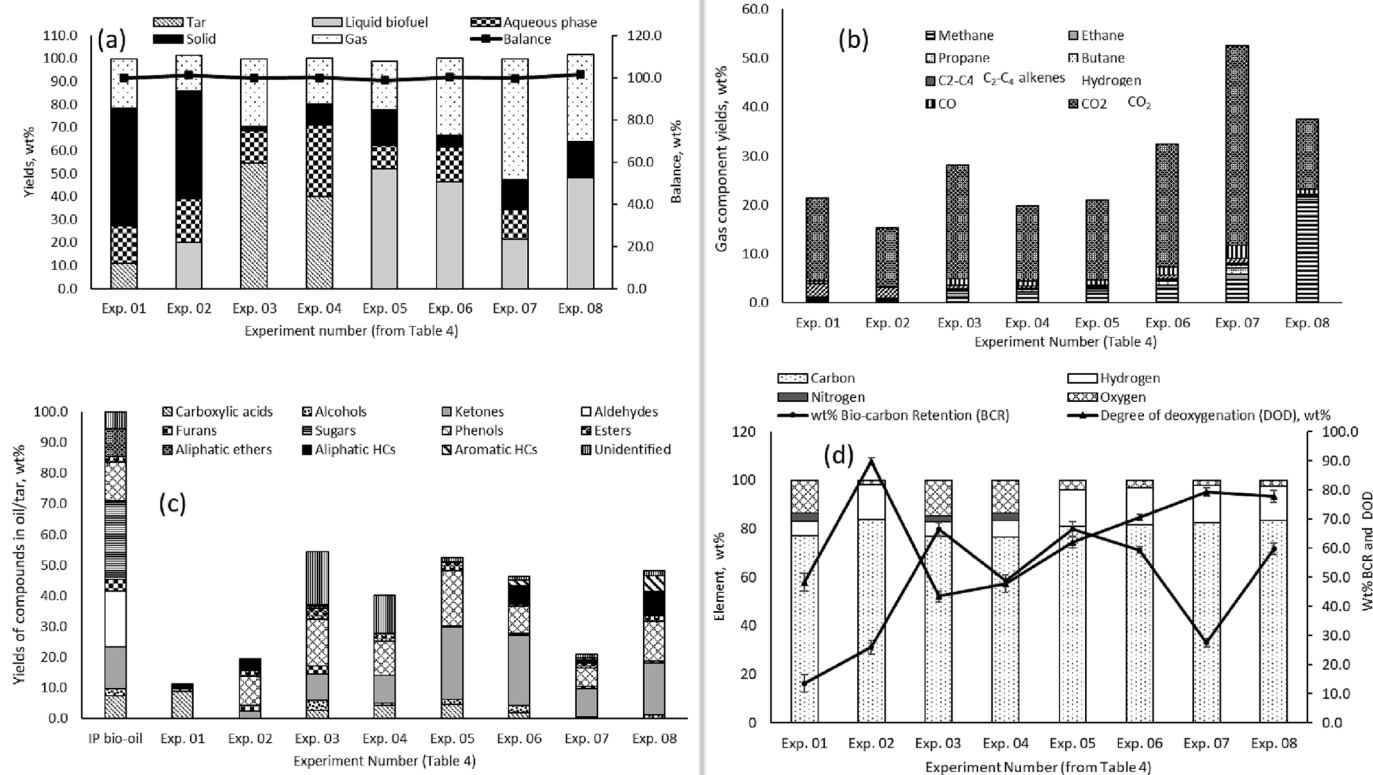
Fig. 3. Results from Stage I upgrading experiments based on IP bio-oil feed; (a) product yields, (b) compositions of gas products, and (c) compositions of tars and organic liquid products compared with IP bio-oil feed; (d) elemental compositions and degree of deoxygenation of organic liquid/tar products.

These first two experiments led to the conversion a large proportion of the IP bio-oil to char via extensive condensation and polymerisation reactions [34,39]. However, the use of dodecane alone as solvent in Stage I (Exp. 02) was marginally only able to minimise char formation in the absence of catalysts. Without the solvent and catalysts, Exp. 01 produced 51.2 wt% of char, no liquid oil and 11.3 wt% of tar in Stage I. Considering that in Exp. 02, the IP bio-oil content in the feedstock was 40 wt%, compared to 100 wt% in Exp. 01, therefore, about 20.5 wt% of char would be produced in Experiment 02. However, Table 4 shows that 18.8 wt% of char was obtained from Exp. 02, which corresponded to 47 wt% of char on IP bio-oil feed basis (Fig. 3). Therefore, the presence of solvent only reduced char formation by about 8.3%. This decrease may be due to the lower concentration of the IP bio-oil in the mixed feedstock or adequate mixing between the solvent and the IP bio-oil, provided by stirring to reduce polymerisation reactions leading to char formation.

In terms of yields of upgraded biofuel, Fig. 3a shows that yields increased to 20.1 wt% in Exp. 02, which was nearly double the results for Exp. 01. Comparing these two experiments, Fig. 3, shows that the main influence of the solvent in the upgrading reaction was to reduce the formation of gas products in favour of upgraded liquid product. Interestingly, Exp. 03 and Exp. 04, in which the IP bio-oil was reacted with Pd/C and Pt/Al$_2$O$_3$, respectively in the absence of dodecane, showed that the catalysts significantly prevented char formation, transforming a large proportion of the bio-oil into tar as the main organic product.

In direct comparison to Exp. 01 results, Table 4 shows that the presence of Pd/C (without solvent) in Exp. 03 led to significant decrease in char yield by 96%. Instead, 54.4 wt% of a dark tarry material, with a strong coal tar smell, was obtained from the IP bio-oil feed. In addition, lower yield of aqueous phase and higher yield of gas product were obtained in Exp. 03 compared to Exp. 01. Indeed in Exp. 03, the Pd/C prevented the extensive char formation that was observed in Exp. 01; it also reduced dehydration (water formation) and slightly improved gas

yields. Li et al. [39] reported that 5 wt% Pd/C catalyst led to lower char formation of between 1.5 wt% and 9.5 wt% during the hydrotreating of fast pyrolysis bio-oil within a temperature range of 150 °C and 300 °C with 100 bar hydrogen pressure. The authors indicated that the lowest char formation occurred at the highest temperature of 300 °C used in their work [40].

Similarly, in the absence of solvent, the use of Pt/Al$_2$O$_3$ in Exp. 04 produced a very clear aqueous phase and a very dark tarry material, which also looked and smelled like coal tar. As with the tar obtained from Exp. 03, the tarry product *(Supplementary Information Figure SI2)* from Exp. 04 was difficult to recover from the reactor without solvent (dichloromethane). Thereafter, the organic solution was filtered to obtain the solid residue (catalyst and char). The char yield from Exp. 04 was 9.13 wt%, representing an 82.2% char reduction compared to Exp. 01. Exp. 04 produced 40.1 wt% of tar, which was 21.1% less than what Pd/C gave in Exp. 03. However, Pt/Al$_2$O$_3$ gave lower gas product (19.8 wt%) and higher aqueous phase (30.9 wt%), compared to Pd/C in Exp. 03. Hence, Pt/Al$_2$O$_3$ produced nearly 2.2 times more aqueous phase and compared Pd/C in their respective Stage I reactions without solvent. Therefore, the two catalysts behaved similarly in terms of their reaction mechanisms. Both Pd/C and Pt/Al$_2$O$_3$ were seemingly good at reducing char and gas formation and promoted deoxygenation via hydrogenolysis of C-OH bonds (hydro-dehydroxylation) to produce water. However, Pt/Al$_2$O$_3$ appeared to be better than Pd/C at promoting water loss and gave the highest yield of aqueous phase obtained in this work.

The remaining Stage I reactions involving the combined use of catalysts and dodecane (Exp. 05, Exp. 06, Exp. 07 and Exp.08) gave char yields of 15.8 wt%, 5.25 wt%, 12.8 wt%, 15.5 wt%, respectively (on IP bio-oil feed basis only). These represented reductions in char formation of 69.3%, 89.7 wt%, 75.1% and 69.8%, respectively, in the presence of the catalysts compared to Exp. 01 (without catalysts and solvent). Hence, Fig. 3a shows that during the Stage I reactions, the use of Pt/

Al_2O_3 in the presence of dodecane solvent, gave the lowest char yield, indicating the superior activity of the catalyst to reduce char formation.

Literature shows that converting bio-oil into hydrocarbons via direct HDO without the use of solvents in the presence of noble catalysts (Ru, Pd, and Pt), led to excessive formation of char [21,23,41]. In the absence of solvents, the highly unstable but active oxygenated compounds in bio-oil easily coverts to coke, even under mild conditions, through an initial formation of large quantities of asphalt-like products [21]. However, the use of solvents during HDO has been reported to help prevent coke formation, causing subsequent deactivation of these noble catalysts. The results from the present work agree with those reported in literature [15,23] showing that the presence of the solvent reduced char formation, through the solubilisation of less polar compounds formed during the upgrading reactions. This apparent *in situ* combination of extraction and dilution process prevented the polymerisation and condensation of char-forming intermediate compounds.

