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LCA case study: comparison between independent and coproduction pathways for the production of ethyl and *n*-butyl acetates

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Abstract

Purpose The production of ethyl acetate and *n*-butyl acetate was investigated through two different pathways: either by independent reactions or by coproduction. In the coproduction pathway, the *n*-butyl acetate was produced by reusing the by-products of the synthesis of ethyl acetate. This study provides a comparison of the environmental impacts of these two pathways using a life cycle assessment (LCA). A discussion about the use of LCA on chemicals and its challenges was also developed.

Methods Ethyl acetate and *n*-butyl acetate were synthesized with maximum respect to the principles of green chemistry (use of heterogeneous catalyst, energy savings, minimum steps). An innovative pathway was developed to avoid waste production, by reusing all the by-products of syntheses. After characterizing the feasibility of using these solvents in paint formulations, their potential impacts on the environment were evaluated through a cradle to gate analysis, up to the synthesis at laboratory scale. Most of the foreground data were directly collected with experimental trials. The background data that were not available in the Ecoinvent 3.1 database were estimated thanks to literature or proxys. Evaluations were then performed on the SimaPro 8.1.1 LCA software, using a derivative of ILCD 2011 1.05 as life cycle impact assessment methodology.

Results and discussion The coproduction of both acetates led to the synthesis of purified ethyl acetate (purity of 92.1% *w/w*) and *n*-butyl acetate (purity of 97.1% *w/w*), after distillation. These results were quite similar to those obtained when independent syntheses were carried out. On an environmental point of view, it was found that the reagents preparation was always the step of the process responsible of the majority of the environmental impacts. The comparison between independent syntheses and coproduction showed that recycling the acetic acid produced during the first esterification (ethyl acetate from ethanol and acetic anhydride) led to a decrease of the impacts from 5 to 23% for all the impact categories.

Conclusions This innovative coproduction of ethyl and *n*-butyl acetates led to interesting results from both a technical and environmental perspective, with a clear reduction of the environmental impacts. In a context of sustainable chemistry, this appears to be a very interesting way of production. Concerning the LCA of chemicals, a lot of work is still needed in order to improve the accuracy and the reliability of the assessment.

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1 Introduction

Nowadays, the global consumption of solvents is significant, with almost 28 million metric tons consumed in 2012 (Linak and Bizzari 2013). The most important users are the producers of paints and coatings (60.6% in 2011 of the total consumption). This demand is predicted to increase by 2.9% per year until 2019 (Ceresana 2014). Solvents in the paint industry can be used as integral part of the formulation for homogenization

or adjustment of the viscosity, as paint thinner by post-addition to adjust application properties or even as cleaning agent for equipment for example.

Ethyl acetate (EtAc) and *n*-butyl acetate (*n*-BuAc) are one of the most used solvents (Steinigeweg and Gmehling 2002; Khire et al. 2012). They have been commonly synthesized through direct esterification of acetic acid with the corresponding alcohol (ethanol for ethyl acetate and *n*-butanol for *n*-butyl acetate), in the presence of a homogeneous acid catalyst, usually sulfuric acid or *p*-toluenesulfonic acid (PTSA) (Chen et al. 1999; Peters et al. 2006; Bamunusingha et al. 2016). The use of these homogeneous catalysts presents many disadvantages such as the production of by-products due to multiple side reactions, the difficult product/catalyst separation, and the equipment corrosion. In order to avoid these problems and in a context of sustainable development, the use of heterogeneous catalysts for esterification such as ion exchange resins (Steinigeweg and Gmehling 2002; Gangadwala et al. 2003; Sert and Atalay 2011), montmorillonite (Gurav and Bokade 2010), or even sulfated zirconia (El-Sharkawy and Al-Shihry 2004; Khire et al. 2012) has been studied.

However, as the esterification is an equilibrium-limited reversible reaction, the yield and conversion of the reactants are generally quite low (limited to 66%), due to thermodynamics limitations (Sert and Atalay 2011; Cho et al. 2014). In order to increase the ester formation, either the alcohol can be introduced in excess or one product, usually water, can be removed from the reactive medium all along the reaction. The equilibrium will be thus shifted to the products formation. In the literature, the most reported technique to achieve this goal is to use reactive distillation process (Hanika et al. 1999; Lederer et al. 2002; Arpornwichanop et al. 2008; Fernandez et al. 2013; Santaella et al. 2015). Indeed, in the case of the synthesis of acetates using acetic acid, the reaction is rather complicated to handle as the esterification leads to the formation of an important quantity of water that will be difficult to separate from the acetate due to azeotropes formation (Gould 1973). The reactive distillation process, where chemical reaction and distillation are combined in a single unit, helps this separation. Nevertheless, it presents many drawbacks: the process is complex, expensive, and not easily transposable at different scales and several disadvantages were observed, linked to the experiment itself (volatility requirement, temperature and pressure compatibility, and long catalyst lifetime) (Lutze and Górak 2016).

In this project, in order to avoid these problematics while maximizing the reaction yield, it was decided to replace the reactive distillation process by a simple esterification. Moreover, acetic acid was replaced by acetic anhydride. The use of anhydride avoids azeotropes formation and thus enhances the products separation through distillation. A coproduction pathway to produce both ethyl and *n*-butyl acetates was thus investigated (Fig. 1): the use of acetic anhydride for

the ethanol esterification led to the production of ethyl acetate and acetic acid (AcA) that can be reused for *n*-butanol esterification; the same catalyst being also reused for the second reaction. This process can minimize reaction steps and so waste production.

A coproduction of EtAc and *n*-BuAc, through reactive distillation, has already been presented by Tian et al. (2015) but only by simulation, with acetic acid as starting material. In our case, these consecutive syntheses were carried out, through experiments, in the simplest reactor that can be easily adapted either at laboratory or industrial scale and abiding by the principles of green chemistry (use of heterogeneous catalyst, soft reaction conditions).

In order to evaluate from an environmental point of view the chemical pathway developed, life cycle assessment (LCA) was used as a decision tool. Indeed, this standardized and accurate method consists in measuring and comparing the potential environmental impacts of these production processes on their entire life cycle, i.e., from cradle to the laboratory gate (in our case).

In this study, both independent syntheses of the esters (scenario 1) and coproduction (scenario 2) were modeled, after a complete inventory at laboratory scale. The results were compared to highlight the interest of this new coproduction pathway on an environmental point of view.

2 Materials and methods

2.1 Esterification of ethyl acetate and *n*-butyl acetate

2.1.1 Chemicals

Ethanol, *n*-butanol, acetic anhydride, acetic acid, cyclohexane, and methyl isobutyl ketone, all at analytical grade, were purchased from Sigma-Aldrich Co. (France). Sodium chloride and Dowex 50WX8 resin (measured capacity = 4.8 meq/g) were also obtained from Sigma-Aldrich Co. (France).

2.1.2 Procedure

Scenario 1 (Sc 1): independent syntheses Both esterifications were carried out in a 2-L glass jacketed stirred reactor.

For the production of ethyl acetate, ethanol (EtOH, 400 g) and acetic anhydride (AcAn, 889 g) were added into the reactor, followed by the incorporation of the dried heterogeneous catalyst, Dowex 50WX8 (20 g, i.e., 5 wt.% respect of the mass of ethanol). The reagent amounts were calculated according to the desired molar *ratio* (1:1 EtOH–AcAn).

The system was left at room temperature for 4 h, the reaction being highly exothermic, under mechanical stirring. After the reaction, the produced ethyl acetate (665 g) was recovered
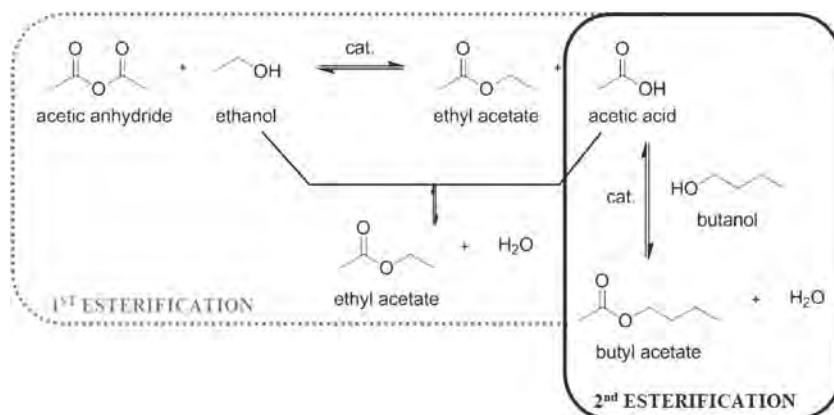
through distillation in order to improve the purity of the de-
sired ester (yield = 87%, purity = 92.1% *w/w*).

