INTEGRATION OF SUPERCRITICAL CO$_2$ EXTRACTION INTO EXISTING BIOETHANOL PRODUCTION PLANT: A TECHNICAL ECONOMICAL ASSESSMENT

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ABSTRACT
In this work the problem of extraction in the recovery of bioethanol from fermentation broth is addressed. Different options are examined to obtain ethanol at suitable purity through a single purification step. First the thermodynamics of the ternary ethanol-water -CO$_2$ vapour liquid equilibrium is studied and implemented in the simulation software Aspen Plus^{TM}, then simulation of the whole dry grind process is performed. The results are used in order to estimate the number and the size of the required pieces of equipment as well as the utilities needs. This allows the determination of the investment of capital and operating costs of the new process, which are finally compared with these of the conventional process.

INTRODUCTION
Among the different biofuels for automotive transportation bioethanol is the most produced and important one. It can be obtained by fermentation starting from different kinds of raw materials, such as simple sugars, starch and cellulose.

The dry-grind process from corn is the most widely used method in the U.S. (the world top bioethanol producer), and it is likely to be the favourite process that will be implemented in Europe and especially in Italy in the next years.

The economical analysis of the current dry-grind process underlines that the economics of fuel ethanol production is mostly influenced by the cost of raw materials, which accounts for more than half of the total production cost, while the energy demand of the process (including electrical energy, thermal utility and natural gas) covers around 15% of it [1]. The urgent need of introducing bioethanol in fossil fuels due to the increasing concern about environmental and greenhouse effects, can be a significant driver to develop new processes in order to decrease the production energy duties.

On the other hand during glucose fermentation a large amount of CO$_2$ is obtained and so there is great availability of this gas in bioethanol plants (about 1 kg/kg of ethanol). CO$_2$ could be captured, sold and used in carbonating soft drinks and beverages, manufacturing dry ice and in other industrial processes, but in this case it is a lower value product as very pure CO$_2$ is difficult to obtain. So, this gas is usually purged to the atmosphere.

This work is focused to develop a viable way to re-use CO$_2$ as a free resource in the process itself.

Previous research works addressed the use of supercritical carbon dioxide for the extraction of ethanol from water mixtures [2,3] and proposed this application as a way to obtain absolute grade fuel ethanol avoiding azeotropic distillation or molecular sieve purification [4]. These authors experimentally proved that the separation is possible, so that the azeotrope can be broken and an ethanol weight fraction of 0.999 can be achieved by supercritical extraction only. However, the effect of this technical option on the economy of a large scale plant has not been studied yet.

PROCESS DESCRIPTION

The most common processes for the production of bio-ethanol are the so-called Dry Grind and Wet Mill. The Dry Grind one is the most performing in terms of ethanol yield and it will be the theoretical basis of this work. In Figure 1 the Block Flow Diagram of the Dry Grind process (DGP) presently considered is shown. The first four steps of the process are exactly the same of the conventional DGP (details are given in a previous work [1]), while supercritical extraction replaces the distillation and the dehydratation in the downstream processing section. It was shown by Budich and Brunner [2] that supercritical CO_2 extraction of bioethanol at 100 bar and 333.15K is able to break the azeotrope.
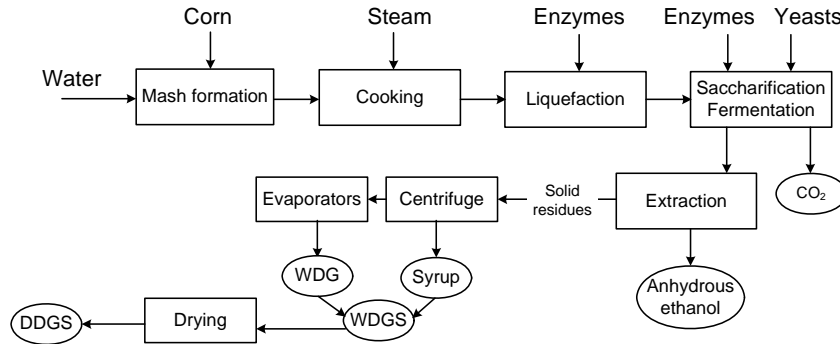

Figure 1 *Block Flow Diagram of the Dry Grind process with supercritical extraction (WDG=Wet Distillers Grains; WDGS=Wet Distillers Grains with Solubles; DDGS=Dried Distillers Grains with Solubles).*

The aim of this work is to study the effect of the integration of supercritical CO_2 extraction of ethanol in a medium scale bioethanol plant from corn, and the comparison of capital costs and operating costs of different technical options with the current process.