Interestingly, in the presence of solvent and Pd/C (Exp. 05) there was a 29% reduction in gas yields, while the yield of aqueous phase and char yields increased 7.7 times and 2.2 times, respectively compared to Exp. 03 (Pd/C without solvent). Both Exp. 05 and Exp. 06 produced light brown organic liquids (mixtures of biofuel and dodecane), rather than the tarry materials obtained from the corresponding experiments without solvents (Exp. 03 and Exp. 04) *(Supplementary Information Figure SI2)*. Therefore, the combination of these catalysts and solvent, eliminated the formation of tars. Even though the presence of solvent reduced the concentration of IP bio-oil processed, compared to Exp. 02 (with solvent but no catalyst), the reduction in char formation and elimination of tar could be ascribed to the combined effects of the solvent and catalysts.

3.3.2. Compositions of gas products from Stage I

Fig. 3b presents the yields and compositions of gas products obtained after Stage I reactions. Significant gas formation was observed across all Stage I experiments, ranging from 15.3 wt% (Exp 02) to 52.5 wt% (Exp. 07). Indeed, the presence of each of the catalysts gave gas yields of around or greater than 20 wt%, so that Exp. 07 involving the use of Pd/Al_2O_3 gave the highest gas yield. It can be seen from Fig. 3b that the gas products were dominated with CO_2 for the different reactions, indicating that decarboxylation was the main deoxygenation reaction in these Stage I tests. Exp. 02 (with solvent alone) and Exp 07 (with solvent and Pd/Al_2O_3), produced the lowest and highest CO_2 yields, respectively in these tests. Pd-based catalyst are known to promote deoxygenation via decarboxylation [42,43].

In addition, the three experiments with Pd/C, Pt/Al_2O_3 and Ru/Al_2O_3 catalysts (Exp. 04, Exp. 05 and Exp. 08) contained the least amount of hydrogen gas in their gas products (0.0049 g, 0.0055 g and 0.0084 g, respectively). Considering that 10 bar hydrogen gas at room temperature was used in each reaction (i.e. 0.0686 g H_2 gas), these results indicated 87% hydrogen consumption in the presence of these noble metal catalysts in Stage I. In contrast, hydrogen gas contents in the gas products from experiments other experiments indicated lower hydrogen consumption. Indeed, Exp. 01 and Exp. 07 gave the hydrogen contents in the gas products at 0.0375 g (45.3% H_2 consumption) and 0.0341 g (50.3% H_2 consumption), respectively. Fig. 3b also shows that the presence of the catalysts led to appreciable formation of methane gas, whereas this became more pronounced when both catalysts and solvents were present.

Thus, it was possible that the solubilising and fluidising effect of the solvent within the reactor (rather than IP bio-oil remaining stuck at the bottom of the reactor) was important to avoid exotherms (hotspots), enhance molecular diffusions and collisions to cause relevant reactions to occur. Considering that barely any gas was produced from reacting dodecane and the catalysts alone, it could be inferred that methane formation came from demethylation reactions and/or the hydrogenation of CO and CO_2. The presence of CO may indicate partial reduction of CO_2 [44].

For Exp. 08 (using Ru/Al_2O_3), the gas product was dominated by methane and CO_2 as shown in Fig. 3b. Ru-based catalysts are known to catalyse the breaking of C-C bonds in organic molecules or materials and the presence of water can promote such reactions due to the possibility of redox equilibria between Ru^0 and Ru^{IV} or Ru^{II} [45]. In such reactions, water is used as a reactant for the conversion of organic molecules to produce methane, hydrogen, and CO_2 [45]. Indeed, Exp. 08 produced no aqueous phase, supporting the redox mechanism of Ru-based catalysts in the presence of water to produce methane and CO_2.

3.3.3. Compositions of organic liquid products from Stage I

The compositions of the organic compounds (less dodecane) in the liquid products from Stage I reactions are presented in Fig. 3c, following GC/MS analysis (*see Supplementary Information Figure SI3 for example of GC/MS chromatograms*). The results show that the combined use of catalysts and solvent in Stage I led to considerable refining of the organic compounds in the resultant organic liquid products compared to the IP bio-oil feed. Hence, the formation of char, aqueous phase and gas during Stage I led to dramatic reduction in the yield of tars and organic liquid products derived from IP bio-oil.

The organic liquids from Stage I contained some well-defined compounds that could be transformed to biofuels by further upgrading. Fig. 3c shows that after Stage I, some compounds such as sugars, furans aldehydes and aliphatic ethers nearly or completely disappeared. These compounds along with the 'unidentified' accounted for 62.4 wt% of the IP bio-oil. The surviving compounds after Stage I included mainly ketones and phenols, with some carboxylic acids, alcohols and esters. While the disappeared compounds may have formed mostly char and gas products, it could be considered that these compounds may have contributed to the organic liquid products from any Stage I experiment with more than 40 wt% biofuel yields. However, it may also be more useful to incorporate a bio-oil pre-treatment step that would remove the thermally unstable compounds for other applications prior to the upgrading process. For example, sugars may be removed by extraction and converted via fermentation [46]. The experiments without catalysts (Exp. 01 and Exp. 02) produced the lowest yield of stable compounds in Stage I. In contrast, the dark tarry material obtained from experiments without solvent (Exp. 03 and Exp. 04), contained appreciable yields of ketones and phenols. However, large fractions of the tars included unidentified large molecular weight compounds, formed from condensation reactions. These results were corroborated by the degree of deoxygenation presented in Fig. 3d, which reached over 80% in the cases involving catalysts and solvent. Giving that wt% DOD does not account for the yield of organic liquid products, a truer picture of the extent of bio-oil survival after the Stage I experiments is given by the wt % BCR presented in Fig. 3d. Not surprisingly, the wt% BCR mirrored the yields of liquid product derived from bio-oil only, so that Exp. 03, Exp. 05, Exp. 06 and Exp. 08 retained the highest amounts of bio-carbon in the corresponding organic liquid/tar products. Apart from Exp. 03 which produced tarry material, these other high wt% BCR experiments indicate the important role of the solvent to ensure that the upgraded bio-oil components were prevented from being lost as char and gas. The low wt% BCR from Exp. 07 was attributed to carbon loss from the formation of large amounts of gas, especially as CO_2.

The experimental conditions used in Exp. 05, Exp. 06 and Exp. 08, which produced more than 40 wt% liquid biofuel contents in the organic liquid, could therefore be considered as appropriate for Stage I bio-oil upgrading. Hence, Pd/C, Pt/Al_2O_3 and Ru/Al_2O_3 can be regarded as suitable catalysts for bio-oil hydrotreatment (stabilisation) [15,22]. As shown in Fig. 3c, ketones and phenols were the dominant compounds in the organic liquid products, suggesting that ketonization and aromatisation reactions, respectively played key roles in the Stage I in the presence of Pd/C, Pt/Al_2O_3 and Ru/Al_2O_3. In Stage I, appreciable yields of the target liquid hydrocarbon compounds obtained from Exp. 02 (3.29 wt%), Exp. 06 (5.94 wt%) and Exp. 08 (8.03 wt%) (see *Supplementary Information Table SI2* for peak area % for hydrocarbons from
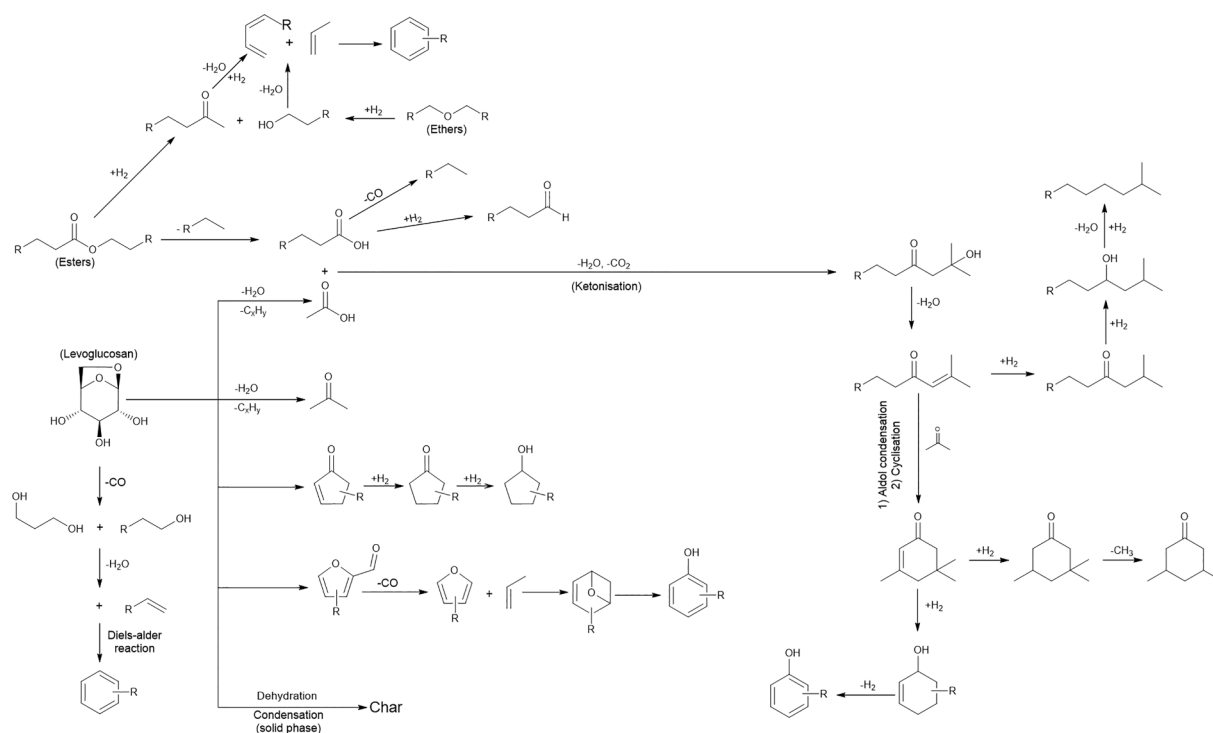
Scheme 1. Plausible main reactions and mechanisms during Stage I IP bio-oil upgrading.

