The 6th International Conference on Life Cycle Management in Gothenburg 2013

GRAVE-TO-GATE LCA OF POROUS MATERIALS MADE FROM BLACK LIQUOR: COMPARISON OF TWO SCENARIOS INCLUDING VEGETABLE OIL OR PETROCHEMICAL

Amandine Foulet (1), Guido W. Sonnemann(1), Hervé Deleuze(1) and Philippe Garrigues(1)*
(1) Université Bordeaux 1, ISM-UMR CNRS 5255

Univ. Bordeaux, ISM, UMR 5255, F-33400 Talence, France.
CNRS, ISM, UMR5255, F-33400 Talence, France.
E-mail: a.foulet@ism.u-bordeaux1.fr

Keywords: black liquor; castor oil; petrochemical; porous polymer; life cycle assessment

ABSTRACT

The Kraft black liquor is an aqueous solution allowing to prepare oil-in-water emulsions with a hydrophilic surfactant. Emulsion-templated porous monoliths based on castor oil-in-black liquor and on dichloroethane-in-black liquor emulsions were obtained by using two different techniques including recycling phases. In both cases the inputs and the outputs were collected in order to conduct a grave-to-gate life cycle assessment at laboratory scale. The early results showed that using a vegetable oil leads to a low potential impact on climate change but is less advantageous than using a petrochemical in most other environmental indicators studied.

INTRODUCTION

The preparation of biobased materials aims for the development a new generation of materials that are ecofriendly and biodegradable. In the worldwide Kraft pulping process, the dissolved wood together with the spent pulping chemicals forms a liquid stream called weak black liquor containing organic matter such as degraded lignin. Everyday tons of Kraft black liquor are produced and merely used for energy production whereas it could be a source of biopolymers. Kraft lignin valorization has been investigated in our research group (Forgacz, 2013). This consists in using Kraft black liquor (KBL) and castor oil (CO) for the preparation of microcellular materials through polymerization of a Medium Internal Phase Emulsion (MIPE). Combining a vegetable oil with an industrial waste to prepare polyMIPEs seems to be in line with the green chemistry principles (Anastas and Warner, 1998). In this paper, the validity of this assumption is being determined by a comparative life cycle assessment (LCA) like it was previously done for soybean-based lubricants (Miller, 2007). To draw up a comparison, CO has been replaced by a petrochemical, the 1,2-dichloroethane (DCA).The resulting preparation technique allows to establish the recycling of all solvents used in the process including DCA, unlike CO. Experimental data along with existing databases are incorporated within the analysis and allow to conduct a grave-to-gate LCA.

EXPERIMENTAL

Materials

The as-received KBL comes as a thick, black liquid (Smurfit Kappa Cellulose du

Pin, Facture, France). density ρ = 1.3 g.cm^{-3}; dry matter amount =50 wt.%. castor oil (CO), Kolliphor® EL, epichlorhydrin (≥99%) and 1,2-dichloroethane (ACS reagent, ≥99%) were obtained from Sigma-Aldrich and were used as received.

Formulation of stable CO-in-black liquor MIPE

This synthesis has been previously described by our research group (Forgacz, 2013). Briefly, a mixture of KBL (25g), epichlorhydrin (2.77g), CO (23.67g) and Kolliphor® EL (1.1g) was placed into a double syringe-pump device. Backwards and forwards movements of the pistons are induced by a specific engine for 80 min (E=0.111 kWh).

Formulation of stable dichloroethane-in-black liquor MIPE

A mixture of KBL (82.5g), epichlorhydrin (8.8g) and Kolliphor® EL (18.7g) was placed into a batch stirred reactor equipped with an overhead agitation impeller and 1,2-dichloroethane (129g) was slowly added to the former mixture for 2h (E=0.440 kWh).