SIMULATION MODEL

A model of the process considered was developed using Aspen Plus™ as a process simulator.
Material and energy balances were accounted for and solved for all the process units, whereas no chemical kinetic models were considered in reactor simulation. The plant capacity was 99,378 t/y of bio-ethanol, starting from approximately 41,900 kg/h of corn grain.
The thermodynamics of the vapor-liquid equilibrium at ambient pressure was described by using the NRTL model [5]. Carbon dioxide is defined as a Henry component. For some pairs of compounds the binary parameters of this thermodynamic model are not available in the simulator databank and have been regressed from experimental data. A simplified non fermentable solids composition has been implemented because solids are not involved in VLE equilibrium but they influence the specific heat capacity. In order to represent the high pressure equilibrium an external routine to calculate the partition coefficients, K_i,

$$K_i = \frac{y_i}{x_i} \tag{1}$$

replaced the equation of state models. EOS were not used because of the difficulty to fit accurately the experimental data points available for the ternary system ethanol-water-CO_2 at high pressure. Note that also Peng Robinson equation of state with Wong Sandler mixing rule [6] gave insufficient results. The experimental VLE data from Budich and Brunner [2] were fitted as follows:
First, as shown in Figure 2a, the correlation between the ethanol mole fraction in the liquid phase and its pseudobinary mole fraction in the same phase was obtained. The pseudobinary mole fraction of ethanol in the mixture ethanol –water – CO_2 is defined as:

$$X_{EtOH} = \frac{x_{EtOH}}{x_{EtOH} + x_{H_2O}} \tag{2}$$

where x_i is the mole fraction of component *i* in the liquid phase. The value of the mole fraction of the other components in the liquid phase is easily calculated from X_{EtOH} by means of:

$$x_{H_2O} = \frac{1 - X_{EtOH}}{X_{EtOH}} \cdot x_{EtOH} \qquad (3)$$

$$x_{CO_2} = 1 - x_{EtOH} - x_{H_2O} \qquad (4)$$

Second, also the relation between the ethanol K- value and the pseudobinary ethanol mole fraction in the liquid phase, as well as the relation between the pseudobinary ethanol mole fraction in the supercritical phase and that in the liquid phase were obtained (Figure 2b and 2c).
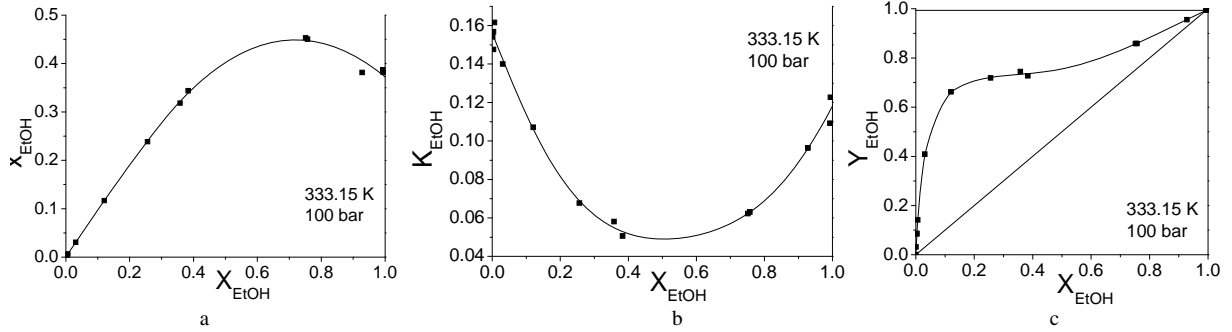

a   b   c

Figure 2 *Fitting of ethanol mole fraction in the liquid phase (a), of the ethanol K value (mole basis) (b) and of the pseudobinary mole fraction of ethanol in the supercritical phase (c) as function of the pseudobinary mole fraction of ethanol in the liquid phase.*

On the base of the VLE equilibrium representation of Figures 2a, 2b, 2c the ethanol mole fraction in the supercritical phase was obtained through:

$$y_{EtOH} = K_{EtOH} \cdot x_{EtOH} \qquad (5)$$

while water and CO_2 mole fraction, in the supercritical phase could be calculated by:

$$y_{H_2O} = \frac{1 - Y_{EtOH}}{Y_{EtOH}} \cdot y_{EtOH} \qquad (6)$$

$$y_{CO_2} = 1 - y_{EtOH} - y_{H_2O} \qquad (7)$$

In order to perform the simulation the extraction column was conveniently split into a cascade of theoretical stages, and Aspen Plus™ was used to solve their mass balances, while energy balances were neglected. The effect of the other components in the extraction unit and also the possibility that using supercritical CO_2 corn oil can be extracted from the ground corn were not taken into account.