Exp. 06 and Exp. 08).

3.3.4. Plausible Stage I reaction mechanisms

The yields and composition of gas products, along with those of the liquid products (aqueous phase and organic phase) could be used to explain the main deoxygenation mechanisms occurring during the Stage I reactions (Reaction Scheme 1). The liquid biofuel products from Stage I were dominated by ketones and phenols, so that their formation depended on the prevailing reaction mechanisms at this stage. Formation of the target liquid hydrocarbons in Stage II would depend on the further deoxygenation of these classes of compounds (phenols and ketones).

The production of ketones indicated that the main stabilisation reactions were ketonization of carboxylic acids [47–49] and aldol condensation [50–52]. While aldol condensation is known to generate enones, the presence of hydrogen gas may have ensured the saturation of C═C bonds, so that saturated ketones were the dominant compounds in the liquid organic products, along with phenols. Although, phenols were the dominant group of compounds in the initial IP bio-oil, their enhanced presence in the upgraded organic liquid indicated that more phenolic compounds were formed during Stage I.

The formation of phenols would involve a series of aromatisation reactions (Diels-Alder cycloaddition reactions and cyclisation of six-carbon compounds followed by dehydrogenation) [53,54]. Ketonization produces CO_2 and water as co-products, aldol condensation produces water, while combined process of cyclisation and aromatisation can also produce CO_2, CO and hydrogen gas. These mechanisms could therefore explain the dominance of CO_2 and the presence of other gases in Stage I gas products as well as formation of water. The classes of compounds that survived the Stage I upgrading experiment were similar to those reported in literature under similar conditions [15,23]. For example, In their work Xu et al., [15] reported that the peak area % of compounds in organic liquid product from the first stage of their tetralin solvent-assisted bio-oil upgrading experiment at 300 °C were dominated by 28.9% phenols and 28.7% aromatic hydrocarbons with 83% naphthalene (which most probably came from the tetralin hydrogen-donor solvent). In addition, the authors reported the presence of some carboxylic

acids (5.5%), ketones (5.6%) and alcohols (1.6%) in the first stage upgraded oil.

In summary, based on the reaction products, the catalysts and solvent aided the Stage I transformations via; (1) disappearance of sugars, furans, ethers and esters mainly to form char, gas and aqueous phase but other classes of compounds (carboxylic acids and phenols) may have been formed as well; (2) ketonization of carboxylic acids and aldol condensation of carbonyl compounds to produce hydroxy ketones with $C_5 - C_{10}$ carbons. (3) formation of phenols through either aromatisation (dehydrogenation) of cyclic compounds and/or Diels-Alder cycloaddition reactions. Hence, the Stage I organic liquid products obtained in the presence of catalysts and solvent were dominated by ketones and *phenols (Supplementary Information Table SI2).*

3.4. Stage II (hydrodeoxygenation) results

3.4.1. Stage II product distribution and mass balances

Table 5 shows the product distribution after the Stage II upgrading reactions, using the tars (from Exp. 03 and Exp. 04) and organic liquids (from Exp. 02, Exp. 05 - Exp. 08) in Stage I. All Stage II experiments were carried out in the presence of Pt/Al₂O₃ catalysts to make results comparable. Due to the low yield of organic liquid product from Exp. 01 (11 wt%), there was no real incentive to carry out several repeat experiments to generate sufficient feedstock for a Stage II test, as was done for other conditions studied. For instance, it would have taken about 10 repeats of Exp. 01 to generate sufficient organic liquid products for Stage II, whereas Exp. 02 to Exp. 08 only required 2 or 3 repeats. For Stage I experiments involving the use of dodecane, the organic liquid products in Table 5 obtained consisted of both dodecane and compounds originating from IP bio-oil. Therefore, using the same data treatment described in Section 3.3.1, Fig. 4a – 4d were produced on IP bio-oil feed basis. Both Table 5 and Fig. 4a show excellent mass balance closures, indicating the accuracy of the experimental work. Fig. 4a shows that Exp. 10 and Exp. 11, which were based on the tar products the corresponding experiments (Exp. 03 and Exp. 04) produced even more viscous tars.

The lowest yield of liquid biofuel was obtained from Exp. 09, which

Table 5
Product yields from Stage II upgrading of tars/organic liquid products from Stage I in the presence of Pt/Al$_2$O$_3$ catalyst.

Exp. #	Feedstock	Product yields (wt%)					
		Tar	[a] Organic liquid	Aqueous liquid	Solid	Gas	Total
9	Organic liquid product from Exp. 02	–	93.4 ± 0.15	1.26 ± 0.43	3.89 ± 0.05	1.05 ± 0.00	99.6
10	Tar product from Exp. 03	47.8 ± 0.78	–	1.89 ± 0.68	35.1 ± 0.91	4.08 ± 0.04	98.9
11	Tar product from Exp. 04	68.1 ± 0.09	–	1.24 ± 0.01	26.6 ± 1.42	3.39 ± 0.37	99.3
12	Organic liquid product from Exp. 05	–	95.2 ± 0.13	1.61 ± 0.02	0.28 ± 0.41	2.72 ± 0.27	99.8
13	Organic liquid product from Exp. 06	–	96.4 ± 1.18	0.00 ± 0.01	1.12 ± 0.63	2.58 ± 0.08	100
14	Organic liquid product from Exp. 07	–	96.8 ± 1.10	0.00 ± 0.01	2.8 0 ± 0.81	0.20 ± 0.01	99.6
15	Organic liquid product from Exp. 08	–	90.6 ± 0.07	1.24 ± 0.76	1.20 ± 0.12	6.4 ± 1.50	99.4

a = monophasic organic liquid containing dodecane and biofuel (upgraded bio-oil) after Stage II.

was based on Exp. 02 (with solvent and no catalyst), with 9.2 wt% on IP bio-oil feed basis. In contrast, Exp. 12 produced the highest yield of liquid biofuel in Stage II after the Stage I stabilisation using Pd/C in the presence of dodecane. The second highest liquid biofuel yield came from Exp. 13, which involved the use of Pt/Al$_2$O$_3$ during the Stage I stabilisation. The general trend indicated that the Stage I stabilisation reactions were the most important determinants of the final yields of products in Stage II, particularly, the yields of liquid biofuel and char. This showed the combined influence of the catalysts, the solvent and the moderate processing temperature of up to 300 °C, compared to up to 400 °C commonly used in literature [15]. For instance, although stabilisation with Pd/C without solvent (Exp. 03) produced a large yield of tar in Stage I, the HDO reaction in Stage II led to extensive formation of char (19.1 wt%, on IP bio-oil basis). This indicated a 35.1% conversion of the Stage I tar product to char, with 47.8 wt% remaining as tar after Stage II.