Preparation and characterization of the monoliths

The obtained emulsions were placed in PTFE cylindrical moulds and crosslinked for 24h at 60°C in an oven (E=2.57 kWh). The CO contained in the resulting monoliths was extracted by refluxing with ethanol (48h) in a Soxhlet apparatus (E=14.375 kWh). The monoliths were finally dried under hood and ethanol was recovered by a rotary evaporator (E=0.122 kWh) and then reused as it is. A solid waste was also collected and characterized. As for the dichloroethane monoliths the solvent extraction was carried with 1-propanol (48h) and the monoliths were dried in a vacuum oven at 60°C to constant weight (E=4.23 kWh). Propanol and dichloroethane were then distilled by a spinning band distillation (E=7.31 kWh) and then reused as it is.

The porosity and the connection size distribution of each sample were determined by mercury intrusion porosimetry using a Micrometrics Autopore IV 9500 porosimeter. The morphology was observed by scanning electron microscopy (SEM) in a Hitachi TM-1000 microscope.

LCA METHODOLOGY

Goal and Scope

The goal of this study is to compare the use of a vegetable oil with a petrochemical for the production of activated carbons-to-be porous monoliths from black liquor, as a waste that becomes a resource. The use and end of life of the monoliths were not taken into account. Therefore, this paper presents a grave-to-gate LCA conducted on a laboratory-scale process for the production of porous monoliths mainly made from black liquor directly recovered as a waste stream in the production of Kraft paper. The life cycle of black liquor being common to the two scenarios, not taking it into account wouldn’t change the results. As functional unit, we chose to compare 1 kg of porous monoliths preceded by a medium internal phase emulsion (MIPE) presenting a volume fraction of 0.54.

For the preliminary investigation, all the environmental impact categories are taken into account and compared for both scenarios. Life cycle impact assessment was done following the ReCiPe Midpoint (Hierarchist) V1.06 method (Goedkoop, 2012).

Inventory analysis

All life cycle inventory calculations were performed using SimaPro 7.3.3. The inventory analysis is based on the flow chart reported in Figure 1. Since the waste stream of black liquor was used as the “original” resource entering into the system of a grave-to-gate LCA, its inputs and outputs were not taken into account. DCA, 1-propanol and ethanol were found in EcoInvent database. We managed to found a study on LCA of biodiesel made from CO led by the Industrial University of Santander (Castro Orduz, 2009) and the synthetic pathways of epichlorhydrin and Kollipohor® EL were also available (Bell, 2008; BASF, 2008).

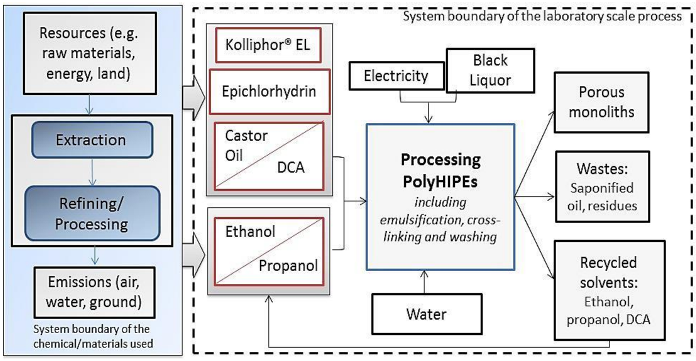

Figure 1: The system boundary of the preparation of porous monoliths from black liquor via laboratory scale process

The consumption of electricity for all included laboratory equipment has been measured directly using a power meter providing an accuracy of 0.5%. According to the geolocation, Brazilian and French electricity productions were used from the EcoInvent database for energy calculations of CO (Latin America) production and laboratory process (France), respectively. We acknowledge that using Brazilian electricity data for the geolocation in Latin America is just an approximation. Transport stages between the manufacturing plants and the laboratory have been ignored due to uncertainties regarding modes of transport and distances travelled.