For the production of *n*-butyl acetate, *n*-butanol (*n*-
BuOH, 800 g) and acetic acid (AcA, 648 g) were added
into the reactor in the appropriate amount (molar *ratio* 1:1
alcohol–acid). The catalyst, previously dried, was then in-
corporated to the reactor (40 g, i.e., 5 wt.% respect of the
mass of butanol). A Dean-Stark apparatus was used, in the
presence of a small amount of cyclohexane (80 mL, i.e.,
5% *v/v* respect of the volume of the reaction mixture), in
order to remove the produced water from the reaction me-
dium and so improve the yield of esterification. The reac-
tion was carried out at 105 °C, under mechanical stirring,
until all the water was distilled out (approximately 8 h).
The remaining cyclohexane was then removed from the
system through a simple distillation. The *n*-butyl acetate
(953 g) was finally collected after catalyst separation
(yield = 76%, purity = 97.4% *w/w*).

**Scenario 2 (Sc 2): coproduction of ethyl acetate and *n*-butyl
acetate** In the coproduction scenario, ethyl acetate was syn-
thesized following the protocol described in scenario 1.

After ethyl acetate distillation, the remaining media, con-
taining the acetic acid formed during the EtAc synthesis and
the catalyst Dowex 50WX8, was respectively used as reagent
and catalyst for the production of *n*-butyl acetate. *n*-Butanol
(BuOH, 498 g) was then added into the reactor in an equimo-
lar amount compared to the acetic acid.

On the reactor, a Dean-Stark apparatus was used, in the pres-
ence of a small amount of cyclohexane (50 mL, i.e., 5% *v/v*
respect of the volume of the reaction mixture), in order to elim-
inate the produced water and so improve the esterification yield.
The reaction was carried out at 105 °C, under mechanical stir-
ring, until all the water was distilled out (approximately 8 h). The
remaining cyclohexane was then removed from the system
through a simple distillation. The *n*-butyl acetate (538 g), obtain-
ed by coproduction, was collected after catalyst filtration
(yield = 69%, purity = 97.1% *w/w*).

2.1.3 Analyses methods

Gas chromatography analyses, for the quantification of alco-
hol, acid, and ester, were carried out using a Varian 3900 gas
chromatograph equipped with a flame ionization detector
(FID). Separation was made in a capillary column (DB-624,
Agilent—30 m × 0.25 mm, 1.4 μm film thickness). Helium
was used as carrier gas at a flow rate of 1.1 mL/min. The
injector and detector were both maintained at the temperature
of 300 °C. The oven temperature was programmed as follows:
50 °C for 2 min, then rise at 100 °C at a rate of 5 °C/min, and
finally rise at 190 °C at a rate of 25 °C/min. The injected
volume was 1 μL with a split *ratio* of 1:100. Quantitative
analyses were performed thanks to the use of an internal stan-
dard (methyl isobutyl ketone).

The water content of the solution was characterized by Karl
Fisher titration.

2.2 Life cycle assessment

The life cycle assessment was undertaken using the ISO
14040 (2006) and ISO 14044 (2006) standards: the first one
defining the principles and the framework and the second one
describing the different stages of the analysis.

2.2.1 Goal and scope definition

The life cycle assessment was conducted on the solvent pro-
duction process in order to analyze the environmental impacts
of the developed synthetic pathways and identify the process
unit that presents the strongest impacts through a hot spot
analysis. The comparison between the two scenarios (inde-
pendent or coproduction syntheses) was also investigated.

In order to build the inventory of production, it was neces-
sary to define the functional unit. The functional unit chosen
was the production of 1 kg of solvent, with a purity deter-
mined experimentally, as presented typically in the literature
(Wang et al. 2013; Dias et al. 2014; Pereira et al. 2015).

To focus only on the impacts related to the production of these solvents in the laboratory, it was decided to carry out a "cradle to gate" analysis centered on the raw material acquisition and on the production step (Fig. 2).

For the modeling, initial hypotheses were defined as follows:

- The energy used was considered as a French energy mix.
- The cleaning of all the devices is neglected.
- The transportation of the chemicals is estimated as follows: 600 km by train followed by 100 km by lorry with a capacity greater than 32 tons (EVEA 2015).
- The depreciation of the infrastructures is estimated to be equal to $4 \cdot 10^{-10}$ p/kg of product (value based on a production of 50.000 tons of products over 50 years) (estimation as described in the Ecoinvent database).
- 0.2% of the mass of the used chemicals are emitted directly into the air (estimation as described in the Ecoinvent database).
- The whole wastes and emissions are fully treated by the sewage plant, i.e., the sewage plant is considered with an efficiency of 100%.

2.2.2 Life cycle inventory

The most important task in a LCA study is the data collection. Two types of data have to be distinguished: the foreground data and the background data.

The foreground data, on the one hand, refer to specific data needed to model the system. They include all the measurements collected directly on experimental devices and all the estimated data that are not directly available. On the other hand, the background data are usually related to energy, transport, and waste materials. They are mostly available in databases (in our case, the Ecoinvent 3.1) or in the literature.

System description For the life cycle inventory, all the inputs and outputs of the system were listed for the different stages of the syntheses, either for the independent pathways (scenario 1) or for the coproduction (scenario 2).

The flowcharts, showing the different steps of the processes with the associated flows, are presented in Fig. 3 for the independent esterifications and in Fig. 4 for the coproduction.

Noteworthy, all the foreground data detailed in Figs. 3 and 4 present their own life cycle that are taken into account for modeling the global life cycle of the ester syntheses.

Some differences between the two flowcharts (Figs. 3 and 4) can be highlighted. Indeed, the aim of the coproduction is to recycle the remaining mixture after ethyl acetate distillation. These wastes are used, without any treatment, as reagents for the second esterification performed in series. The catalyst that is in the remaining mixture is still active after the first cycle. Indeed, the value of the ion exchange resin capacity was not modified after the synthesis of ethyl acetate (4.8 meq/g).

Data collection The inventory data, also called foreground data, were collected directly in the laboratory by the experiments. They were considered relatively reliable compared to those from the literature.

The emission and extractions data, or background data, were obtained from the Ecoinvent 3.1 database. If possible, the French (FR) or even the European (RER) data were used in order to be consistent on the geographic point. In other cases, the data from the global market (GLO) were considered.

Unfortunately, all the chemicals were not available in the used database. In order to overcome this problem, that could affect the modeling of the environmental performance of the syntheses, proxys and bibliographic study were used.

The data used in the analyses and their sources are presented in Table 1.

Before any modeling, the quality of the data needed to be estimated in order to guarantee the value and reliability of the