In contrast to the Pd/C, the tar product from Exp. 04 with Pt/Al$_2$O$_3$ catalyst, was converted to 26.8 wt% of char and 68.1 wt% of tar in Stage II. These yields corresponded to 10.7 wt% char and 27.3 wt% tar from the initial IP bio-oil, respectively. Hence, both Pd/C and Pt/Al$_2$O$_3$ produced similar yields (26 wt% and 27.3 wt%) of tar in the absence of solvent after Stage II. However, based on the nature of the tars, they could not be regarded as attractive energy products. Most Stage I reactions produced significant yields of gas products, such that at Stage II only minimal gas products were formed. The maximum gas yield (12. 5 wt%) occurred in Exp. 15 from the organic liquid obtained in the presence of Ru/Al$_2$O$_3$ in Stage I. The lowest gas yield (0.20 wt%) was formed in Exp. 14 from the organic liquid obtained from Stage I in the presence of Pd/Al$_2$O$_3$. Recall that the Stage I reaction with of Pd/Al$_2$O$_3$ produced the highest gas yield among all the experiments in that stage. Hence, gas formation became seemingly limited at Stage II for Exp. 14, possibly due to absence of gas-forming compounds.

3.4.2. Compositions of gas products from Stage II

The compositions of gas products from Stage II of IP bio-oil upgrading are presented in Fig. 4b. The dominant gases were methane, CO$_2$, hydrogen and CO. Decarboxylation and decarbonylation have been reported as dominant reactions during catalytic bio-oil upgrading, and these reactions produce CO$_2$ and CO, respectively. For example, Boscagli et al., [55], reported that the gas products from the catalytic upgrading of bio-oil derived from beech wood, were dominated by CO$_2$, methane and CO. The formation of methane was attributed to methanation of CO$_2$/CO in the presence of Ni-Cu/Al$_2$O$_3$ and Ru/C catalysts. In addition, methane could also be produced from the hydrogenolytic demethylation of some compounds in the tars/organic liquids from Stage I.

The highest content of hydrogen in the gas products from Stage II experiments were obtained in Exp. 10 and Exp. 11, which corresponded to experiments with the tarry materials from Exp. 03 and Exp. 04, showing poor hydrogenation of these products. The formation of hydrogen gas in Exp. 10 and Exp. 11 was possible during char formation (dehydrogenation) or through water–gas shift reaction. However, the

large partial pressure of added hydrogen gas would not favour water–gas shift reaction (limited by equilibrium). Therefore, it would be plausible to think that most hydrogen gas formation occurred via dehydrogenation to during the formation of coal tar-like products obtained in the absence of solvents. As reported by Wildschut [21], the combination of dehydrogenation, cyclisation, aromatisation and condensation of the resultant aromatic compounds would lead to char formation.

3.4.3. Compositions of tars and organic liquid products from Stage II

Fig. 4c shows the compositions of tars (Exp. 10 and Exp. 11) and liquid biofuels (Exp. 09; Exp. 12 to Exp. 15) obtained from the Stage II upgrading reactions. Where dodecane had been used in the upgrading reactions, its content in the organic liquid products was determined using Table 3 and eliminated to obtain the corresponding data from Fig. 4c. Apart from Exp. 10 and Exp. 11, most of the compounds in the liquid biofuel compounds were identified by GC/MS (*see Supplementary Information Figure SI3 for example of GC/MS chromatogram*). So, these two experiments carried out without solvents in the presence of Pd/C and Pt/Al$_2$O$_3$, respectively produced dark tarry liquid products in Stage I, and the nature of the products did not change much in Stage II. However, they both smelt strongly like coal tar and the identified compounds were mostly aromatic hydrocarbons and alcohols. Appreciable amounts of these tars (7.57 wt% and 15.0 wt%, respectively) were unidentified by the GC/MS NIST Library used in this work.

All other experiments gave organic liquid products in Stage II with high contents of aliphatic hydrocarbons derived from IP bio-oil as shown in Fig. 4c (*see also Supplementary Table SI3*). Exp. 12 and Exp. 13, which were based on Stage I liquid products obtained from the use dodecane (solvent) with Pd/C and Pt/Al$_2$O$_3$, respectively, produced the highest yields of hydrocarbons by far. These were followed by Exp. 15, which was based on Stage I liquid product made with Ru/Al$_2$O$_3$ in the presence of dodecane. Therefore, the combined used of the solvent and these catalysts (Pd/C, Pt/Al$_2$O$_3$ and Ru/Al$_2$O$_3$), promoted the extensive deoxygenation of the Stage I liquids, to produce high yields of liquid hydrocarbons in Stage II. The dominant hydrocarbons in the Stage II organic liquid products included alkylated pentanes, hexanes, cyclopentanes, cyclohexanes and C$_{14}$ – C$_{21}$ n-alkanes). Interestingly, some aromatic compounds (toluene, ethylbenzene, propyl benzene, naphthalene, methyl naphthalene and retene) were present but at much lower yields compared to the aliphatic hydrocarbons. The aromatics were the main unsaturated hydrocarbons in the Stage II liquid products; with just one alkene identified from Exp. 12 and Exp. 13 organic liquid product (*Supplementary Information Table SI3*).

Large molecular weight hydrocarbons, aldehydes and ketones were also found in some of the biofuels (*Supplementary Information Table SI3*). These include cholestane, retene, methyl dehydroabietate and phenanthrenecarboxaldehyde. These large structures appeared to have similar carbon framework related to diterpenoid resins found in biomass, and their presence may indicate the different levels of transformations that occurred during the thermal upgrading reactions. For instance, retene has been reported in the emissions from combustion of soft woods as
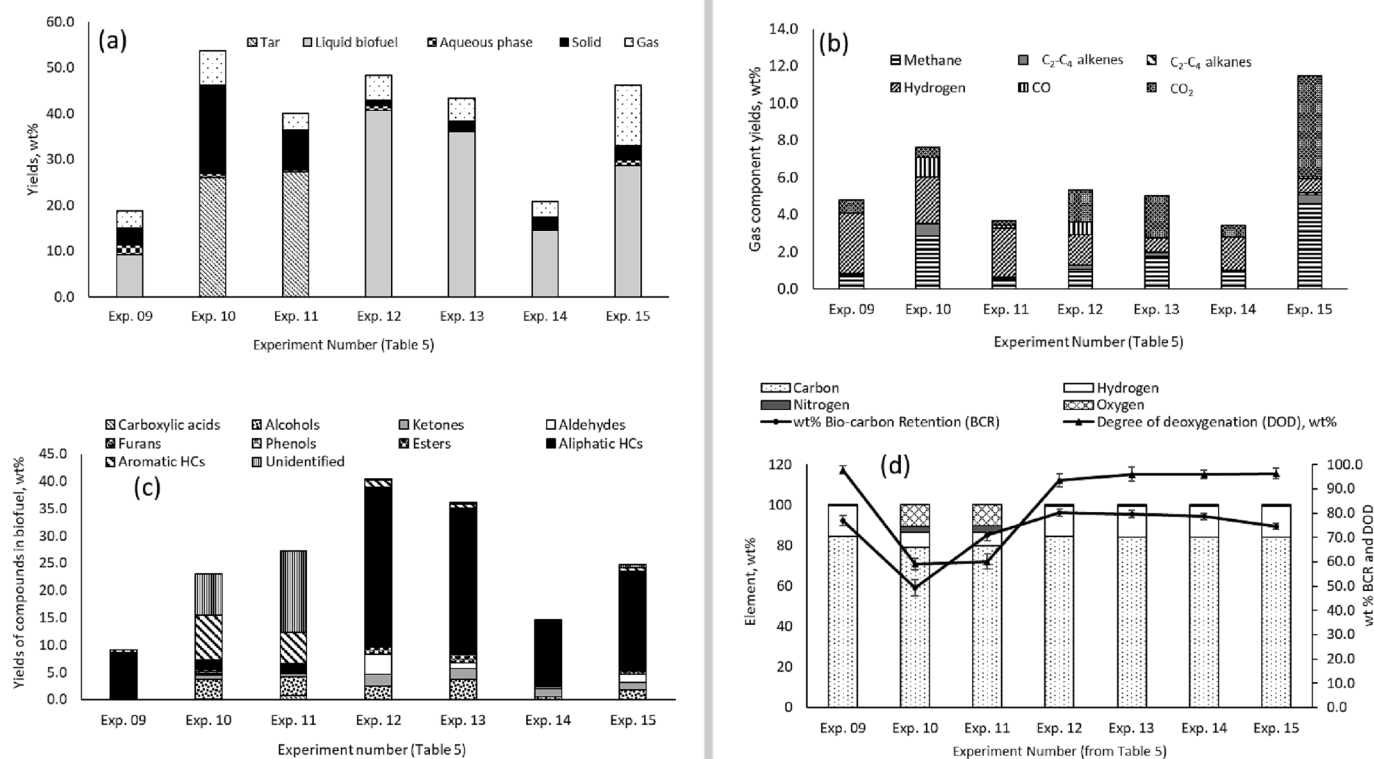
Fig. 4. Results from Stage II upgrading experiments on bio-oil feed basis; (a) product yields, (b) compositions of gas products, and (c) compositions of tars and organic liquid products; (d) elemental compositions and degree of deoxygenation of organic liquid/tar products.

residential solid fuel [56]. Their presence in the organic liquid products rather than in the char or forming char may be attributed to the solubilising effect of the dodecane solvent. However, these large compounds could also be formed from the cyclisation of the large, branched chain hydrocarbons produced during the reactions.