THECNICAL EXTRACTION OPTIONS
A number of technical options have been investigated in this work both for the ethanol recovery from the supercritical phase output stream at the top of the extraction column and for the extraction itself. These are summarized as follow:

1st option: In this case supercritical extraction is carried out at 100 bar and 333.15 K while the recovery of the ethanol from the extract (top) is achieved by using an activated carbon adsorber system as proposed by Hagen and Hartwig [7]. In Figure 3a the scheme of the corresponding extraction section is illustrated. The supercritical stream at the top of the extraction columns is sent to an activated carbon column, where only ethanol and water (which is only 0.2%) are absorbed; the whole CO_2 flow rate is recycled to the extraction unit without pressure change except for the friction loss. The regeneration of the activated carbon (removal of alcohol and water) is achieved with CO_2 at 200°C and 10 bar. In this way the ratio between the extraction and the regeneration CO_2 flow rates is around 1.28.
The CO_2 make up and the recompression of the CO_2 hold up in the activated carbon bed can be done by compression of gas from 10 bar to 100 bar (with a compressor) or in two steps: by compressing the gas up to 40 bar with a compressor and then, after condensation, by a pump from 40 bar to 100 bar.

We have identified as 1st/a option the use of compressor up to 100 bar (for both make up and compression of the holdup) whereas 1st/b indicates the coupled system compressor + pump.
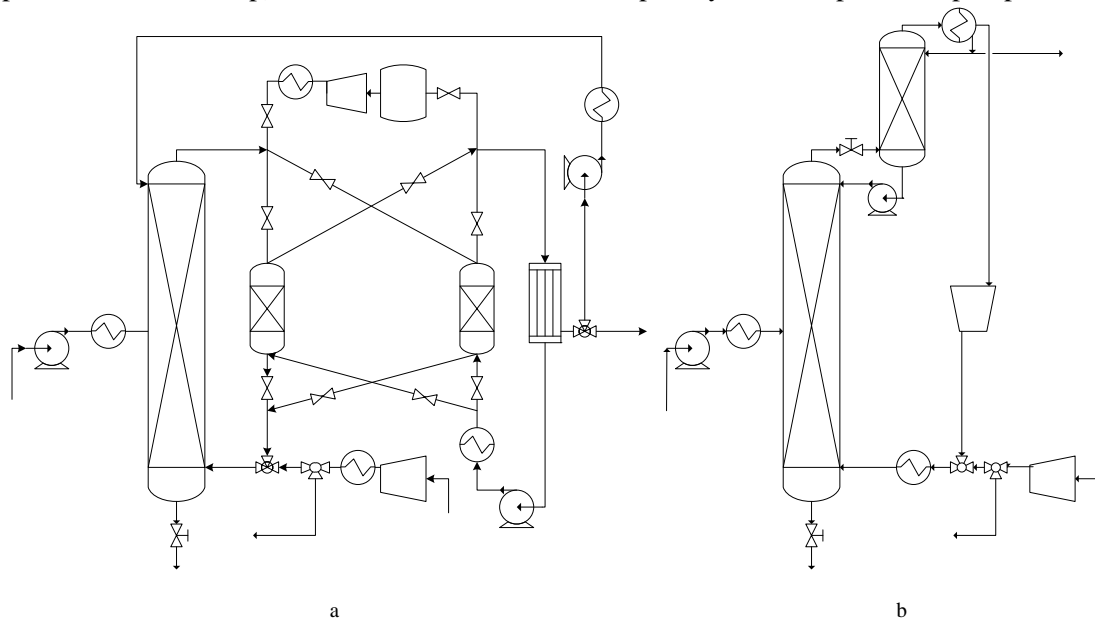
a   b