RESULTS & DISCUSSION

Monoliths characterization

The analysis of the solid waste obtained in the CO based process presents typical fatty acids signals especially ricinoleic acid signals among many unidentified signals. The supposed saponification of CO doesn't allow yet to recycle it. In contrast the use of DCA enables to establish a recycling process by taking into account the boiling points of different solvents and the absence of possible azeotropes, resulting in using 1-propanol as the washing solvent. The morphology of the different samples were observed using SEM in order to estimate the size and size distribution of the voids. In both cases the average voids size values are around 12 μm. The size distribution is more regular when using DCA than CO.

Life Cycle Impacts Assessment & Interpretation

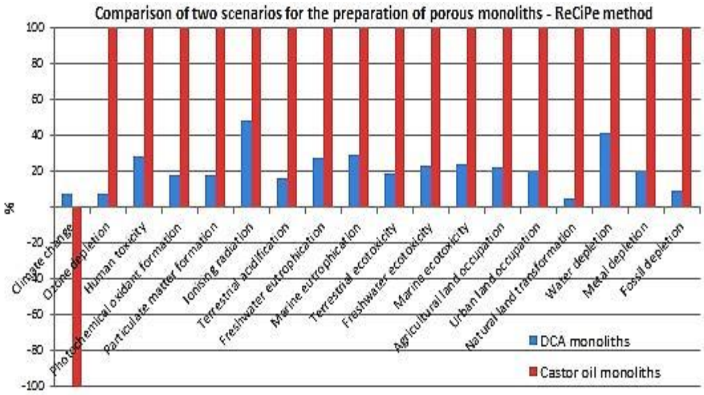

Figure 2: Comparison of the environmental impacts of both scenarios

Figure 2 presents the LCA results according to the ReCiPe Midpoint (Hierarchist). This provides us with the environmental profile of the two studied scenarios. It seems that using CO would be better for the climate change but otherwise more impactful than using DCA for the preparation of porous monoliths. In order to understand that fact, it is necessary to look at each step of the two processes by complementary characterization calculations on SimaPro. For both monoliths preparation, two steps are highly responsible for the presented potential impacts: emulsification and drying.

Emulsification implies the use of electricity and raw materials. The electricity used for this step is below 0.5 kWh and thus negligible. In contrast, as all the raw materials, except for the dispersed phase (DCA and CO), are common to the two emulsifications, it means that the choice of the dispersed phase is substantial. The extraction method, the farming constraints and the non-recyclability (in the studied process) of CO are the criteria to be found the most impactful in most environmental impact categories. To dry the monolith, it requires heat, stirring and ethanol for the CO case and stirring and propanol for the DCA case. The choice of these solvents is certainly addressed by the LCA results but the biggest difference between the two drying scenarios comes from energy. Indeed, the required energy to totally remove CO from monolith matrix is up to 14.38 kWh whereas for DCA removal it only takes 4.23 kWh.

The recycling of DCA and propanol within the process has a positive influence on the LCA results as it allows to significantly decrease the potential impacts values except for a few categories (ionizing radiation, terrestrial ecotoxicity, and water depletion). As for the castor-oil-based process, the recycling of ethanol also helps to moderate the potential impacts values but not enough to compete with DCA recycling. With regard to climate change CO is more advantageous considering the photosynthesis implication during the growth of plants. Eventually this gives a negative value (-35.13 kgCO_2/eq for 1 kg of porous monoliths) for Global Warming Potentials (GWP) compare to DCA monoliths GWP (2.81 kgCO_2/eq).

CONCLUSIONS

The use of castor oil for the production of activated-carbon-to-be materials seemed to be a judicious choice in green chemistry and it has allowed to obtain the desired polyMIPE structure. However castor oil was degraded by the alkali media and is thus non reusable. Judicious choice of a petroleum substitute such as dichloroethane allows the recycling of all raw materials. According to LCA results, environmental impacts are higher when using castor oil instead of dichloroethane as the dispersed phase for emulsions preparation. It appears that the production of castor oil and the technique to prepare its resulting monoliths are responsible for that latter fact. Considering that among the studied impact categories, climate change shows the advantage of using castor oil further research needs to strive towards good GWP results while avoiding the transfer of environmental pressure to other impact categories.

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