The presence of simple oxygenates (e.g., residual alcohols, esters and ketones) was observed but these may be beneficial during fuel combustion, providing internal oxygen to improve combustion and lower harmful emissions [57]. Alternatively, an additional hydrotreatment may be incorporated to achieve complete deoxygenation or minimal oxygen content. A study on the combustion and emission characteristics of a fuel blend prepared with 10 vol% of the organic liquid obtained from using of Pt/Al_2O_3 in both stages, has been recently published [58]. The test carried out by blending the upgraded fuel with commercial diesel in a conventional diesel engine, with results showing comparable and improved performance compared to diesel and kerosene [58].

Fig. 4d shows that the degree of deoxygenation of the bio-oil component of the feed. For the experiments involving the combination of solvents and/or catalysts, the degree of deoxygenation ranged from 93 wt% to 97.6 wt%. In contrast, the tars from Exp. 10 and Exp. 11 still contained significant amount of oxygen with similar degree of deoxygenation of around 60 wt%. Again, the careful combination of catalyst, solvents and reaction conditions has led to almost complete deoxygenation of the bio-oil with the production of hydrocarbon-rich biofuel contents in the organic liquid products. In addition, Fig. 4d also shows that apart from Exp. 10, all the Stage II reactions led to high wt% BCR in the final liquid/tar products. As for Exp. 10, the low wt% BCR in the Stage II resulting tar may be attributed to its high yield of solid and gas products (especially methane) products as observed in Fig. 4a and Fig. 4b, respectively. The formation of other carbon-containing products apart from oil/tar clearly represented carbon loss and therefore low wt% BCR. Hence, comparing Exp 10 and Exp. 11, results showed that Pd/C

promoted more char formation that Pt/Al_2O_3 in the absence of solvent. All other Stage II experiments gave BCR of between 71 wt% and 80 wt%, showing that much of the bio-carbon that survived the Stage I experiments were retained in the Stage II organic liquid products, indicating the success of the Stage I stabilisation step.

3.4.4. Plausible Stage II reaction mechanisms

Stage II reactions appeared to be much simpler so that once the rather more stable compounds (mainly ketones and phenols) had been formed and retained in Stage I, the yields and compositions of the final organic liquid products depended on their conversion. The dominance of naphthenes in the Stage II organic liquid products pointed to evidence of hydrogenation of aromatic rings and cyclodeoxygenation of aliphatic compounds (Reaction Scheme 2). Apart from five-membered and six-membered naphthenes in the Stage II organic liquid products, several compounds with chain lengths ranging from C_{14} - C_{21} were also identified. Interestingly, these longer-chain compounds were either missing or observed at low concentrations in the Stage I organic liquid products. While using tetralin as solvent during catalytic HDO of bio-oil, Xu et al., [15] reported the formation of $C_{11} – C_{27}$ alkanes and suggested that their formation could be from the solvent and the oxygenated compounds in the oil. Hence, their formation during Stage II reactions could be attributed to the continuation of aldol-condensation of the predominant ketones. Therefore, the resulting formation of hydrocarbons such as butyl cyclohexane, octyl cyclohexane and $C_{13} – C_{21}$ n-alkanes appeared to be from the combination of the carbon-chain elongating aldol condensation, followed by hydrodeoxygenation [49,59]. These deoxygenation reactions would remove oxygen mainly as water, and to some extent, CO and CO_2. In addition, the conversion of alcohols (from aldol condensation) and phenols via hydrogenolysis-type hydro-dehydroxylation seemed to have occurred.

In their two-stage mild and deep HDO of bio-oil, [60] used Ru/C
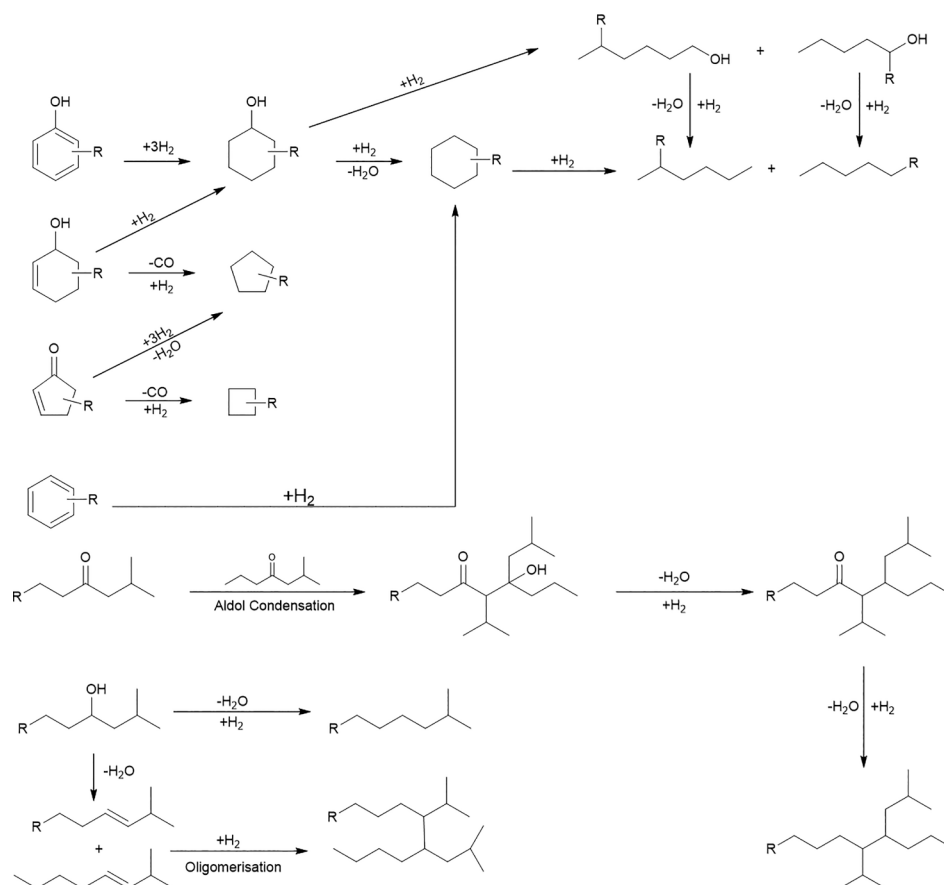
Scheme 2. Plausible main reactions and mechanisms during Stage II IP bio-oil upgrading.

catalyst to achieve up to 90 wt% deoxygenation with up to 60 wt% yield of oil composed mainly of aromatic hydrocarbons, alkanes and phenols. At the end of the second stage at 350 °C, the authors reported between 5 wt% and 11 wt% of oxygen remaining in the upgraded oils, without the use of solvents. Unlike in this present work, the authors reported a selected composition of the final oil products in peak area% with 6.39% alkanes, 3.79% phenols, 0.9% alkylbenzenes and naphthalenes [60]. In addition, Xu et al [15] used as two-stage solvent-assisted method to achieve up to 94 wt% deoxygenation as the oxygen content of the upgraded organic liquid fell to only 0.5 wt%, which they attributed to the combined effects of Ru/C and the tetralin solvent. The reactions were carried out at 300 °C and 100 bar hydrogen for 3 h for the first stage, while the second stage was carried out in a continuous fixed bed reactor at 400 °C using 130 bar hydrogen [15]. Compositional analysis of the final upgraded oil obtained from the use of tetralin showed that compounds apparently formed from the solvent accounted for 55% of oil components (on peak area % basis) [15].

In this present study, similarly high degree of deoxygenation has been obtained but at milder conditions, especially at the second stage. This has been achieved by using mild reaction conditions of temperatures (between 160 °C and 300 °C) and only 10 bar hydrogen with the advantage of keeping the solvent stable. The experimental design used in this work and stability of the solvent has made it possible to estimate the fraction of upgraded bio-oil in the organic liquid products.

In summary, further deoxygenation in Stage II seemed to involve the following reactions: (1) aldol condensation of ketones to form compounds with even longer carbon chains of up to 21 carbon atoms; (2) deoxygenation of aldol compounds and phenols via hydrogenation and hydrogenolysis-type hydro-dehydroxylation to form hydrocarbons and water; and (3) final hydrogenation of aromatic rings to saturated hydrocarbons and naphthenes. The Stage II upgraded biofuels contained

mainly alkylated pentanes and cyclopentanes, alkylated hexanes and cyclohexanes, and well as $C_{10} - C_{21}$ n-alkanes (*Supplementary Information Table SI3*).