Fig. 2 System boundaries of the life cycle assessment of this study
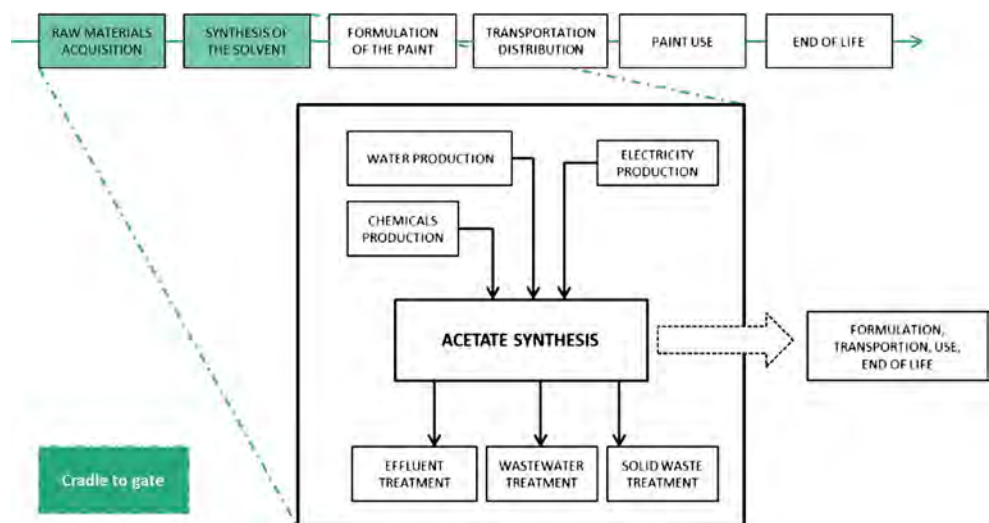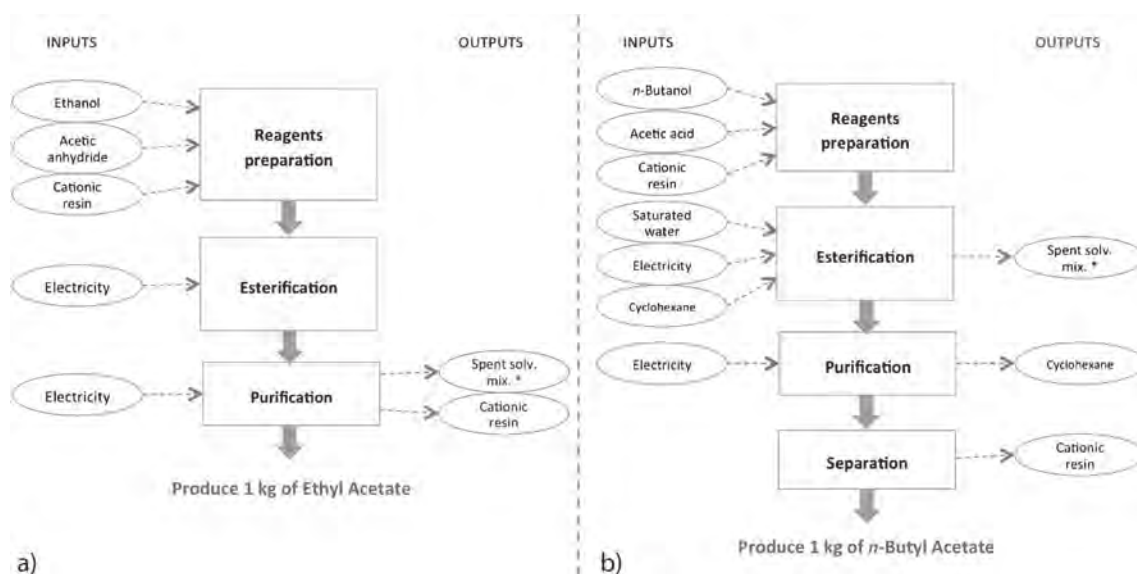
Fig. 3 Process flowchart of the independent syntheses of ethyl acetate (**a**) and *n*-butyl acetate (**b**) (the *asterisk* represents spent solvent mixture)

data used in the life cycle assessment. In this study, all the data were not of equivalent accuracy and uncertainty existed between them. It was thus necessary to evaluate this uncertainty that could affect the interpretation of the results.

For this, the quality indicators developed by Weidema and Wesnaes (1996) were used. Table 2 summarizes the reliability ratings of each type of data (the reliability being assessed by a score from 1 for the maximum to 5 for the minimum).

2.2.3 Impact assessment

To characterize the different environmental impacts, a derivative of the ILCD 2011 1.05 method was used. Indeed, in the existing method, indicators of resource depletion (water and mineral, fossil, or renewable resources) were not sufficiently reliable (EVEA 2015). These indicators have thus been replaced by a water flow indicator (corresponding to the "water depletion" indicator of the ReCiPe method) and an energy consumption indicator, based on the cumulative energy demand method. The 17 midpoint impact categories used are presented in Table 3.

The inventory and the impact calculations were performed on the SimaPro 8.1.1 software.

3 Results and discussion

3.1 Synthesis of ethyl acetate and *n*-butyl acetate

3.1.1 Independent pathways

Synthesis of ethyl acetate The strategy to use ethanol and acetic anhydride, instead of acetic acid used mostly in the literature for the production of ethyl acetate (Gurav and

Bokade 2010; Santaella et al. 2015), was developed in order to avoid the formation of water during the synthesis.

Indeed, starting from ethanol and acetic acid, for 1 mol of ethanol, 1 mol of water is produced. At the end of the esterification, this production of water lead to difficulties in purification, as the ethyl acetate forms azeotropes with water and also with the remaining ethanol (Tavan and Hosseini 2013). One promising solution to break this azeotrope water/ethanol/ethyl acetate is the pervaporation (Hasanoğlu et al. 2009; Hu et al. 2012; Ong and Tan 2016). In our case, starting with a mixture of ethanol and acetic anhydride at an equimolar ratio leads to the formation of ethyl acetate and acetic acid, easily separable by distillation. Noteworthy, as the reaction is highly exothermic, there is a competition between the reaction of ethanol with acetic anhydride and the acetic acid that was formed during this reaction. The acetic acid reacts with the remaining ethanol, all along the synthesis and thus led to a nearly total conversion of the ethanol and the formation of a small amount of water that will not disrupt the purification of the acetate.

The composition of the obtained crude reaction medium, before distillation, is presented in Table 4.

In order to separate and purify ethyl acetate, a distillation was carried out and the results are presented in Table 5.

After the laboratory distillation, ethyl acetate was obtained at a purity of 92.1% *w/w*, acetic acid and water still being present in the distillate.

When the distillation was stopped, 43.8% *w/w* of the medium still remained in the reactor, with a composition of 77.5% *w/w* of acetic acid and 22.5% *w/w* of ethyl acetate. Thus, a way of recycling needed to be considered.

Synthesis of *n*-butyl acetate In the case of *n*-butyl acetate, the use of *n*-butanol and acetic acid at a molar *ratio* of 1:1, in the presence of a heterogeneous catalyst, led to the formation of

Fig. 4 Process flowchart of the coproduction of ethyl acetate and *n*-butyl acetate
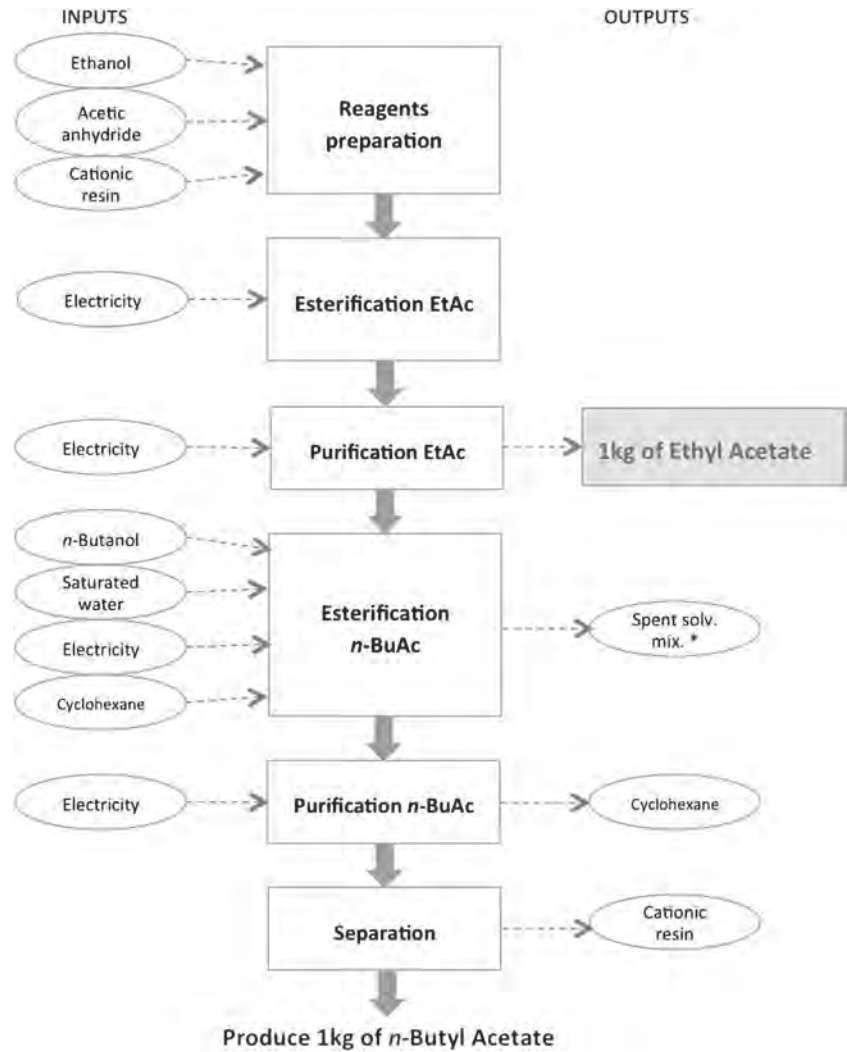
1 mol of water per mole of *n*-butyl acetate. It is thus mandatory to remove continuously the produced water in order to shift the equilibrium and so enhance the ester formation. The use of a Dean-Stark apparatus, in the presence of a small

