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Multi-scale characterisation of chars mineral species for tar cracking

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HIGHLIGHTS

- Multi-scale characterisation of mineral species of chars was performed.
- Original data on mineral species within chars were provided by Raman spectroscopy.
- Multi-scale techniques complementarity provided a precise description of minerals.
- Amount, speciation and availability of minerals influence the catalytic activity.

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ABSTRACT

Syngas from thermochemical conversion of waste or biomass is a renewable energy carrier that may contain pollutants – such as tar – that should be removed before further syngas utilisation. Chars have proved to be promising catalysts for tar cracking, but the influence of the physico-chemical properties on their reactivity is still unclear. This work aimed to better understand the structure and the composition of the mineral species of pyrolysis char, as well as their catalytic role in tar cracking. For this purpose, a characterisation of the minerals has been performed at bulk, surface (studied at micro and nano-scale) and crystallite scale. Pyrolysis chars were produced from wastes generated on cruise ships – namely used wood pallets (UWP), food waste (FW) and coagulation flocculation sludge (CFS) – having different mineral amount and content. Ethylbenzene was used as surrogate of light aromatic hydrocarbons in a tar cracking process. The results showed that ethylbenzene was converted into lighter gases meaning that the chars were efficient for this. Ethylbenzene conversion at 650 °C was found to be significantly higher with the char from a mixture of sludge and food waste (c.FW/CFS) compared to that of wood-based char (c.UWP): 71 wt.% against 45 wt.%, respectively. The combination of multi-scale and complementary techniques has highlighted that the higher catalytic activity of this char was mainly attributed to the mineral content. Well dispersed mineral particles with various morphologies and natures were observed on the surface of c.FW/CFS using Scanning and Transmission Electron Microscopy (SEM and TEM). Especially, Ca, Al and P were the main mineral species identified using XRFS and SEM. These mineral species in form of oxides and hydroxyapatite were considered to be the main active mineral components for tar cracking. Oxides were identified using EDX-analysis. XRD analysis highlighted the presence of crystalised particles of hydroxyapatite ($Ca_5(PO_4)_3(OH)$), while Raman spectroscopy revealed that these particles were embedded in the carbon matrix.

1. Introduction

To cope with the increase of energy demand, the depletion of fossil fuel resources and the increase of greenhouse gas emissions, the research of alternatives for clean energy production is one of the twenty-first century challenges. Among those alternatives, the energetic valorisation of biomass and waste using pyro-

Abbreviations: UWP, used wood pallets; FW, food waste; CFS, coagulation-flocculation sludge; c.UWP, char from UWP; c.FW/CFS, char from a mixture of FW (50wt.%) and CFS (50wt.%); c.UWP/FW/CFS, char from a mixture of UWP (50wt.%), FW (25wt.%) and CFS (25wt.%); AAEM, alkali and alkaline earth metallic species.

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gasification is one of the most promising options. Pyro-gasification consists in converting biomass and/or waste into gaseous energy carrier by partial oxidation at high temperature (800–1000 °C) with an oxidising agent (air, steam, oxygen or carbon dioxide). Synthetic gas ($CO + H_2$), the main expected product, usually needs to be purified before further utilisation. The elimination of pollutants such as tars, H_2S, and fine particles in the synthetic gas is one of the main industrial challenges of the pyro-gasification process.

The pyro-gasification process encompasses four steps: drying, pyrolysis, gasification and finally, reforming of the pyrolysis chars and condensable gases. During pyrolysis, biomass is decomposed at moderate temperatures (<700 °C) under reducing atmosphere and solid residues, namely chars, are formed. They represent 15–30 wt.% of the initial biomass and contain about 25% of the initial recoverable energy. Chars are carbonaceous materials with a variable part of mineral species depending on the initial biomass. They can be used as fuel in gasification process only if their concentrations of heavy metals and mineral species are low. Above ash contents of 5%, clinkering and slagging problems occur due to the fact that the gasification temperature is often higher than the melting point of the biomass ash [1]. Moreover, chars with high mineral and metal content have low energy potential and their gasification leads to the production of a heavily polluted syngas. Otherwise, chars can be used in higher added-value applications than if used for energy, such as environmental remediation (removal of pollutants in air or wastewater) and catalysis (as catalysts or catalyst supports). As an example, pyrolysis chars with or without modification are already known to be efficient sorbent or catalyst for gas cleaning [2,3]. This byproduct of thermochemical process is also relatively inexpensive compared to other synthetic catalysts used in tar cracking processes [4]. Due to important differences in the structure and mineral content of the initial feedstock, the resulting chars can display significant variations in physical and chemical properties [4]. Moreover, the pyrolysis process conditions strongly influence the properties of the resultant char [5]. The catalytic activity of pyrolysis chars is mainly determined by four characteristics: (a) the disorganized and porous structures [6,7]; (b) the presence of O-containing groups on the char surface [8,9]; (c) the structure of the carbonaceous matrix [10,11]; (d) active sites formed by the alkaline (Na, K) and alkaline earth (Mg, Ca) species distributed in the char matrix [7,12,13].