3.5. Cumulative yields of products

As stated earlier, the results of dodecane thermal stability tests showed that the liquid biofuel contents of the organic liquid products could be estimated using dodecane data in Table 3. In addition, it could be assumed that the char, aqueous phase (water) and gas products originated almost entirely from the IP bio-oil. To support this assumption, Equation 10 was used to obtain the cumulative yields of char, aqueous phase and gas products from the corresponding Stage I and Stage II experiments and presented in Fig. 5a. Along with the yields of liquid biofuel, Fig. 5 shows excellent mass balance closures, which indicated the validity of the assumption.

From Fig. 5, Exp. 02 and Exp. 09 produced the highest cumulative yield of solid residue (char) of 53.6 wt%. Therefore, over the two upgrading stages, the yields of products were similar to those obtained in the Stage I Exp. 01 (11 wt% tar and 51.2 wt% char). However, the solvent prevented the formation of tarry materials or solubilised them, so that organic liquid products were obtained in Exp. 02 and the corresponding Exp. 09. All the other experiments that involved the use of catalysts, solvent or their combinations in Stage I reactions, gave different cumulative yields of products over the two stages. In general, the presence of solvent and catalysts gave organic liquid products with colours ranging from light brown (Stage I) to light yellow (Stage II) *(Supplementary Information Figure SI2)*. Without the solvent, corresponding experiments, Exp. 03/Exp. 10 and Exp. 04/Exp.11, produced higher cumulative char yields over the two stages, with 21.1 wt% and 19.8 wt%, respectively than their counterpart experiments that involved
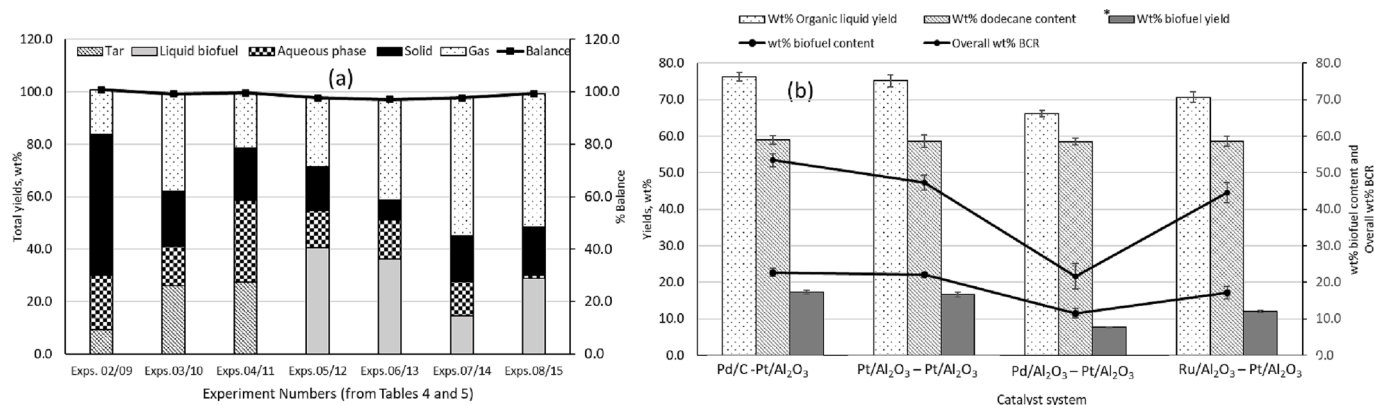
Fig. 5. Cumulative yields; (a) products from Stage I and Stage II upgrading experiments on IP bio-oil feed basis; (b) compositional yields and biofuel contents of final organic liquid products involving catalysts and solvent (* calculated using data in Table 2).

both the solvent and catalysts in Stage I (Exp. 05/Exp. 12 and Exp. 06/Exp. 13). These were followed by the experiment in which Ru/Al$_2$O$_3$ was used in Stage I, so that the cumulative yield of char across Exp. 08/Exp. 15 was 17.8 wt% on IP bio-oil basis.

Again, these results showed that the overall yields of products depended heavily on the Stage I product distributions as well as the compositions of the tars or organic liquids. For instance, with Pd/Al$_2$O$_3$, IP bio-oil was converted to give the highest gas yields in Stage I (Exp. 07), thereby reducing the biofuel contents of the organic liquid processed in Stage II (Exp. 14). Therefore, among the solvent-assisted reactions, the use of Pd/Al$_2$O$_3$ in Stage I gave the overall lowest yield of liquid biofuel and highest gas yield over the two upgrading stages. In contrast, while Ru/Al$_2$O$_3$ produced the second highest biofuel yield (48.3 wt%) in Stage I, after Stage II, the biofuel yield reduced to 28.7 wt %, a decrease of nearly 41% due to increased gas formation from the compounds in the Stage I organic liquid product. Comparatively, the highest yields of liquid biofuels were obtained from Stage I experiments that involved Pd/C and Pt/Al$_2$O$_3$ in the presence of solvent, so that across the two stages, on the basis of the initial IP bio-oil feed, 40.6 wt% and 36.2 wt% of liquid biofuels were obtained, respectively. Therefore, compared to the Ru/Al$_2$O$_3$ – Pt/Al$_2$O$_3$ system (Exps. 08/15), the Pd/C – Pt/Al$_2$O$_3$ (Exps. 05/12) and Pt/Al$_2$O$_3$ – Pt/Al$_2$O$_3$ (Exps. 06/13) systems, led to much less reduction in biofuel yields of 27.8% and 26.0%, respectively.

Such results supported the fact that the combination of Pd/C or Pt/Al$_2$O$_3$ and dodecane in Stage I caused significant hydro-stabilisation of the IP boil-oil, thereby minimising mass losses during the processing of obtained organic liquids in their respective Stage II reactions. In addition, Fig. 4c shows that across the two stages, the use of the two catalyst systems (Pd/C – Pt/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ – Pt/Al$_2$O$_3$) produced 29.3 wt% and 26.8 wt% of liquid hydrocarbons on IP bio-oil basis, respectively.

These results are among the highest ever reported in literature from bio-oil upgrading, providing a good basis for further research towards large-scale industrial application. With its high carbon content (62 wt%) and relatively low oxygen (26 wt%) content compared to raw biomass and fast pyrolysis bio-oils, these results showed that IP bio-oils are highly suitable for upgrading to give high yields of hydrocarbons. Typically, IP bio-oils have about half the oxygen contents of fast pyrolysis bio-oils (up to 50 wt%), mainly due to operational differences of the pyrolysis reactors (especially, solid and vapour residence times, which influence secondary reactions) [5,9–12]. Therefore, in theory, complete deoxygenation of IP bio-oils would produce about twice as much hydrocarbon yields compared to fast pyrolysis oils. This means that to produce the same quantity of hydrocarbon fuels, fast pyrolysis bio-oils would require higher feedstock throughputs, larger-sized equipment and potentially higher processing costs than would IP bio-oils.

The percentage by mass of the liquid biofuel contained in each final organic liquid product was calculated using Equation 7. These results are presented in Fig. 5b for the four sets of experiments that involved catalysts and dodecane. These were the experiments that gave well over 60 wt% clear organic liquid products and therefore certainly contained product derived from the bio-oil (dodecane was 60 wt% of feedstock). Fig. 5b therefore shows that 22.1 wt% and 22.7 wt% of cumulative biofuel contents were obtained from the Pd/C - Pt/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ - Pt/Al$_2$O$_3$ catalytic systems, respectively. This was followed by Ru/Al$_2$O$_3$ - Pt/Al$_2$O$_3$ system, which gave 17.2 wt% biofuel content in the final organic liquid product. The lowest biofuel yield was obtained with the Pd/Al$_2$O$_3$ – Pt/Al$_2$O$_3$ system (11.6 wt%), across the two stages, mainly due to the high conversion to gas observed in Stage I with Pd/Al$_2$O$_3$. Fig. 5b also shows that overall wt% BCR for all these four combinations of experiments. Clearly, the experiment with Pd/C- Pt/Al$_2$O$_3$ catalyst system gave the highest overall bio-carbon retention capacity (53.4 wt %), closely followed by Pt/ l$_2$O$_3$ – Pt Al$_2$O$_3$ (47.3 wt%) and Ru/Al$_2$O$_3$ – Pt/Al$_2$O$_3$ (44.6 wt%) catalyst systems over the two stages of bio-oil upgrading. The Pd/ Al$_2$O$_3$ – Pt/ Al$_2$O$_3$ catalyst system produced the lowest wt% BCR due to its first Stage I massive carbon loss through mainly gas (CO$_2$) formation. The overall wt% BCR also mirrored that cumulative wt% biofuel contents of the organic liquid products in Fig. 5b.