Table 1 Source of the data used in the LCA

Data	Source
Ethanol without water in 99.7% solution slate, from ethylene {GLO} / market for	Ecoinvent 3.1
1-Butanol {GLO} / market for	Ecoinvent 3.1
Acetic anhydride {RER} / market for	Ecoinvent 3.1
Acetic acid, without water, in 98% solution slate {GLO} / market for	Ecoinvent 3.1
Cationic resin {GLO} / market for	Proxy
Cyclohexane {GLO} / market for	Ecoinvent 3.1
Sodium chloride, powder {GLO} / market for	Ecoinvent 3.1
Water, deionized, from tap water, at user {GLO} / market for	Ecoinvent 3.1
Transport, freight train {CH} / market for	Ecoinvent 3.1
Transport, freight, lorry >32 metric tons, EURO 3 {GLO} / market for	Ecoinvent 3.1
Chemical factory, organics {GLO} / market for	Ecoinvent 3.1
Electricity, medium voltage {FR} / market for	Ecoinvent 3.1
Spent solvent mixture {CH} / treatment of hazardous waste incineration	Ecoinvent 3.1

Table 2 Evaluation of the reliability of the inputs and outputs (with score from 1 being the best and 5 the worst)

Data	Comments	Quality rating (reliability)
Inputs		
Chemicals mass	The mass of chemicals has been precisely measured during the synthesis.	1
Energy	The quantity of energy needed for the synthesis has been calculated, by using the operation time of each devices and their technical characteristics. These data could not have been measured.	3
Transportation distances	The transportation distances, either by lorry or train, have been determined through hypothesis. This is an estimation of average distance for the transport of chemicals.	3
Infrastructure depreciation	The depreciation of the infrastructure (regarded as a chemical plant) is estimated from the mean values over the entire life of the plant.	3
Outputs		
Emissions into air	Emissions to air are derived from assumptions.	3
By-products masses (avoided products)	The masses of avoided products that can be recycled or recovered are measured precisely during the synthesis.	1
Masses of waste treatment	The masses of waste treatment are measured precisely during the synthesis.	1

amount of cyclohexane, was decided in order to produce and remove the azeotropic mixture cyclohexane/water and so increase the reaction yield. The composition of the medium obtained after the separation is presented in Table 6.

Table 3 Midpoint impact categories used for the evaluation method (a derivative of the ILCD 2011 1.05 method)

Midpoint impact categories	Description	Unit
Climate change	Emissions of greenhouse gases that cause an increase in temperature of the lower atmospheric layers (for example CO_2, CH_4, N_2O, CFC, CO…)	kg CO_2 eq
Ozone depletion	Air emissions of substances that destroy the stratospheric ozone layer (for example CFC, HCFC, CCl_4…)	kg CFC −11 eq
Human toxicity, cancer effects	Emissions to soil, water, and air of substances that harm human health (for example heavy metals, dioxins, VOC, NOx, SO_2, particulates…) with carcinogenic effects	CTUh
Human toxicity, non-cancer effects	Emissions to soil, water, and air of substances that harm human health (for example, heavy metals, dioxins, VOC, NOx, SO_2, particulates…) with non-carcinogenic effects	CTUh
Particulate matter	Air emissions of particulate matter less than 2.5 µm	kg PM2.5 eq
Ionizing radiation, human health	Ionizing radiation, with impacts on human health	kgBq ^{235}U eq
Ionizing radiation, ecosystems	Ionizing radiation, with impacts on ecosystems	CTUe
Photochemical ozone formation	Air emissions of substances that cause the production of tropospheric ozone or smog (for example NOx, VOC, CH_4, CO…)	kg NMVOC eq
Acidification	Air emissions of substances that cause acid rain (for example NOx, SO_2, NH_3, VOC, HCl...)	molc H^+ eq
Terrestrial eutrophication	Emissions to air and water of substances that cause an excess of nutrients (for example components containing N and P)	molc N eq
Freshwater eutrophication	Emissions to air and water of substances that cause an excess of nutrients in lakes, rivers, and oceans (for example components containing N and P)	kg P eq
Marine eutrophication	Emissions to air and water of substances that cause an excess of nutrients in marine water (for example components containing N and P)	kg N eq
Freshwater ecotoxicity	Emissions to water and air of substances that damage the ecosystems (flora and fauna) in fresh water (for example heavy metals, acids, pesticides…)	CTUe
Land use	The occupation by men of a certain area of agricultural land for a certain period for agriculture and the landscape changes or space resulting	kg C deficit
Mineral, fossil, and renewable resources depletion	Environmental depletion of mineral, fossil, and renewable resources. The calculation performed is based on the remaining stocks and on the current consumption rates	kg Sb eq
Water flow	Environmental depletion of water. The calculation performed is based on the remaining stocks and on the current consumption rates	m3
Non-renewable energy consumption	Quantification of the energy content of non-renewable energy resources (fossil, nuclear, and biomass)	MJ

Table 4 Quantitative analysis of the crude reaction medium, without purification (standard deviation = ±2%)

Conversion of EtOH (%)	Yield of EtAc (%)	Composition of the reaction medium			
99.4	98	AAc (mol %)	EtOH (mol %)	EtAc (mol %)	H_2O (mol %)
		48.4	0.3	48.5	2.8
		AAc (% w/w)	EtOH (% w/w)	EtAc (% w/w)	H_2O (% w/w)
		40.1	0.2	59.0	0.7

After distillation, *n*-butyl acetate was obtained at a purity of 97.1% *w/w*, containing very small amounts of butanol, acetic acid, and water. The yield of formation of *n*-butyl acetate is a bit lower than the one of ethyl acetate (76% compared to 87%) as two successive distillations are needed to recover the desired acetate (water elimination followed by cyclohexane distillation). In each distilled fractions, traces of *n*-butyl acetate were revealed.

3.1.2 Coproduction of ethyl acetate and n-butyl acetate

After studying both ethyl acetate and *n*-butyl acetate separately, their coproduction was investigated. The wastes of the ethyl acetate purification, i.e., a mixture composed of 77.5% *w/w* of acetic acid and 22.5% *w/w* of ethyl acetate, were reused as reactants for the *n*-butyl acetate production. The heterogeneous catalyst was also recycled in the second esterification. The composition of the distillated *n*-butyl acetate after the coproduction process is presented in Table 7.

The use of acetic acid mixed with ethyl acetate, recycled from the first esterification, did not affect the production of the desired ester as a mixture highly enriched in *n*-butyl acetate (97.1% *w/w* of purity after coproduction vs 97.4% *w/w* after the independent esterification) was obtained. It is thus an interesting way of production of *n*-butyl acetate that minimizes waste production and so treatment by sewage plants.

3.2 Life cycle assessment

After characterizing the products obtained either by independent esterifications (scenario 1) or by coproduction (scenario 2), the feasibility of using them as part of paint formulation was evaluated by TECNALIA (European project ECOBIOFOR pending).

As both solvents presented interesting properties, their processes were compared through a life cycle analysis. The environmental impacts of the chemical reactions were assessed according the functional unit (FU) defined previously as the production of 1 kg of purified solvent. Only the purified esters (ethyl acetate and *n*-butyl acetate) were considered for this study.

3.2.1 Life cycle assessment of the independent syntheses (scenario 1)

In this study, the acetates were only produced at laboratory scale: the scale-up optimization was not investigated. Therefore, the developed processes were not compared to the industrial ones, available in the databases, as this comparison would not be relevant.

Life cycle assessment of the ethyl acetate production
According to the process flowchart of the ethyl acetate production through Sc 1 (Fig. 3) and the experimental analysis of the obtained medium (Table 5), the inventory data (Table 8) have been collected via experiments and by using the hypotheses described in Section 2.2.1.

The results of the assessment of the ethyl acetate production are presented in Fig. 5.