Figure 3 *Scheme of the 1st /a technical option (a), and of the 2nd /a (b) option.*

2nd option: it includes a supercritical extraction that is carried out at 100 bar and 333.15 K, while the recovery of the ethanol is done by a second distillation column i.e. a distillation tower running at 50 bar of pressure. This idea has been proposed by both Ikawa *et al.* [3] and Budich and Brunner [2]. The distillation is necessary because the simple depressurization to 50 bar does not allow the recovery of enough ethanol from the gas stream to permit the required reflux flow to the extraction unit. The process scheme is in Figure 3b. The CO$_2$ make up from 1 bar to 100 bar can be done as previously outlined, by using a compressor up to 100 bar or by using a compressor up to 40 bar followed by condensation and a pump up to 100 bar. At the same time the recovery of the CO$_2$ at the top of the column can be done by using either a pump if the total condensers is used, or a compressor if the condenser is a partial one. We have identified as 2nd/a option the one which refers to the use of compressor up to 100 bar for both make up and recovery of CO$_2$, instead the 2nd/b option indicates the use of a compressor up to 40 bar and then of a pump up to 100 bar for the make up, while the recompression of the recycled CO$_2$ is done by means of a pump.

3rd option: the extraction is carried out with two different CO$_2$ cycles, as suggest by Zetzl *et al.* [4]. The extraction column works at 100 and 333K but a system of 2 mixer settlers, working at 140 bar and 333.15 K, are added at the bottom of the column in order to strip the ethanol and obtain pure water with less theoretical units and avoiding flooding problems.

SIMULATION AND ECONOMICAL ANALISIS RESULTS
The simulations were carried out for all the three options, and the results obtained were used as input data for the economical analysis.
Basically, our results show that in order to obtain a pseudobinary mass fraction of ethanol of 99.8% at the top and of 0.1% at the bottom of the extraction column an high flow rate of supercritical CO$_2$ is needed (the ratio between CO$_2$ and feed mass flow rates is 19.9 for the 1st option and 20.1, and for the 2nd); also, a large reflux ratio of about 7.2 is required. There is a need of a little CO$_2$ make up, because the most part of the CO$_2$ is recycled. The make up is of 7,571 kg/h for the 1st technical option, and of 4,883 kg/h for the 2nd technical option in both cases they are supplied by the CO$_2$ produced in the fermentation. A calculation based on 80% of the flooding operating condition suggest that 19 extraction columns in parallel have to be arranged, if a Sulzer CY structured packing is used. Plant

investment and operating costs of the traditional distillation process are calculated in another work [1]; here ,to estimate the total costs, the distillation section costs of the traditional process are replaced with the costs for the extraction operations.In Table 1 the capital investment and operating costs of the 1st technical options are compared with those of the traditional process.

Table 1 *Capital investment and operating costs of the conventional process compared with the 1st option ones.*

	traditional process	*1st/a option*	*1st/b option*
Capital investment [€]	70,000,000	275,101,000	266,482,000
Electrical energy [€/y]	5,858,155	14,621,000	10,979,000
Thermal utilities [€/y]	6,101,171	1,928,000	5,873,000

Table 1 underlines that a process that uses supercritical CO_2 extraction needs a much higher capital investment, principally due to the activated carbon system (see the pie charts in Figure 4). At the same time the compressors and pumps need a lot of electrical energy because of the high pressure involved. The option 1st /b requires less energy than 1st /a because compressors are partially replaced by pumps, but at the same time the CO_2 have to be condensed and then warmed up so the use of thermal utilities greatly increases if options 1st/b is adopted.
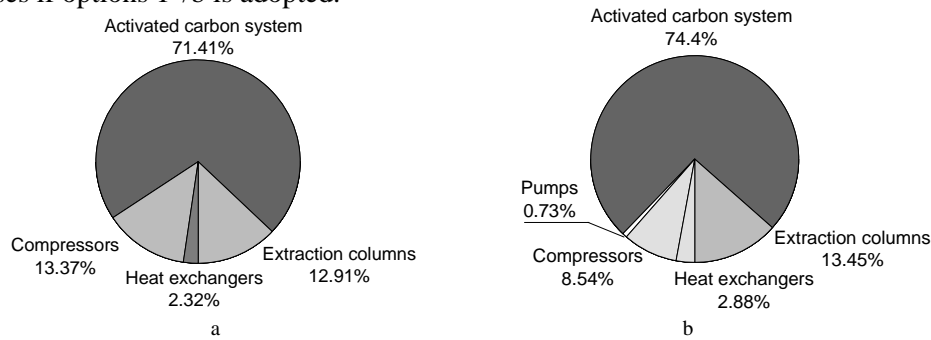

Figure 4 *Distribution of equipment costs for the extraction section for both 1st /a option (a) and 1st /b option (b).*

Table 2 and Figure 5 show that the capital investment for a process with supercritical extraction according to 2nd option is greater than that of the traditional process but is lower than in the case of 1st option.

