Impact of supercritical extraction on solid fuel wood pellet properties and off-gassing during storage

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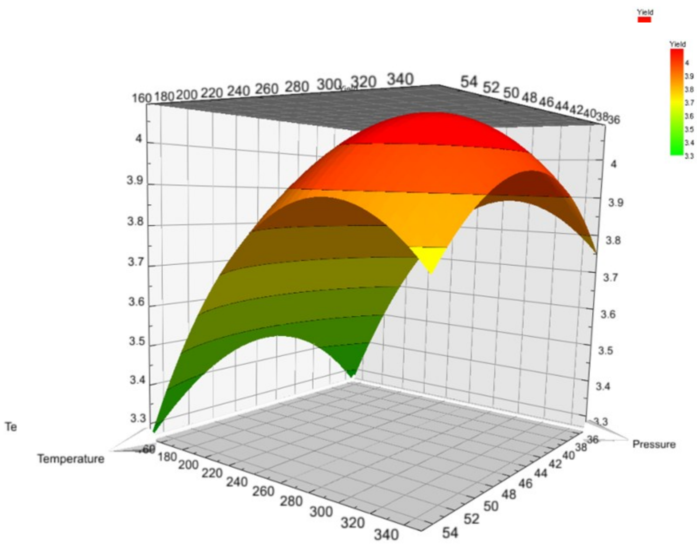

Figure S1: Contour plot showing optimum conditions for fatty acid and resin acid using $scCO_2$

Economic Assessment of Supercritical process

The economic assessment carried out on the supercritical extraction of FRAs from sawdust was based on a model by Turton *et al.*[1] In this model, the cost of manufacture (COM) is based on three main types of costs: direct costs (DC), fixed costs (FC) and General expenses (GE)

$$COM = DC + FC + GE$$

These three components making up the COM can be estimated in terms of five main costs: fixed capital investment (FCI), cost of operational labour (C_{OL}), Cost of utilities (C_{UT}), cost of waste treatment (C_{WT}) and cost of raw materials (C_{RM}). The equation used to calculate the final COM is as follows[1]:

$$COM = 0.280FCI + 2.73C_{OL} + 1.23(C_{RM} + C_{WT} + C_{UT})$$

It is assumed that the supercritical extraction of the sawdust will be part of a holistic biorefinery so some of the costs will obviously be distributed to other areas of the biorefinery.

Fixed Capital investment (FCI)

This involves the cost of the supercritical extraction unit. Literature indicates that a typical industrial supercritical extraction unit used for the extraction of natural pigments, spices, nutraceuticals, essential oils etc. is €1,400,000, consisting of two 0.4 m^3 extractors as well as a number of flash tanks, a CO_2 reservoir, pump and heater.[2, 3] Multiplying the total investment by the depreciation rate (assumed to be 10% per year and is used in the calculation of the COM) gives the fraction of investment. Although another fraction of the investment is the initial amount of CO_2 that is needed to fill the reservoir this is negligible in comparison to the cost of the extraction unit.

Cost of Operational Labour (C_{OL})

The total C_{OL}, in terms of man-hour per operation hour, is estimated by utilising tables that are presented by Ulrich (1984) and based on literature.[2-4] It is assumed that the operational time (time when the extractors are under operation) is 7920 hours of continuous extraction (which is 330 days per year of 24-hour per day shifts). Furthermore, two operators per shift will be working in the industrial SFE unit, with the C_{OL} taken to be €5.00 per hour (per person). This cost is only for the SFE extraction; since the operators will have to perform other duties in the biorefinery, their overall wage will be higher than that stated here.

Raw Material costs (C_{RM})

The C_{RM} takes into account all of the materials that are directly related to the production. In the case of $scCO_2$ extraction, this involves all of the solid substrate (sawdust) which contains the solute that needs to be extracted, and includes all of the pre-processing steps (e.g. communition, cleaning, storing, transportation etc.) that lead to the final biomass product.

Personal communication with a production manager from an industrial Lulea pellets production company (Bioenergi i Luleå) indicated that the C_{RM} for sawdust (as received) was found to be €34 per tonne of sawdust.[5]

Cost of waste (C_{WT})

In $scCO_2$ extraction, no solvent waste is typically generated since the CO_2 is recycled. Therefore, the only waste from the extraction process is the minimal amount of CO_2 that leaks from the system as well as the biomass. Since the $scCO_2$ extraction is part of a biorefinery, the latter (sawdust biomass) will be passed on for production of pellets and this is therefore not a waste. The CO_2 that leaks from the system is negligible and therefore it is assumed that there are no C_{WT}.