It clearly appears that the reagents preparation step presents the most significant environmental impacts (between 53 and 84%) for 13 of the 17 impact categories. These results can be explained by the strong impacts generated by the production of acetic anhydride involving in particular the use of acetic acid. In the case of the four other impact categories (ozone depletion, ionizing radiation HH, ionizing radiation E, and non-renewable energy consumption), the purification step

Table 5 Quantitative analysis of the isolated ethyl acetate, after purification (standard deviation = ±2%)

Conversion of EtOH (%)	Yield of EtAc (%)	Composition of the reaction medium			
99.4	87	AAc (mol %)	EtOH (mol %)	EtAc (mol %)	H_2O (mol %)
		9.1	0.0	85.4	5.4
		AAc (% w/w)	EtOH (% w/w)	EtAc (% w/w)	H_2O (% w/w)
		6.7	0.0	92.1	1.2

Table 6 Quantitative analysis of the isolated *n*-butyl acetate, after purification (standard deviation = ±2%)

Conversion of *n*-BuOH (%)	Yield of *n*-BuAc (%)	Composition of the reaction medium			
99	76	AAc (mol %)	*n*-BuOH (mol %)	*n*-BuAc (mol %)	H_2O (mol %)
		0.8	1.7	91.2	6.4
		AAc (% w/w)	*n*-BuOH (% w/w)	*n*-BuAc (% w/w)	H_2O (% w/w)
		0.4	1.1	97.4	1.1

has the greatest impact on the environment, due to a large consumption of electricity during 8 h. For example, the potential "human toxicity, cancer effects" impact was $3.85 \cdot 10^{-7}$ CTUh, with a contribution of the reagents preparation step of $2.53 \cdot 10^{-7}$ CTUh and of acetic anhydride itself of $1.98 \cdot 10^{-7}$ CTUh, corresponding to 51.5% of the total impact. These results are in line with those presented in the works of Domènech et al. (2002), Wang et al. (2013), and Groslambert and Léonard (2014). They highlighted that the main environmental impacts came from the burdens associated with the production of reactants. One way for improving these LCA results could be the use of greener reactants produced either from biomass or with a greener and more direct process.

Life cycle assessment of the *n*-butyl acetate production
Before modeling the chemical production of *n*-BuAc, the inventory data were collected and are reported in the Table 9.

The results of the assessment of the *n*-butyl acetate production are presented in Fig. 6.

As for the ethyl acetate production, the reagents preparation step is responsible for the majority of the environmental impacts (12 impact categories out of 17). This observation can be explained by the use of *n*-butanol as a reactant and especially the use of propylene related to its production. For the five other impact categories (ozone depletion, ionizing radiation HH, ionizing radiation E, freshwater ecotoxicity, and non-renewable energy consumption), the impact of the electricity consumption can be highlighted, with a major role for the esterification and purification steps. Noteworthy, as the cyclohexane was recovered after distillation and recycled, it does not contribute to environmental impacts in the esterification step.

These conclusions (high quantity of reactants and energy intensive processes such as distillation) are also presented in Jödicke et al.'s work (1999) as important contributors on the LCA.

3.2.2 Life cycle assessment of the coproduction (scenario 2)

After studying both esterifications separately (scenario 1), they were investigated according to a coproduction process (scenario 2) where the coproducts of the first synthesis were recycled in the second one. As presented in the process tree detailed in Fig. 4, the functional unit of this coproduction is the production of 1 kg of *n*-BuAc, using the acetic acid from the synthesis of EtAc. It is thus needed to determine the quantity of initial reactants to obtain the sufficient amount of acetic acid to produce 1 kg of *n*-BuAc, knowing the characteristics of the esterifications (Tables 5 and 7). According to our calculation, 1.141 kg of EtAc must be synthesized in order to recover the 0.749 kg of acetic acid needed for the production of 1 kg of *n*-BuAc.

The inventory data of this coproduction were collected directly through our experiments at laboratory scale (Table 10).

Noteworthy, the spent solvent mixture considered as wasted from the "Esterification *n*-BuAc" step (as presented Fig. 4) was composed of a mixture of reagents and products (*n*-butanol, acetic acid, ethyl acetate, *n*-butyl acetate, and water).

These inventory data were then connected to the environmental damages caused by the substances inventoried, as presented in Fig. 7.

The results obtained through LCA, for the coproduction (scenario 2), seem to be quite similar to those obtained for

Table 7 Quantitative analysis of the distilled *n*-butyl acetate, obtained by coproduction (standard deviation = ±2%)

Conversion of *n*-BuOH (%)	Yield of *n*-BuAc (%)	Composition of the reaction medium					
94	69	AAc (mol %)	*n*-BuOH (mol %)	EtOH (mol %)	*n*-BuAc (mol %)	EtAc (mol %)	H_2O (mol %)
		0.2	2.9	0.0	92.7	0.2	3.9
		AAc (% w/w)	*n*-BuOH (% w/w)	EtOH (% w/w)	*n*-BuAc (% w/w)	EtAc (% w/w)	H_2O (% w/w)
		0.1	1.9	0.0	97.1	0.2	0.6

Table 8 Inventory data for the ethyl acetate esterification

	Reagents preparation	Esterification	Purification
Inputs			
Ethanol (kg/FU)	0.601	–	–
Acetic anhydride (kg/FU)	1.332	–	–
Cationic resin (kg/FU)	0.030	–	–
Transport, train (kgkm/FU)	1177.7	–	–
Transport, lorry (kgkm/FU)	196.3	–	–
Chemical factory (p/FU)	$4 \cdot 10^{-10}$	–	–
Electricity (kWh/FU)	–	1.4	18.8
Outputs			
Ethanol—into air (kg/FU)	$1.202 \cdot 10^{-3}$	–	–
Acetic anhydride—into air (kg/FU)	$2.664 \cdot 10^{-3}$	–	–
Cationic resin—avoided product (kg/FU)	–	–	0.030
Spent solvent (kg/FU)	–	–	0.847

independent esterifications (scenario 1): the reagents preparation step is still the one responsible of the majority of the environmental impacts for 13 impact categories. A deeper comparison between both scenarios has been made. Noteworthy, as the scenario 2 generates 1.141 kg of ethyl acetate and 1 kg of *n*-butyl acetate; the same factors were used for the scenario 1, i.e., the impacts caused by the synthesis of the ethyl acetate were multiplied by 1.141.

Actually, by studying these results deeper and comparing in more details those two different processes, it appears that the coproduction presents lowest impacts on the environment (Fig. 8).

These results have been confirmed by a Monte Carlo analysis, over 5000 iterations (Fig. 9).

Indeed, for all the 17 impact categories evaluated in the method, processing the ethyl acetate and *n*-butyl acetate syntheses in parallel (Sc 1) had a higher probability of occurrence than the coproduction (Sc 2), that is to say

that there is more chance that Sc 1 creates more impacts on the environment than Sc 2.

These results can essentially be explained by the recycling of the acetic acid produced through the ethyl acetate esterification, by using acetic anhydride. This recycling also led to a reduction of the quantity of spent solvent to be treated by incineration or wastewater treatment plant, and so the substances emitted by these treatments. Moreover, as the ion exchange resin was also recycled; it avoided effluent consumption needed for potential treatment.

3.3 Challenges for life cycle assessment of chemical syntheses

In this study, we have faced several problems due to the lack of LCA perspective in the chemical field.