3.6. Characterisation of used catalysts

The used catalysts from the Stage I and the Pt/Al$_2$O$_3$ used in Stage II reactions were characterised and presented in Table 2 for comparison with the fresh catalysts. Apart from Pd/C, the used catalysts were characterised before and after recalcination and the results presented in Table 6. The recalcination was carried out at 600 °C for 2 h in a muffle furnace. Due to using carbon support, calcination of the used Pd/C would lead to carbon burn-off, leaving behind the metal and metal oxides [28]. Hence, giving the large amount of char formed in Stage I experiments, it appeared that Pd/C would not be suitable for easy regeneration and reuse, even though its use in the presence of dodecane resulted in both the highest yields of liquid biofuel and yield of hydrocarbons. Abdullah et al. [25] alluded to this fact, leading the authors to focus on metal catalysts with supports such as alumina, silica and other metal oxides that were suitable for thermal regeneration.

Table 6 shows that the properties of the catalysts used in Stage I changed dramatically after the experiments. However, recalcination of the alumina-supported spent catalysts restored their properties to similar values as the fresh catalysts (Table 2). Fig. 6 shows the XRD pattern of the used and recalcined (except Pd/C) catalysts, which corroborates the data presented in Table 6. For the Pd/C, which was not suitable for calcination, the used catalyst was reduced post-reaction and

Table 6
Some properties of spent (recalcined and/or reduced) catalysts.

|	Bulk density (kg/m³)	BET surface area (m²/g)	Pore diameter (nm)	Pore volume (cm³/g)
Pd/C uncalcined S1	523	102	1.91	0.37
Pd/C uncalcined, reduced SI	452	196	1.92	0.43
Pd/Al$_2$O$_3$ recalcined S1	548	18.9	6.08	0.33
Pd/Al$_2$O$_3$ recalcined, reduced S1	563	146	13.0	0.61
Pt/Al$_2$O$_3$ recalcined S1	712	27.8	5.87	0.36
Pt/Al$_2$O$_3$ recalcined, reduced S1	716	180	8.86	0.69
Ru/Al$_2$O$_3$ recalcined S1	607	25.4	6.62	0.41
Ru/Al$_2$O$_3$ recalcined, reduced S1	612	167	9.03	0.82
Pt/Al$_2$O$_3$ recalcined S2	718	175	7.14	0.68
Pt/Al$_2$O$_3$ recalcined, reduced S2	720	181	8.89	0.70

S1 = Stage I and S2 = stage II.

the XRD patterns compared well with the unreduced catalyst.

In Fig. 6, the peaks for the various phases found in each catalyst are shown. The peaks were assigned based on the International Centre for Diffraction Data's (ICDD) Powder Diffraction File-2 2012 (PDF-2 2012) and Inorganic Crystal Structure databases ICSD. In addition, the recalcined catalysts were also reduced under hydrogen as previously described and their XRD patterns shown in Fig. 6. Among the Stage I catalysts, only Ru/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ showed significant presence of oxidised species (RuO$_2$ and PdO, respectively). The existence of PdO from Pd/Al$_2$O$_3$ indicates that the reduced Pd was more easily oxidised than in Pd/C, which may explain why substantial gas formation was observed from Stage I reaction with Pd/Al$_2$O$_3$ due to redox catalysis. Similar redox catalysis has been reported for Ru/Al$_2$O$_3$, which also led to increased gas formation [45]. Further research would be needed to confirm this hypothesis. However, the peaks corresponding to these oxidised species disappeared following reduction under hydrogen, so that the recalcined reduced catalyst exhibited similar XRD patterns to the fresh catalysts (please see Section 3.8 for Pt/Al$_2$O$_3$).

3.7. Catalytic stability tests for Pt/Al$_2$O$_3$ catalyst

As shown from the results so far, the final yields and compositions of upgraded biofuel depended on the products from Stage I reactions. The two catalysts that gave the lowest char yields during Stage I were Pd/C and Pt/Al$_2$O$_3$. The Stage I reactions involving Pd/C produced the highest yield of liquid biofuel, but this was because, among the experiments with solvent and catalyst, it contained the highest yield of carboxylic acids and the lowest yield of hydrocarbons (*Supplementary Information Table SI2*). Moreover, the challenge of thermally regenerating carbon-supported catalysts has been highlighted by many researchers [25,48]. Therefore, in terms of progress of reaction towards the deoxygenation target and ease of catalyst recovery, regeneration and reuse, the Pt/Al$_2$O$_3$ catalyst, which gave the second highest yield of upgraded biofuel across the two stages, was considered a more suitable catalyst than Pd/C.

Three cycles of experiments were carried out with the same Pt/Al$_2$O$_3$ catalyst for Stage I IP bio-oil upgrading. In the procedure, the used catalyst from each cycle was recovered as part of solid residue, which was then dried in an oven at 110 °C for 2 h and, then recalcined and
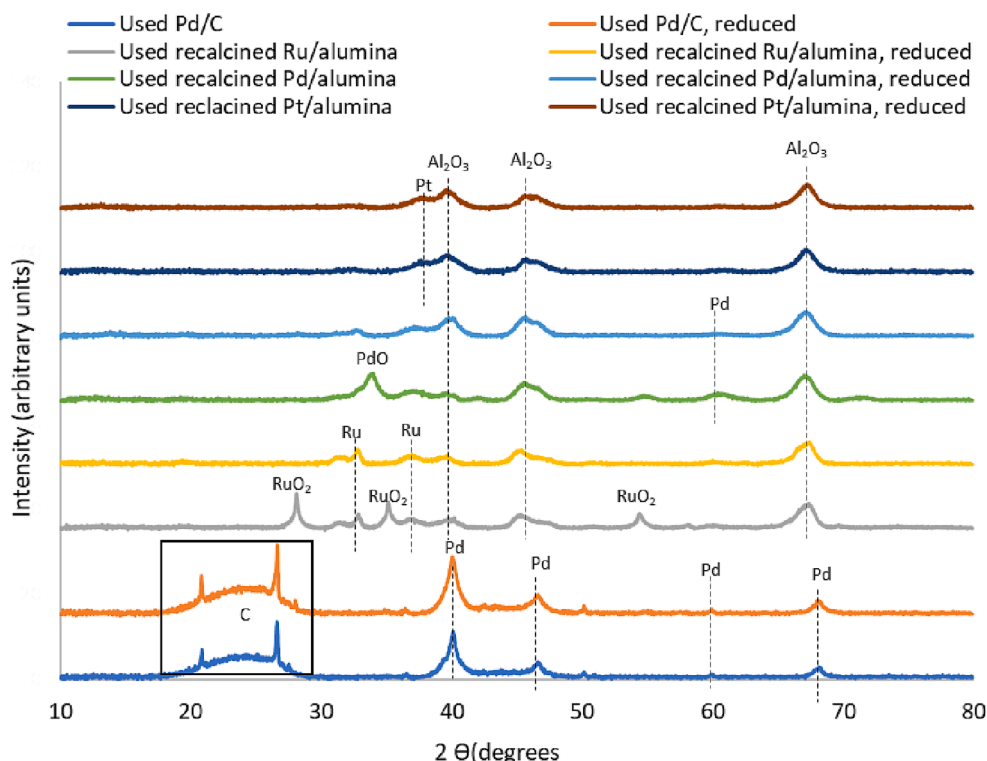
Fig. 6. XRD patterns of the used recalcined catalysts from Stage I reactions before and after reduction (only reduction for Pd/C).
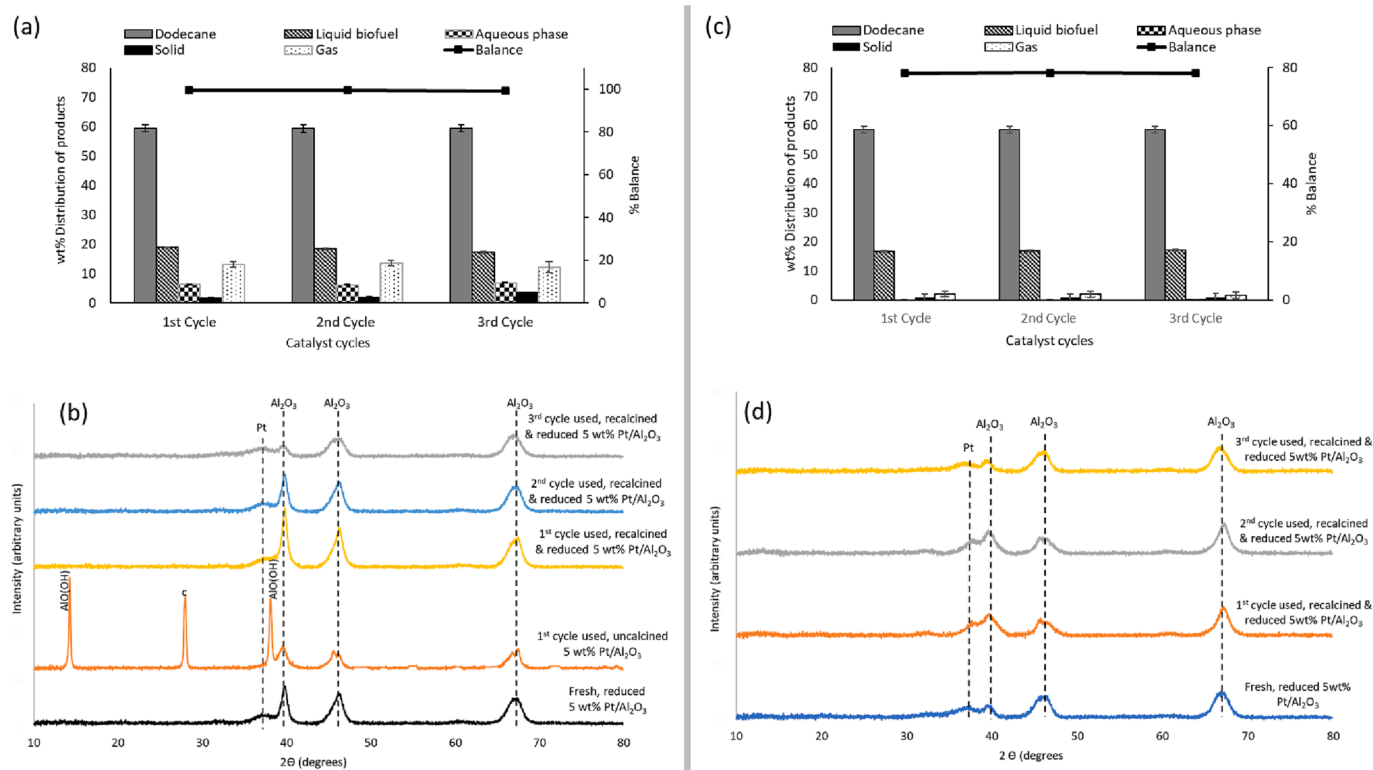
Fig. 7. Results from Pt/Al$_2$O$_3$ catalyst stability and activity tests over three cycles; (a) yields of upgrading products from Stage I; (b) XRD patterns of fresh and used Pt/Al$_2$O$_3$ catalyst during Stage I; (c) yields of upgrading products from Stage II; and (d) XRD patterns of fresh and used Pt/Al$_2$O$_3$ catalyst during Stage II.