Cost of utilities (C_{UT})

When looking at utility costs, a number of factors have to be considered including (i) Costs associated with the CO_2 pump (ii) Costs associated with the CO_2 heater and (iii) Refrigeration.

Costs associated with the electric power used in the CO_2 pump

In terms of electrical costs associated with the power supplied to the CO_2 pump the following have to be taken into consideration: (i) Pressure and temperature used in the extraction process (ii) CO_2 flow rate (iii) Experimental bed density (iv) Duration of the extraction (extraction time). From data that was obtained from the optimisation experiments of sawdust FRAs extraction, it was found that the highest yields were obtained using a pressure of 350 bar and 55 ^{o}C.

The pressure and temperature parameters are required in order to obtain the specific enthalpy. The total energy used in the extraction process can be determined by multiplying the variation of specific enthalpy by the extraction time and the flow rate of CO_2. In the case of sawdust, the specific enthalpy of CO_2 using 350 bar and 55 ^oC is 297.20 kJ/kg.
The CO_2 flow rate in the laboratory-scale extraction experiments was 6.7 x 10^{-4} kg/s (based on earlier studies on supercritical extraction from sawdust) and therefore the CO_2 flow rate that is required for an industrial-unit is around 2875.1 kg/hr.

The experimental bed density of the sawdust utilised in this study was found to be 360 kg/m^3. Therefore, it was calculated that on an industrial scale, for each extraction, 150 kg of sawdust can be loaded into the extractor.

The extraction time was taken to be 40 minutes per extraction. This is based on earlier studies in literature on the supercritical extraction of lipophilic molecules from biomass, whereby 40 minutes was found to extract around 80% of the total extraction yield (total extraction time was around 4 hours).[3, 4, 6] When analysing cost of raw materials, it was found that it was more profitable to carry out 40 minute extractions than longer extraction times (leading to only minimal increases in FRA quantities). The cost of electricity was taken to be €0.112/kwh.[7]

The costs associated with the pump were found to be €31.14/h (calculations worked out in the attached spreadsheet).

Costs associated with the CO_2 heater

To determine the costs associated with the CO_2 heater, the energy associated with the heating process need to be estimated. It is assumed that the heaters have a 50% efficiency. This was done using :

$$Q = MC_p\Delta T$$

Where Q is the energy required, M is the mass of CO_2, Cp is the specific heat capacity of CO_2 and ΔT is the temperature change. CO_2 needs to be heated from 4 ^oC (temperature of the pumps) to 55 ^oC. The CO_2 mass used per hour is 2875.1 kg, Cp at 55 ^oC is 0.874 kJ kg^{-1} k^{-1} and ΔT is 51 ^oC.

The energy required (see attached spreadsheet) was calculated to be approximately 300 MJ/h. It is possible to obtain this energy by combusting some of the residual sawdust biomass following the extractions. Burning of the residual sawdust will supply around 20.19 MJ kg^{-1}, and therefore the system would require around 14.87 kg per hour or 10% of the extracted sawdust. As such, the costs associated with heating the extractors are negligible.

Costs associated with heating the biomass

To determine the costs associated with the heating the biomass, the energy associated with the heating process has to be estimated. Once again, it is assumed that the heaters have a 50% efficiency. This was done using:

$$Q = MC_p\Delta T$$

Where Q is the energy required, M is the mass of biomass per extraction, Cp is the specific heat capacity of the sawdust and ΔT is the temperature change. The biomass needs to be heated from 20 °C (room temperature) to 55 °C. The sawdust used per extraction is 150 kg, Cp of sawdust is 0.9 kJ kg^{-1} k^{-1} [8] and ΔT is 35 °C.

The energy required (see attached spreadsheet) was calculated to be approximately 9.45 MJ/run. Once again, it is possible to obtain this energy by combusting some of the residual sawdust biomass following the extractions. Since burning of the residual sawdust will supply 20.19 MJ kg-1 the system would only require around 0.47 kg per hour or 0.3% of the extracted sawdust to provide the required energy to heat the biomass for extraction. As such, the costs associated with heating the biomass are negligible.