Fig. 5 Hot spot identification of the ethyl acetate production—impact characterization by a derivative of the ILCD 2011 1.05 method
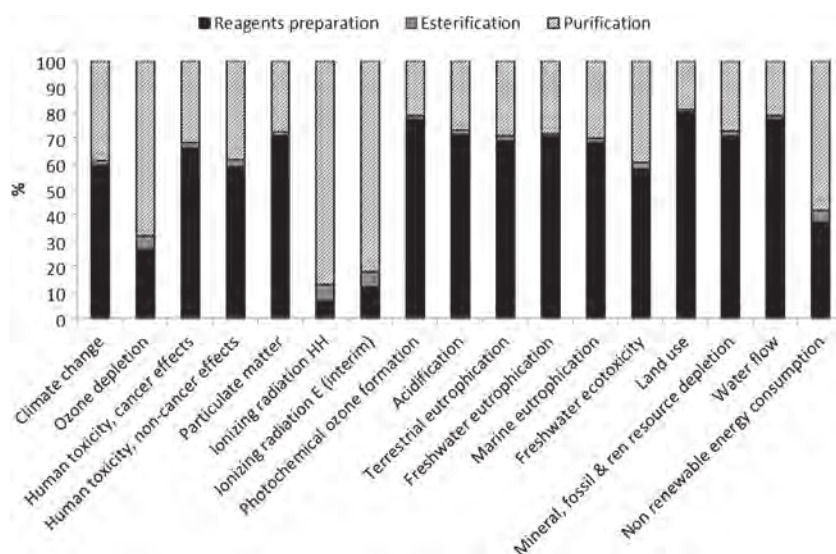
Table 9 Inventory data for the *n*-butyl acetate production

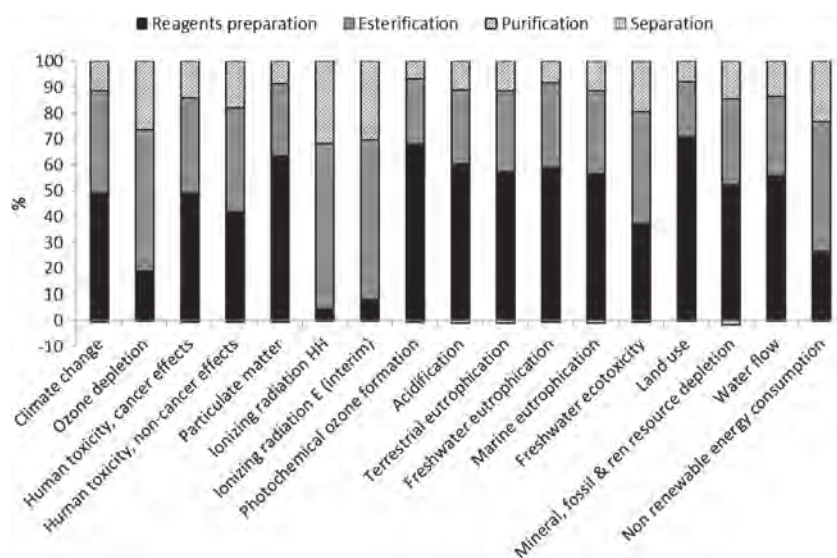|	Reagents preparation	Esterification	Purification	Separation
Inputs				
1-Butanol (kg/FU)	0.840	–	–	–
Acetic acid (kg/FU)	0.680	–	–	–
Cationic resin (kg/FU)	0.042	–	–	–
Cyclohexane (kg/FU)	–	0.050	–	–
Sodium chloride (kg/FU)	–	0.010	–	–
Water, deionized (kg/FU)	–	0.010	–	–
Transport, train (kgkm/FU)	937.1	36	–	–
Transport, lorry (kgkm/FU)	156.2	6	–	–
Chemical factory (p/FU)	$4 \cdot 10^{-10}$	–	–	–
Electricity (kWh/FU)	–	18.8	9.4	–
Outputs				
1-Butanol—into air (kg/FU)	$1.68 \cdot 10^{-3}$	–	–	–
Acetic acid—into air (kg/FU)	$1.34 \cdot 10^{-3}$	–	–	–
Cyclohexane—into air (kg/FU)	–	$0.1 \cdot 10^{-3}$	–	–
Cyclohexane—avoided product (kg/FU)	–	–	0.050	–
Cationic resin—avoided product (kg/FU)	–	–	–	0.042
Spent solvent (kg/FU)	–	0.493	–	–

3.3.1 Problematic of the data collection

Only few LCAs have been carried out on chemicals and syntheses (Aresta and Galatola 1999; Domènech et al. 2002; van Kalkeren et al. 2013). An important lack of data has been highlighted: nowadays, about 84,000 substances are used but only 1500 are available in life cycle inventory (LCI) databases, such as Ecoinvent, Agribalyse, or GaBi (Subramanian and Golden 2016). This lack of data can be explained by the fact that collecting data is complex, time consuming, and expensive. When possible, data were directly collected in laboratories or chemical industries such as BASF (Saling et al. 2002) or GlaxoSmithKline (Jiménez-González et al. 2004), but due to confidentiality issues, the results of the assessment were barely published. The scarcity of the data availability is problematic to correctly determine the potential environmental impacts of these chemicals.

To overcome this lack of data, the inventories are mostly estimated. Different techniques exist to fill these gaps such as an estimation of the inputs/outputs derived from heuristics and

Fig. 6 Hot spot identification of the *n*-butyl acetate esterification—impact characterization by a derivative of the ILCD 2011 1.05 method

Table 10 Inventory data for the coproduction of ethyl and *n*-butyl acetate—scenario 2

	Reagents preparation	Esterification EtAc	Purification EtAc	Esterification *n*-BuAc	Purification *n*-BuAc	Separation
Inputs						
Ethanol (kg/FU)	0.686	–	–	–	–	–
Acetic anhydride (kg/FU)	1.520	–	–	–	–	–
Cationic resin (kg/FU)	0.034	–	–	0.012	–	–
1-Butanol (kg/FU)	–	–	–	0.925	–	–
Cyclohexane (kg/FU)	–	–	–	0.050	–	–
Sodium chloride (kg/FU)	–	–	–	0.010	–	–
Water, deionized (kg/FU)	–	–	–	0.010	–	–
Transport, train (kgkm/FU)	1343.7	–	–	598.0	–	–
Transport, lorry (kgkm/FU)	224.0	–	–	99.7	–	–
Chemical factory (p/FU)	$4 \cdot 10^{-10}$	–	–	–	–	–
Electricity (kWh/FU)	–	1.4	18.8	18.8	9.4	–
Outputs						
Ethanol—into air (kg/FU)	$1.371 \cdot 10^{-3}$	–	–	–	–	–
Acetic anhydride—into air (kg/FU)	$3.039 \cdot 10^{-3}$	–	–	–	–	–
1-Butanol—into air (kg/FU)	–	–	–	$1.85 \cdot 10^{-3}$	–	–
Cyclohexane—into air (kg/FU)	–	–	–	$0.1 \cdot 10^{-3}$	–	–
Cyclohexane—avoided product (kg/FU)	–	–	–	–	0.050	–
Cationic resin—avoided product (kg/FU)	–	–	–	–	–	0.046
Spent solvent (kg/FU)	–	–	–	0.664	–	–

on-site data on chemical production processes (Geisler et al. 2004), the use of stoichiometric equations from technical literature (Hischier et al. 2004), the use of chemical engineering process design (Jiménez-González et al. 2004), or even the use of substitutes or proxys (Subramanian and Golden 2016). For all, uncertainty analysis must be undertaken to avoid under or overestimations of the potential environmental impacts, especially in product comparisons.

In our case study, all the chemicals needed were not available in the database used (Ecoinvent 3.1). To overcome this problem, proxys and bibliographic study were used.

For example, the ion exchange resin used in our experiments, Dowex 50WX8, is not presented in Ecoinvent 3.1. It was thus decided to substitute this chemical by the data "Cationic resin {GLO}, market for" that considers the production of 1 kg of moist resin, containing 50 wt.% of moist and with 6–8 wt.%

