U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 3, 2010 ISSN 1454-2331

ENVIRONMENTAL ASSESSMENT OF CITRIC ACID PRODUCTION

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Acidul citric se obține uzual utilizând filamente ale ciupercii Aspergillus niger. Un avantaj al lui Aspergillus niger este abilitatea de a fermenta substraturi ce provin ca deşeuri ale altor procese. Utilzarea zerului ca sursa de carbon este foarte atractivă, deoarece această materie primă este ieftină. În această lucrare se prezintă o investigare originală a evaluării ecologice a procesului industrial de obținere a acidului citric din zer. Rezultatele corespunzătoare sunt confruntate cu un proces alternativ de obținere a acidului citric utilizând amidonul. Respectivele evaluări ecologice sunt realizate folosind metoda practică propusă de Biwer şi Heinzle.

Citric acid is traditionally produced using the filamentous fungus Aspergillus Niger. One advantage of Aspergillus Niger is its ability of fermenting substrates which come as waste products from other process. The use of whey as carbon source is very attractive because this raw material is cheap. In this work is presented an original investigation on the environmental assessment of the industrial process of citric acid production using whey. The corresponding results are confronted with an alternative process of citric acid production using starch. The corresponding environmental assessments are realized using the practical method proposed by Biwer and Heinzle.

Keywords: environmental assessment, citric acid, Aspergillus niger, zer, amidon

1. Introduction

The consideration of the environmental aspects of the process and plant plays an ever increasing role in the bioindustries. Citric acid is produced commercially by fermentation of carbohydrates derived from corn starch from beet molasses, and recently from yeast. Citric acid is soluble in water with a pleasant taste. Citric acid is one of the most versatile industrial organic acids that are used in the food and pharmaceutical industries, due to its high solubility, palatability and low toxicity.

The main areas of citric acid usage are: beverages (45 %), foods (23 %), soaps and detergents (20%), being used in and as a flavor enhancer and

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preservatives. Citric acid is also used in buffers, as an antioxidant, and for complex of metals. In the last three decades the production of citric acid has continuously strongly increased: from 350,000 tons in 1986 to 1.1 million tons in 2006.

2. Environmental assessment method

The environment assessment method used in this work was proposed by Biver and Heinzle [1 – 3]. The method consists on two sides. The firs side is based on the material balance of the process. For this aim, the simulator SuperPro Designer was used. From the overall material balance of the process streams, the so called Mass Indexes (MIs) defined by Heinzle et all. [4] are computed for all input and output components. For input materials, the MI indicates how much of a component is consumed to produce a unit of the final product. For output, the MI defines how much of a component is formed per unit final product. The sum of all input MIs (or output MIs) gives the MI of the entire process, which is a metric for material intensity of the process.

It is obvious that not all the components have the same environmental effect. The second side of the environment assessment method consists in the evaluation of the environmental impact of the components. There are evaluated a wide range of negative effects of a compound on human health and environment [5]. These effects are given by next 14 Impact Categories (IC): Raw Material Availability, Complexity of the Synthesis, Critical Material Used, Thermal Risks, Acute Toxicity, Chronic Toxicity, Endocrine Disruption Potential, Global Warming Potential, Ozone Depletion Potential, Acidification Potential, Photochemical Ozone Creation Potential, Odour, Eutrophication Potential, and Organic Carbon Pollution Potential. On the base of its environmental properties and its potential to involve an environmental burden, the ICs of each chemical and biochemical component of the process are evaluated with an ABC-classification (A-high relevance, B-medium relevance, C-low relevance). The ABC analysis is usually method used in economic and other disciplines where involve numbers with high uncertainty. Possible synergistic and additive interactions of the components are not taken into account due to the complexity, variability and limited knowledge about them.

The 14 ICs are gathered in 6 Impact Groups: Resources, Grey Input, Component Risk, Organisms, Air, and Water/Soil. The allocations of the ICs to IGs are: Raw Material Availability to Resources, Complexity of the Synthesis and Critical Material Used to Grey Input, Thermal Risks to Component Risk, Acute Toxicity, Chronic Toxicity, and Endocrine Disruption Potential to Organisms, Global Warming Potential, Ozone Depletion Potential, Acidification Potential, Photochemical Ozone Creation Potential, and Odour to Air, Eutrophication

Potential, and Organic Carbon Pollution Potential to Water/Soil. If several ICs are allocated to one IG, the ABC classification of the respective IG will correspond to the most sever class of the ICs. (e.g. if three ICs with the classes A, C and respectively C are allocated to an IG, then IG will be in class A).

