Activated Carbon from biomass, a sustainable acid catalyst for flavor synthesis

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The objective of this work was to develop and study carbon based heterogeneous catalysts for catalytic reactions of interest, within the scope of green chemistry. Activated carbons prepared from biomass via chemical activation as well as a commercial carbon were studied in esterification reactions for the production of flavors.

This material is an eco-friendly choice for catalyst, which combines excellent textural and chemical properties. Also, the preparation of activated carbon from biomass waste is a suitable pathway of valorization of wastes and promotes the processing of biomass in the production of added value products.

The catalysts proved to be efficient in the esterification reaction of hexanol, isoamyl alcohol and octanol with acetic acid to produce pear, banana and orange flavors, respectively. The latter are approved compounds for food additives by the European Food Safety Authority.

1. Scope

Hedychium gardnerianum, better known as Conteira, is an original plant of Asia (India, between the Himalayas and Nepal), which was introduced in the Azores and Madeira (the Portuguese islands), for ornamental reasons. It is an invasive plant that propagates preferentially in wetlands, forest and agricultural areas. Its rapid growth leads to the formation of vast and dense colonies that stifle the development of native vegetation and may lead to the modification of the natural habitat of native animals and thus threat the integrity of ecosystems. For these reasons it is necessary its periodic removal [1].

This is a lignocellulosic material and, therefore, can be considered as a suitable raw material to obtain activated carbons with good adsorption and catalysis properties. The conversion of this raw material in activated carbon will increase its economic value, help reduce the cost of disposal of their waste and provide a potentially cheap raw material for carbons [2]. The application of the obtained carbons in acid catalysis results in a high added value product.

Esterification reactions are traditionally catalyzed by homogeneous mineral acids, for instance sulfuric acid, hydrochloric acid or hydrogen iodide, or heterogeneous solid acids. The purpose of this study was to observe whether the conventionally used acidic catalysts could be replaced by ACs with acidic surface groups, which are more environmentally friendly in terms of production and disposal, not to mention the advantages of heterogeneous over homogeneous catalysis. Since esters are frequently used artificial flavors, the chemical industry could benefit from positive results [3].

In this work, two activated carbons from *Hedychium gardnerianum* wastes were obtained via chemical activation with phosphoric acid (H_3PO_4), presenting high surface area and an acidic surface. These materials were characterized and tested as catalysts in the esterification reaction for the production of flavors. Their catalytic performance was compared with a commercial activated carbon.

2. Results and discussion

Biomass derived carbons were prepared by using two ratios of biomass: activating agent (phosphoric acid) of 1:1 and 1:3. After impregnation at 50ºC, samples were dried and thermally treated at 500ºC for 2 h under nitrogen flow. The obtained activated carbons were named as RCB1 and RCB2 depending on whether of the biomass:H_3PO_4 weight ratio used was 1:1 or 1:3, respectively. For comparison purpose, a commercial carbon (Norit GAC) was used after acid treatment with nitric acid (HNO_3) at 90ºC for 6h (NCN sample).

Table 1 presents the main characterization results. The biomass derived carbons presented very high surface area and a low pHpzc value revealing a very acidic surface without any further post synthesis treatment. RCB2 exhibited the best textural features attaining more than 2000 m^2/g, with a synthesis yield of almost 30% (w/w). These carbons also presented significant mesoporosity. The surface acidity is probably due to the incorporation of phosphorus in the carbon surface as suggested by FTIR studies (not shown) [4]. Interestingly, the increase of phosphoric acid in the activation step did not result in an increase in acidity of the carbon surface.

Table 1: Samples Characterization

Samples	A_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total}	pH_{pzc}
NCN	1030	0.30	0.56	3.8
RCB1	1076	0.29	0.81	2.4
RCB2	2197	0.59	1.37	3.0

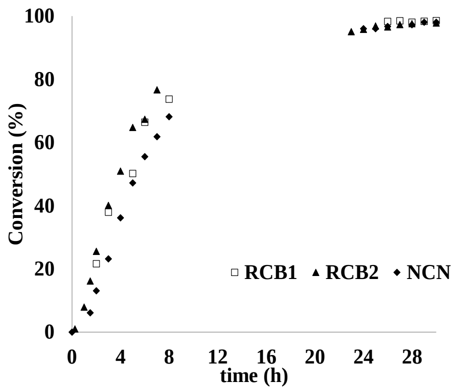

Fig 1: Conversion curve of Octanol esterification

Several esterification reactions were carried out where alcohols octanol, hexanol and isoamyl alcohol reacted with an excess amount of acetic acid resulting in the flavors of orange, pear and banana, respectively. Every reaction was performed with each catalyst (NCN, RCB1, RCB2). All prepared catalysts revealed to be active in the esterification reaction. The biomass derived carbons presented slightly better performance than the commercial carbon, for all the alcohols studied. Fig. 1 displays the reaction behavior for the esterification reaction of octanol in the presence of the 3 catalysts. Observing the ascending part of the curve, even though with a small difference, one can identify the best performance of carbon RCB2 which present the best textural properties (Table1). The commercial carbon has a similar surface area to RCB1 but seems to be less efficient probably due to the lower surface acidity. The results were further investigated and a kinetic model was fitted.

3. Conclusions

The objective of this work was to prepare biomass derived carbons based heterogeneous catalysts and determine their suitability to be used as catalyst by the example of esterification reactions.

For this purpose, a widely used commercial carbon was compared to the biomass carbons produced under laboratory conditions. Shredded *Hedychium gardnerianum* was the feedstock for the biomass carbon, which was produced by chemical activation in a single thermal treatment. It was possible to produce activated carbons with very good textural properties, attaining high surface area and with suitable chemical properties for acid catalysis, presenting low pHpzc. The biomass carbon achieved the best catalytic results for most of the reactions, even though the commercial AC's results are almost as good. But in addition to the good catalytic results, the RCB2 carbon was made of a feedstock which would otherwise be considered waste, and so there are no further resources needed for the production, which makes this catalyst very environmentally friendly.

References

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