reduced before subsequent use. The recalcination procedure also served to burn-off char products. Fig. 7a shows that the yields of products from these experiments remained fairly similar over the first two cycles but char formation increased at the third cycle. In addition, the organic liquid product from the third cycle became slightly darker than those obtained from first two cycles.

These observations seemed to indicate loss of catalytic activity. To check this, the XRD pattern of the used Pt/Al$_2$O$_3$ catalyst from the three cycles were compared with that of the fresh catalyst and the results provided in Fig. 7b. Before recalcination, Fig. 7b shows that the XRD pattern of the catalyst changed, mainly due to the conversion of Al$_2$O$_3$ to boehmite (AlO(OH)), with peaks at $2\theta = 14.4°$ and $38.5°$. The transformation of alumina to boehmite (Al$_2$O$_3$ + H$_2$O → 2AlO(OH)) under hydrothermal conditions below 350 °C is well documented in literature [61,62]. In this present study, the considerable amount of water was formed during the Stage I reactions would provide hydrothermal conditions for the observed transformation of alumina to boehmite. The sharp AlO(OH) signal at $2\theta = 38.5°$, would have masked the weak signal of the Pt phase ($2\theta = 35° – 38°$) observed in the fresh catalyst. Also, Fig. 7b shows evidence of the presence of graphitic carbon ($2\theta = 28.1°$), from the formed char. Recalcination of the use catalyst (at 600 °C, for 2 h), led to the complete loss of the AlO(OH) and carbon signals due to thermal decomposition of the AlO(OH) to the gamma-Al$_2$O$_3$ phase ($2\theta = 39.4°$, $46.2°$ and $67.3°$) and char burn-off. Hence, coke formation on the catalyst surface and hydrolysis of the alumina could be regarded as the main deactivation mechanisms of the Pt/Al$_2$O$_3$ during Stage I reactions but the catalyst was effectively regenerated by recalcination over the three cycles tested.

Furthermore, activity and stability of the Pt/Al$_2$O$_3$ catalyst was tested over another three cycles for the Stage II reactions using organic liquid samples produced with fresh Pt/Al$_2$O$_3$ catalyst in Stage I. When Pt/Al$_2$O$_3$ was used in Stage I upgrading reaction, an average of 78.3 wt% organic liquid products (dodecane + upgraded bio-oil) was obtained as shown in Table 5. During the Stage II catalytic stability tests, the yields

of organic liquids were 96.4 wt%, 96.6 wt% and 96.9 wt% consecutively over the three cycles, showing consistent results.

Hence, over the two stages, the organic liquid yields were calculated by multiplying yield at Stage I (78.3 wt%) by each of the yields at Stage II to give 75.5 wt%, 75.6 wt% and 75.9 wt%. Hence, the balance of 2.81 wt%, 2.73 wt% and 2.40 wt%, accounted for the char and gas products, as no water was formed. Fig. 7c shows that the catalyst remained active over the three cycles, giving identical product distribution and the organic liquid product appeared to be of the same in colour. Furthermore, Fig. 7d shows that the XRD patterns of the used catalyst were essentially the same with the fresh catalyst over the three cycles. No boehmite and carbon peaks were observed in the used catalysts before recalcination. Recall that the presence of water (hydrolysis) and carbon (poisoning) was considered the main deactivation mechanisms during Stage I. However, only tiny amounts of water and char were formed in the Stage II reactions with Pt/Al$_2$O$_3$, which can be attributed to the observed stability and activity of the Pt/Al$_2$O$_3$ over the three cycles.

4. Conclusions

The use of moderately low-pressure hydrogen gas (10 bar) during a solvent-assisted two-stage catalytic hydrotreatment (stabilisation) and hydrodeoxygenation of sample of intermediate pyrolysis bio-oil has been successfully carried out in this present study. Four supported noble metal catalysts were used in Stage I of the upgrading process, during which Pd/C and Pt/Al$_2$O$_3$ produced the highest biofuel contents, followed by Ru/Al$_2$O$_3$ while Pd/Al$_2$O$_3$ lead to highest gas formation during this stage. During Stage II, Pt/Al$_2$O$_3$ was used for hydrodeoxygenation. Results showed that the use of solvent (dodecane) and the noble metal catalysts were necessary to prevent char formation, thereby promoting reactions leading to high yields of hydrocarbon-rich organic liquid products. This present work showed that the solvent-assisted bio-oil upgrading produced up to 22.7 wt% of upgraded biofuel with more than 70% of hydrocarbons in the resulting organic liquid product across the

two stages. The overall degree of deoxygenation (up to 97.6 wt%) and bio-carbon retention capacity (up to 53.4 wt%) of the two-stage process depended heavily on the outcome of the Stage I hydro-stabilisation reactions, which altered the compositions of the bio-oil by producing ketones and phenols.

In Stage II, more than 90 wt% of the organic liquid feed was recovered as liquid products, with little or no water formation, indicating the effectiveness of stabilising the bio-oil components in the Stage I organic liquid products. A dramatic production of n-alkanes and cycloalkanes within the $C_6 - C_{10}$ range as well as longer chain n-alkanes and cycloalkanes with up to C_8 side chains was observed in the Stage II organic liquid products. The combined results showed that ketonization, aldol-condensation and some hydrogen-promoted deoxygenation reactions were dominant mechanisms in Stage I to form the observed products. The continuation of aldol-condensation was evident during Stage II, and this was followed by hydrodeoxygenation. The order of catalytic activity towards eventual deoxygenation and high yields of biofuel in Stage I were observed Pt/Al$_2$O$_3$ >/Pd/C > Ru/Al$_2$O$_3$ > Pd/Al$_2$O$_3$. Thus, Pt/Al$_2$O$_3$ was considered the best overall catalyst over the two stages. Catalytic stability tests were carried out with the Pt/Al$_2$O$_3$ over three cycles at both stages with different results. Deactivation of the catalyst in Stage I occurred after the second cycle due to hydrolysis of alumina and coke formation, whereas the catalyst remained stable after three cycles in Stage II. Across the two stages, results showed that the use of organic solvents/carrier avoided the formation of exotherms that characterise hydrogenation of chemically-bonded oxygen atoms in bio-oils, that often lead to hotspots and subsequent char/coke formation, especially at higher temperatures. Further work is being planned on techno-economic analysis, life cycle analysis and process development to determine the potential viability of this upgrading process.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

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