Fig. 7 Hot spot identification of the coproduction process (scenario 2)—impact characterization by a derivative of the ILCD 2011 1.05 method
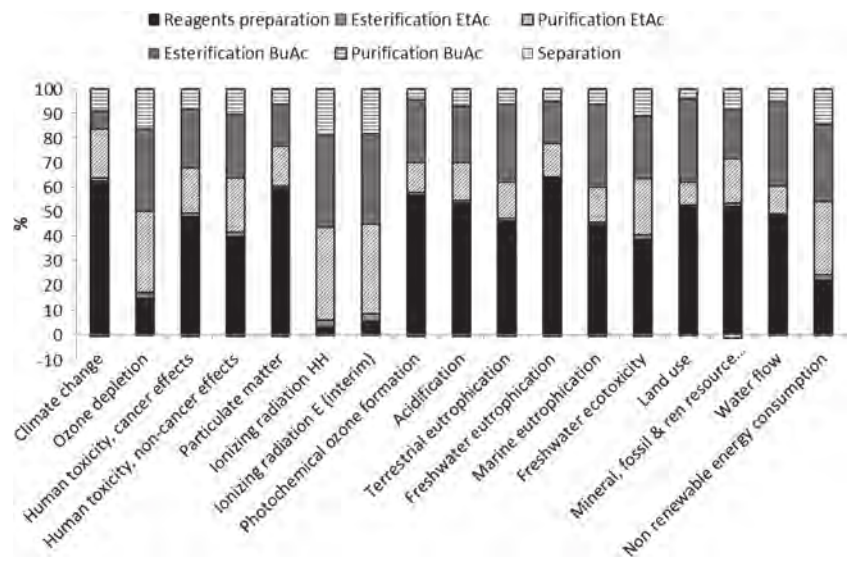
Fig. 8 Comparison between the independent reactions (*Sc 1*) and the coproduction (*Sc 2*)—normalization of the impacts by a derivative of the ILCD 2011 1.05 method
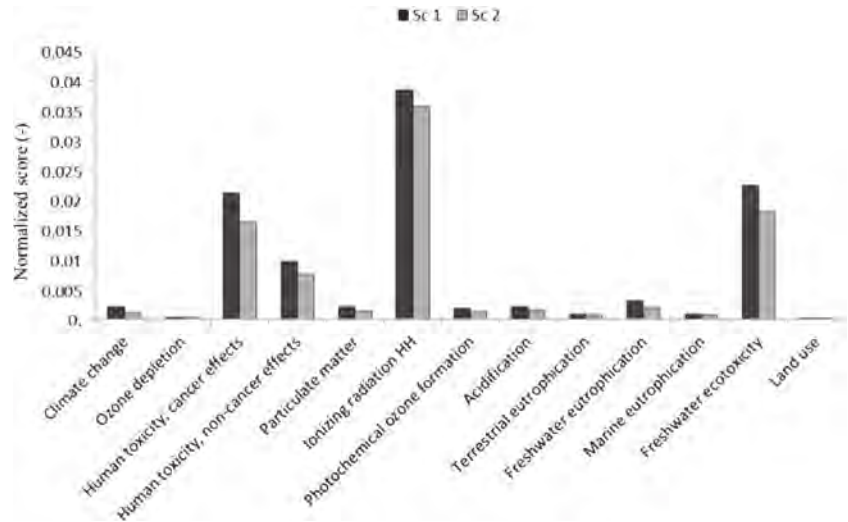
divinylbenzene (DVB) cross-linking. It was also mentioned that the production process of the resin contained lots of uncertainty, leading to a low quality of the data.

3.3.2 Problematic of the functional unit description

The definition of the functional unit has to be done carefully as the results of LCA strongly depend on this choice (Burgess and Brennan 2001).

In this study, we decided to consider, in a cradle to gate approach, the production of 1 kg of the desired solvent, at a purity determined experimentally. The knowledge of the purity of the solvent to be assessed, and furthermore the presence of potential by-products, is essential to correctly estimated the inputs and outputs of the study. Indeed, in the case of the ethyl acetate presented in the "Synthesis of ethyl acetate" section, producing 1 kg of ethyl acetate at

92.1% *w/w*, really means the production of 1.086 kg of mixture including 1 kg of acetate, 0.072 of acetic acid and 0.014 of water, according to the composition of the final reaction mixture (Table 5).

To compare different syntheses, it was essential to use the same functional unit, as reference, i.e., the production of 1 kg of desired solvent (ethyl or butyl acetate).

In our study, the limits of this statement were faced. Indeed, for the coproduction process developed, two syntheses were made consecutively. If we studied the production of 1 kg of ethyl acetate followed by the production of 1 kg of *n*-butyl acetate, there will not be enough acetic acid produced in the first process to be used in the synthesis of *n*-butyl acetate (the process is presented in Fig. 4). It is thus necessary to adapt the functional unit to the study.

Another important point could have been observed if the study was focused on a cradle to gate approach, up to the

Fig. 9 Comparison between the independent reactions (*Sc 1*) and the coproduction (*Sc 2*) through a Monte Carlo analysis—impact characterization by a derivative of the ILCD 2011 1.05 method
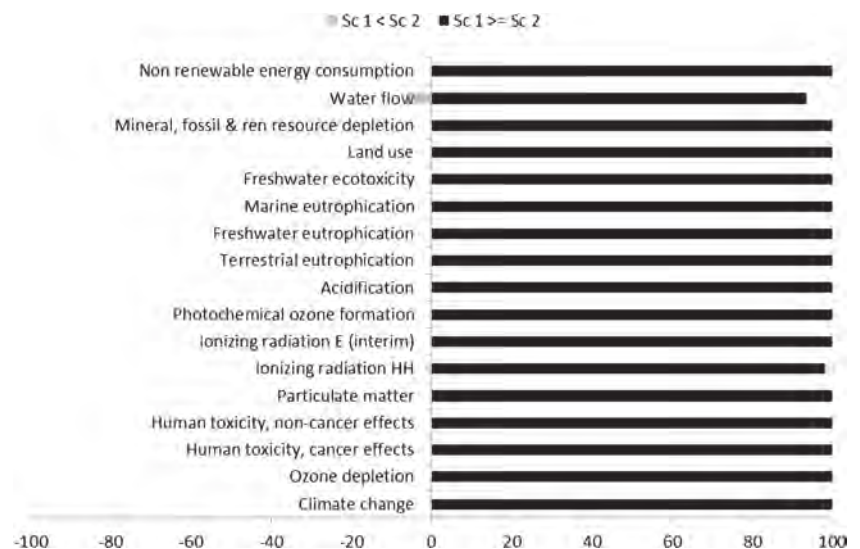
Table 11 Green metrics—comparison between the independent syntheses and the coproduction process

	Atom economy (%)	E-factor	Theoretical percentage of renewable matter[a] (%)
Independent syntheses (Sc 1)	72.4	0.68	57.9
Coproduction (Sc 2)	91.9	0.31	57.9

[a] Theoretical percentage of renewable matter estimated if the reagents (ethanol and *n*-butanol) were biobased

formulation of the paint and its application. Indeed, in this case, the functional unit could have been to cover a wall with a determined opacity. Changing the degree of opacity could completely change the calculations of the LCA.

3.3.3 Contribution of LCA vs green metrics

Usually, the environmental profile of chemicals is undertaken using green metrics, such as the atom economy (AE), the environmental factor (E-factor), or even the percent from renewable sources (Tabone et al. 2010; Pini et al. 2014). These metrics are focusing on the green aspects of a synthesis, i.e., on the respect of the 12 principles of green chemistry: prevention, atom economy, less harmful chemical syntheses, less hazardous solvents, and auxiliaries for instance (Wang et al. 2013).

$$\text{Atom economy} = \frac{\sum \vartheta_{\text{pdt}} M_{\text{pdt}}}{\vartheta_{\text{react}} M_{\text{react}}} \times 100$$

with ϑ_{pdt} the stoichiometric coefficient of the desired product, ϑ_{react} the stoichiometric coefficient of the reactant, M_{pdt} the molar mass of the desired product (g/mol), and M_{react} the molar mass of the reactants (g/mol).

$$\text{E-factor} = \frac{\sum m_{\text{waste}}}{m_{\text{pdt}}}$$

with m_{waste} the total mass of wastes (kg) and m_{pdt} the mass of the desired product (kg).

$$\text{PMR} = \frac{M_{\text{biobased, pdt}}}{M_{\text{pdt}}} \times 100$$

with $M_{\text{biobased, pdt}}$ the molar mass of the biobased content of the product (g/mol) and M_{pdt} the molar mass of the product (g/mol).

The green metrics do not show the environmental contributions of the whole process and the whole life cycle but only of the synthesis. They do not take into account any energy consumption, which could be problematic as their impact usually represents one of the highest contributions of the process. But it is actually a simple tool for a quick analysis of the chemical synthesis that can be easily determined from simple reaction equations like the one presented in this case study. The green metrics of the syntheses of ethyl acetate and *n*-butyl

acetate, through independent or coproduction processes, are reported in Table 11.

Using the green metrics calculated Table 11, it appears that the coproduction presents better results on the three metrics studied with a lower loss of carbon (i.e., higher atom economy) and a lower quantity of wastes (i.e., lower E-factor).

Noteworthy, to conduct a full environmental analysis of a system (for example, our comparison between the two developed processes), it is advisable to conduct a life cycle assessment. This standardized method identifies the process improvement ways to reduce resource consumption and pollutant emissions throughout the life cycle. LCA, however, is more time consuming and requires a larger amount of data but it is very detailed and comprehensive.