Costs associated with refrigeration

Typically, a refrigeration cycle constitutes a working fluid circulated around a loop that comprises a compressor, evaporator, expansion valve or turbine and condenser. Since refrigeration requires electrical power, it is more expensive than heating. The water temperature has to be reduced from 20 °C (around room temperature) to 4 °C. The coefficient of performance, COP, has to be calculated in order to determine energy needed for refrigeration.

The costs associated with refrigeration (calculations in attached spreadsheet) were found to be €2.66/h.

The total utility costs (C_{UT}) (addition of pump costs and refrigeration costs) was calculated to be €33.80/h.

Total COM

Total COM is calculated using the equation mentioned previously

$$COM = 0.280FCI + 2.73C_{OL} + 1.23(C_{RM} + C_{WT} + C_{UT}$$

This has been carried out in the attached spreadsheet and the COM was found to be approximately €642 per tonne of sawdust.

Sensitivity Analysis

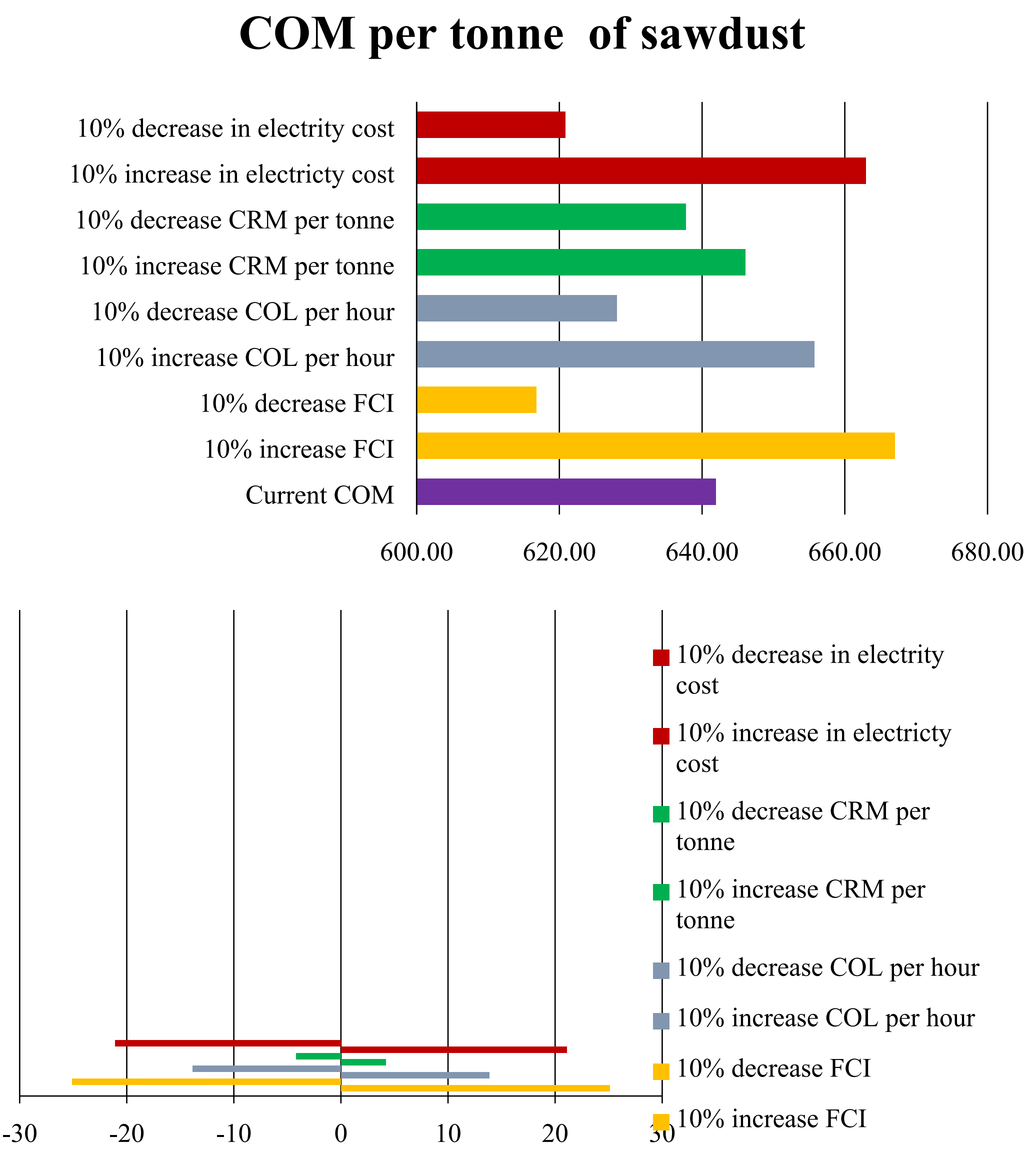

Figure S2: One-at-a-time sensitivity analysis indicating A)Total COM per tonne of sawdust by increasing or decreasing each parameter by 10% B) The difference in COM from the original COM by varying each parameter by 10%

A simple one-at-a-time sensitivity analysis was conducted in order to determine the most relevant parameters (out of FCI, C_{RM}, C_{OL} and C_{UT}). The cost value of each parameter was varied (10% increase or 10% decrease) in order to determine which parameter had the greatest effect on the total COM. The results (Figure S1 and S2) show that the FCI followed closely by the C_{UT} (electricity costs associated with the CO_2 pump and refrigeration) are the two major parameters that have the greatest effect on the COM. The parameter that was found to have the smallest effect on the overall COM was found to be the C_{RM} which is important as the cost of the sawdust biomass could vary from country to country.

Green Metrics

The metrics for the supercritical extraction were carried out for the semi-pilot plant scale and the pilot-plant scale (2000 t/year). The calculations may be found in the attached spreadsheet.

E-factor

The E-factor was calculated using:

$$E - factor = \frac{total\ waste\ (kg)}{product\ (kg)}$$