Table 2 *Capital investment and operating costs of the common process compared with the section option ones.*

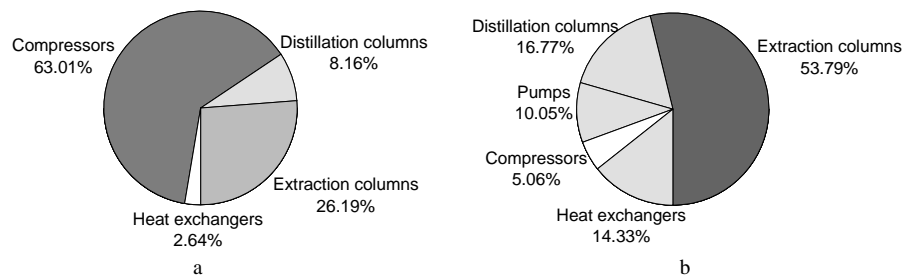|	*traditional process*	*2nd/a option*	*2nd/b option*
Capital investment [€]	70,000,000	166,305, 000	112,052,000
Electrical energy [€/y]	5,858,155	25,465,000	10,226,000
Thermal utilities [€/y]	6,101,171	7,412,000	81,045,000

Figure 5 *Distribution of equipment costs for the extraction section for both 1st /a option (a) and 1st /b option (b).*

Similarly to what occurs for the 1st technical option, the 2nd/a one presents an higher capital investment and electrical consumption than the 2nd/b option, but its thermal utilities consumption is lower.

In these cases the major part of the capital investment is due to the compressor for the 2nd /a option and to the extraction columns for the case 2nd/b. Note that, if activated carbon are used only the hold up has to be compressed from 10 to 100 bar; instead, in the 2nd option, all the CO_2 needed for the supercritical extraction is expanded to 50 bar in order to recover the ethanol, and then has to be recompressed up to 100 bar. For this reason the electrical energy demand of the 2nd /a option is higher than the demand of the 1st /a option and the same thing occurs for the thermal utilities of the 1st /b and 2nd /b options. About 67% of the thermal utilities cost is due to the condensation of the CO_2 in the 2nd /b option. In the diagrams of Figure 5a and 5b the distribution of capital costs are represented

As far as the 3rd option is concerned, its costs are roughly doubled with respect of the option 1 because of the needs of running the extraction section at two different pressures.

Finally it has to be pointed out that the distillation section in the traditional process consist in 3 different distillation columns that work at different pressure (under 5 bar) in order to minimize the energy consumption, while the supercritical extraction needs 19 extraction columns (more expensive because of the high pressure). In addition the 1st option needs a large volume of activated carbon due of their relatively low absorption capacity (417g of ethanol for kg of activated carbon) and each one of these absorption columns (one every extraction column) has to be double because of the batch working condition. The 2nd option, instead, requires distillation columns in order to recover the ethanol but this columns have to treat all the amount of CO_2 and so, because of flooding problem, they are roughly double in number with respect to the extraction columns. Moreover, all the options with supercritical CO_2 would increase the costs further, but they need compressors and pumps. This large number of equipments obviously requires more space and a greater staff in comparison to the traditional process. All these points were not taken into account in the previous economical analysis.

CONCLUSIONS
In this work it was shown by process simulation that the production of anhydrous ethanol by means of CO_2 extraction is technically possible and the amount of CO_2 obtained in the fermenter (13,109 kg/h) is enough to supply the required makeup of the extraction for all the technical options considered. However, due to the low ethanol loading of CO_2, a great quantity of CO_2 is needed and this leads to a large number of extraction columns and great operating costs and capital investment for the recovery of the ethanol by supercritical fluid extraction.
In summary, at present the integration of supercritical CO_2 extraction into existing bioethanol production is attractive, technically feasible, but it is not economic.

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