4 Conclusions

As the solvent market is still going to increase, it is essential to focus on different manners to improve their way of production, especially from an environmental point of view. Even with the petrochemical resource depletion, temporary solution could be investigated to reduce the environmental impacts of the chemical synthesis.

This study was focused on the production of two common esters particularly used in paints and coatings: ethyl and *n*-butyl acetate.

The syntheses of the desired esters, in the presence of heterogeneous catalyst, were first optimized:

- For the purified ethyl acetate: 92.1% *w/w* of purity with a yield of 87%
- For the purified *n*-butyl acetate: 97.4% *w/w* of purity with a yield of 76%

The two developed esterifications were then coupled in order to simplify and make greener the global process: no water is produced during the first step that forms ethyl acetate and acetic acid. This acid was thus recycled for the synthesis of *n*-butyl acetate, after its separation from ethyl acetate. With the proposed process of coproduction, the objectives were completed with an efficient production of acetates in the presence of heterogeneous acidic resin (Dowex 50WX8). The purified acetates, obtained after distillation, showed the following composition:

- For the purified ethyl acetate: 92.1% *w/w* of ethyl acetate, 6.7% *w/w* of acetic acid, and 1.2% *w/w* of water
- For the purified *n*-butyl acetate: 97.1% *w/w* of butyl acetate, 1.9% *w/w* of 1-butanol, 0.6% *w/w* of water, and traces of acetic acid and ethyl acetate

The environmental impacts of this new process were thus evaluated through a life cycle assessment (LCA) and compared to those of the both esterifications, realized in parallel. Using a derivative of the ILCD 2011 1.05 method, it appeared that, for all the 17 midpoint impact categories taken into account, the coproduction presents the lowest impacts on the environment. Indeed, as the by-products of the ethyl acetate esterification, i.e., a mixture of acetic acid and ethyl acetate, were recycled in the second synthesis, the impact of the substances was reduced up to 23%.

In a context of sustainable chemistry, this new way of production of acetates presents many advantages such as comparable results on a technical point of view and above all, a clear improvement of the environmental impacts.

This case study also allowed us to raise the issue of the lack of perspective on the LCA of chemicals, whether in terms of data collection or for the definition of the functional unit. The interest of LCA compared with green metrics was also discussed.

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ELECTRONIC SUPPLEMENTARY MATERIAL

GREEN CHEMISTRY

LCA case study: comparison between independent and coproduction pathways for the production of ethyl and *n*-butyl acetates

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- Production of ethyl acetate - Impact characterization by a derivative of the ILCD 2011 1.05 method

Functional Unit = 1 kg of ethyl acetate	Reagents Preparation	Esterification	Purification
Climate change (kg CO_2 eq)	5,776	0,1582	3,800
Ozone depletion (kg CFC -11 eq)	6,766E-07	1,265E-07	1,735E-06
Human toxicity, cancer effect (CTUh)	2,534E-07	8,288E-09	1,234E-07
Human toxicity, non-cancer effect (CTUh)	1,430E-06	6,668E-08	9,432E-07
Particulate matter (kg PM2.5 eq)	0,00345	7,932E-05	0,00135
Ionizing radiation - Human Health (kgBq ^{235}U eq)	1,122	1,124	15,103
Ionizing radiation - Ecosystems (CTUe)	2,619E-06	1,378E-06	1,854E-05
Photochemical ozone formation (kg NMVOC eq)	0,0213	0,000386	0,00594
Acidification (molc H^+ eq)	0,0351	0,000881	0,0133
Terrestrial eutrophication (molc N eq)	0,0479	0,00129	0,0205
Freshwater eutrophication (kg P eq)	0,00168	3,028E-05	0,000679
Marine eutrophication (kg N eq)	0,00458	0,000125	0,00204
Freshwater ecotoxicity (CTUe)	53,878	2,695	37,364
Land use (kg C deficit)	9,3756	0,144156795	2,221
Mineral, fossil, renewable resources depletion (kg Sb eq)	0,000277	8,069E-06	0,000108
Water flow (m^3)	0,144	0,00292	0,0398
Non renewable energy consumption (MJ)	141,107	16,423	222,032

- Production of *n*-butyl acetate - Impact characterization by a derivative of the ILCD 2011 1.05 method

Functional Unit = 1 kg of n-butyl acetate	Reagents Preparation	Esterification	Purification	Separation
Climate change (kg CO_2 eq)	3,973	3,232	0,932	-0,0698
Ozone depletion (kg CFC -11 eq)	5,789E-07	1,737E-06	8,417E-07	-2,805E-09
Human toxicity, cancer effect (CTUh)	1,666E-07	1,247E-07	4,892E-08	-2,859E-09
Human toxicity, non-cancer effect (CTUh)	9,788E-07	9,463E-07	4,247E-07	-1,555E-08
Particulate matter (kg PM2.5 eq)	0,00299	0,00133	0,000409	-4,108E-05
Ionizing radiation - Human Health (kgBq ^{235}U eq)	1,076	15,109	7,541	-0,00390
Ionizing radiation - Ecosystems (CTUe)	2,422E-06	1,856E-05	9,240E-06	-1,157E-08
Photochemical ozone formation (kg NMVOC eq)	0,0176	0,00646	0,00186	-0,000231
Acidification (molc H^+ eq)	0,0277	0,0133	0,00517	-0,000455
Terrestrial eutrophication (molc N eq)	0,0370	0,0204	0,00760	-0,000662
Freshwater eutrophication (kg P eq)	0,00106	0,000596	0,000155	-1,183E-05
Marine eutrophication (kg N eq)	0,00354	0,00201	0,000733	-6,277E-05
Freshwater ecotoxicity (CTUe)	32,542	37,828	17,318	-0,576
Land use (kg C deficit)	7,516	2,2697	0,872	-0,0523
Mineral, fossil, renewable resources depletion (kg Sb eq)	0,000181	0,000114	5,138E-05	-6,168E-06
Water flow (m^3)	0,0745	0,0411	0,0185	-0,000743
Non renewable energy consumption (MJ)	117,386	226,302	106,116	-1,546

- Coproduction of ethyl and *n*-butyl acetate - Impact characterization by a derivative of the ILCD 2011 1.05 method

	Reagents Preparation	Esterification EtAc	Purification EtAc	Esterification *n*-BuAc	Purification *n*-BuAc	Separation
Climate change (kg CO_2 eq)	6,585	0,158	2,124	1,659	0,932	-0,0764
Ozone depletion (kg CFC -11 eq)	7,717E-07	1,265E-07	1,699E-06	1,783E-06	8,417E-07	-3,073E-09
Human toxicity, cancer effect (CTUh)	2,866E-07	8,288E-09	1,113E-07	1,498E-07	4,892E-08	-3,131E-09
Human toxicity, non-cancer effect (CTUh)	1,609E-06	6,668E-08	8,954E-07	1,072E-06	4,247E-07	-1,703E-08
Particulate matter (kg PM2.5 eq)	0,00393	7,932E-05	0,00107	0,00126	0,000409	-4,500E-05
Ionizing radiation - Human Health (kgBq ^{235}U eq)	1,277	1,124	15,090	15,297	7,541	-0,00427
Ionizing radiation - Ecosystems (CTUe)	2,984E-06	1,378E-06	1,850E-05	1,884E-05	9,240E-06	-1,267E-08

Photochemical ozone formation (kg NMVOC eq)	0,0243	0,000386	0,00518	0,0114	0,00186	-0,000253
Acidification (molc H^+ eq)	0,0400	0,000881	0,0118	0,0180	0,00517	-0,000498
Terrestrial eutrophication (molc N eq)	0,0546	0,00129	0,0174	0,0394	0,00760	-0,000725
Freshwater eutrophication (kg P eq)	0,00191	3,028E-05	0,000407	0,000642	0,000155	-1,295E-05
Marine eutrophication (kg N eq)	0,00522	0,000125	0,00168	0,00416	0,000733	-6,875E-05
Freshwater ecotoxicity (CTUe)	60,673	2,695	36,187	40,832	17,318	-0,630
Land use (kg C deficit)	10,664	0,144	1,936	7,186	0,872	-0,0573
Mineral, fossil, renewable resources depletion (kg Sb eq)	0,000309	8,069E-06	0,000108	0,000122	5,138E-05	-6,756E-06
Water flow (m^3)	0,165	0,00292	0,0393	0,117	0,0184	-0,000813
Non renewable	160,944	16,423	220,534	231,757	106,116	-1,693

energy consumption (MJ)						