The final product was taken to be the sawdust following the extraction while the waste was taken to be the FRAs extracted (even though these are not considered to be a waste but an added-value product) as well as the CO_2 lost during the depressurisation of the extractor following the extraction (amount of CO_2 lost in a 0.005 m^3 extractor for the semi-pilot scale and amount of CO_2 lost in a 0.4 m^3 extractor for the pilot-plant scale). At 55 bar and 20 ^oC (CO_2 density of 177.4 kg/m^3) it was calculated that 0.887 kg of CO_2 and 70.96 kg of CO_2 would be lost in the semi-pilot and pilot extraction process respectively. The E-factor was calculated to be 0.53 for the semi-pilot plant scale and 0.51 for the pilot-plant scale.

Extraction Mass Efficiency

The extraction mass efficiency was calculated using the following equation:

$$EME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ starting\ material} \times 100$$

The starting material was taken to be the sawdust utilised pre-extraction while the isolated product was taken to be the sawdust post-extraction (without the FRAs). This was found to be 97.4% and 97.9% for the semi-pilot plant scale and the pilot plant scale respectively.

Process Mass Intensity (PMI)

The process mass intensity was calculated as follows:

$$Process\ Mass\ Intensity\ (PMI) = \frac{total\ mass\ in\ a\ process\ or\ process\ step}{mass\ of\ product}$$

It is effectively the E-factor +1. The total mass in this case was the biomass utilised in the extraction as well as the mass of CO_2 (solvent) used up in the process. This was found to be 1.53 and 1.5 for the semi-pilot plant and pilot-plant scales respectively.

Renewables Intensity

The renewables intensity is described as:

$$Renewables\ Intensity = \frac{mass\ of\ all\ renewably\ derivable\ materials\ used}{mass\ of\ product}$$

Since in the extraction both the biomass used as well as the solvent are renewable the renewables intensity was therefore found to be 1.53 and 1.5 for the semi-pilot plant and pilot-plant scales respectively.

The **% renewables** was therefore found to be 100%.

Space time yield

$$Space\ time\ yield = \frac{mass\ of\ product}{volume\ of\ reactor\ used\ \times\ reaction\ time}$$

For the semi-pilot plant scale the reaction time was taken to be 6 hours (duration of the extraction) while the volume of the reactor used was 0.005 m^3. The space time yield was found to be 58.44 kg m^{-3} h^{-1}. In the pilot-plant scale, the reaction time was taken to be 40 minutes and the volume of reactor was 0.4 m^3. The space time yield was calculated to be 6.54 kg m^{-3} h^{-1}.

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