The influence of each above mentioned property on the catalytic activity of chars for tar cracking reactions, as well as their combined effects, still remains unclear. A recent study showed that if the tar cracking temperature is higher than the temperature of char production, secondary pyrolysis can occur, resulting in textural properties and carbonaceous structure changes affecting the char activity [7]. Nevertheless, the presence of mineral species has been identified to be of prime importance in the char catalytic activity [8]. Recently, the use of chars as catalysts or catalyst supports in tar cracking reactions has been intensively studied [3,4,6]. However the main studies only concerned the characterisation of the mineral content at the bulk scale. The analysis of mineral content without any details on its distribution and speciation is not sufficient to understand how efficient the catalytic activity of minerals in the char could be. Many parameters (such as speciation, size of crystallites and spatial distribution) could influence this catalytic activity. The speciation and amount of mineral species should be investigated to identify the presence of active and inhibitory species. The size of minerals and their spatial distribution are decisive in the catalytic and inhibitory phenomena. Indeed, small and well-dispersed mineral species on the char surface provide many active sites that promote the catalytic activity of char and reduce the deactivation by coke deposition [14]. In addition, the carbonaceous matrix has been demonstrated to be important feature, as small aromatic rings in carbon structure and defects in graphene like sheets promote the char reactivity [7,12,15].

The aim of this paper is to study the content, the speciation and the distribution of mineral species of pyrolysis chars to better understand the mineral structure of such complex matrix and its catalytic role in tar cracking reactions. Three chars with various mineral contents were produced from three different feedstocks produced on cruise ships. Emphasis was placed on a set of complementary characterisation techniques performed at different scales: bulk, surface (studied at micro and nano-scale) and crystallite scale. The distribution and size of minerals were investigated by SEM and TEM while their speciation and crystallinity were studied by XRFS and XRD. Moreover, original data related to the interactions between the mineral species and the char matrix has been provided by the Raman spectroscopy. This technique was used to characterise the composition, the distribution, the structure of the carbonaceous and the mineral species on the surface and within the char. Finally, the two chars with the most different compositions were used as catalysts in a tar cracking process in order to assess the influence of the mineral species on tar cracking efficiency. These data lead to a complete description of the mineral species in the char and a better understanding of the relationships between minerals and the catalytic activity of chars.

2. Materials and methods

2.1. Raw materials

The materials used in this study were Used Wood Pallets (UWP), Food Waste (FW) and Coagulation-Flocculation Sludge (CFS), all of them were wastes coming from cruise ships. The interests of studying these wastes lie in their very different mineral content and in their large availability. UWP was common softwood (from gymnosperm trees) used in the production of pallets for loading and transportation of food. Food wastes came from feeding activity, and were composed of a mixture of vegetables and animal wastes. Coagulation-Flocculation Sludge was recovered from a wastewater treatment plant present on board the ship. FW and CFS were partially dehydrated in a screw press up to a moisture content of 80 wt.% and dried up to a moisture of 30 wt.% in a steam dryer (Scanship). Before pyrolysis, these wastes were stored in closed bags. UWP was chipped in particles of average diameter of 3 cm and stored indoors.

2.2. Pyrolysis treatment

The chars were produced in a semi-continuous horizontal screw reactor (internal diameter of 0.167 m and 2 m in length). The pyrolysis was performed at 700 °C during 30 min with a heating rate of 22 $°C \cdot min^{-1}$. A slow pyrolysis was chosen in order to maximise the char yield and reduce the volatilisation of mineral species. The details of the experimental procedure were described in a previous paper [16]. From such a treatment, three different pyrolysis chars were produced: (1) c.UWP, only from UWP, (2) c.FW/CFS, from a mixture of 50 wt.% FW and 50 wt.% CFS, and (3) c.UWP/FW/CFS, from 50 wt.% UWP, 25 wt.% FW and 25 wt.% CFS. The mixtures of the feedstocks were hand-made. The flow rate of feedstocks was 8.9 kg/h for c.UWP and c.FW/CFS, and 7.1 kg/h for c.UWP/FW/CFS. In these conditions, the char yields were 22 wt.% for c.UWP and c.UWP/FW/CFS, and 23 wt.% for c.FW/CFS. The char yields are in agreement with the literature results of wood chars produced in similar conditions [6]. These waste mixtures allowed producing three chars with various mineral contents, since CFS and FW contained more mineral compounds than UWP. Chars were sieved to particle size from 0.5 to 1.6 mm. This size fraction represented