In the next step, the Environmental Factors EFs are computed on the base of IGs. For input components EFs are computed on the base of ABC classes of Resources, Grey Input, Component Risk, and Organisms. For output components EFs are computed on the base of ABC classes of Component Risk, Organisms, Air, and Water/Soil. In the absence of any reasonable scientific criteria, Biwer and Heinzle have proposed two options for EFs calculation: multiplication method for EF_{Mult} and averaging method for EF_{Mw}. The EF_{Mult} uses the values A = 4, B = 1.3 and C = 1 and these values are aggregated by multiplication, possible values of EF_{Mult} being between 1 and 256. The EF_{Mw} uses the values A = 1, B = 0.3 and C = 0. The corresponding values of EF_{Mw} computed by averaging are between 0 and 1.

Finally, the amounts of the components in the mass balance are linked with their potential environmental impact by multiplying the corresponding MI with their EF. The resulting Environmental Index (EI) helps to identify those components that are environmentally most relevant in the process.

3. Environmental assessment of citric acid production from whey and glucose

The input involved in acid citric production from whey and glucose are summarized in Table 1.

Four components are categorized at least once as class A (high environmental relevance). Concentrated hydrogen chloride and sodium hydroxide have a high acute toxicity, while ammonium nitrate used as nitrogen source is classified A in the category Thermal Risk, because it can be explosive when mixed with flammable substances. A careful handling of these three substances in the process can minimize the risk. In the output, phosphate is classified A due to its importance to eutrophication process. However, it leaves the process only in very small amounts. The emissions to the environmental are indicated in Table 2.

Table 1

ABC - classification of the input involved in citric acid production from whey and glucose

Component	Avail.	Land use	IG Resources	CS	CM	IG Grey Input	AT &ET	ChT	IG Org.	IG Risk
Ammonium Nitrate	0.3	0	0.3	0.3	0.3	0.3	0.3	0	0.3	1
Biomass	0	0	0	0	0	0	0	0	0	0
Hydrogen Chloride	0	0	0	0	0.3	0.3	1	0.3	1	0
KH2PO4	0.3	0	0.3	0	0	0	0	0	0	0
Magnesium Sulfate	0.3	0	0.3	0	0	0	0	0	0	0
Oxygen consumed	0	0	0	0	0	0	0	0	0	0
Sodium Hydroxide	0	0	0	0	0.3	0.3	1	0.3	1	0
Whey	0	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0	0
Glucose	0	0	0	0	0	0	0	0	0	0

Table 2

ABC - classification of the output involved in citric acid production from whey and glucose

Component	GWP	ODP	AP	POCP	Odor	IG Air	NP	OCPP	IG W/S	AT	ChT	ED	IG Org.	IG Risk
Biomass	0	0	0	0	0	0	0.3	0.3	0.3	0	0	0	0	0
Carbon Dioxide	0.3	0	0	0	0	0.3	0	0	0	0	0	0	0	0
Chloride	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Citric Acid Product	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Citric Acid Loss	0	0	0	0	0	0	0	0.3	0.3	0.3	0	0	0.3	0
Fats	0	0	0	0	0	0	0.3	0.3	0.3	0	0	0	0	0
Glucose	0	0	0	0	0	0	0	0.3	0.3	0	0	0	0	0
Hydrogen Chloride	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Magnesium	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Ions														
Phosphate Ions	0	0	0	0	0	0	1	0	1	0	0	0	0	0
Potassium Ions	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sodium Hydroxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sulfate	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Proteins	0	0	0	0	0	0	0	0.3	0.3	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Galactose	0	0	0	0	0	0	0	0.3	0.3	0	0	0	0	0

The signification of the abbreviations are: Raw Material Availability (Avb), Complexity of the Synthesis (CS), Critical Materials Used (CM), Acute Toxicity (AT), Chronic Toxicity (ChT), Endocrine Disruption Potential (ED), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Acidification Potential (AP), Photochemical Ozone Creation Potential (POCP), Odor (Od), Eutrophication Potential, Organic Carbon Pollution Potential (OCPP), IG (Impact Group).

The results of environmental evaluation are summarized in Table 3. The overall mass index is 15.57 kg/kg product, excluding water. The amount of carbon dioxide produced is low, with only 0.41 kg/kg product. The overall EI_{Mult} of input is 15.72 Index Point/kg Product. The overall mass index MI of output is 13.23 kg/kg product. The overall EI_{Mult} of output is 13.76 Index Point/kg Product.

The environmental indices, both for input and output, are all quite close to their minimum possible values (see Table 3), this indicates a generally low environmental relevance of the substances involved in the process. The most important input materials are carbon sources (glucose, whey), ammonia nitrate used as nitrogen sources, hydrogen chloride need used in ion-exchange column to elute anions and product, sodium hydroxide added to prevent the evaporation of hydrogen chloride during crystallization. The most significant output components are phosphate, unused carbon sources, solid wastes (fats, galactose, proteins, and biomass) and carbon dioxide.

Table 3

Environmental assessment parameters of citric acid production from whey and glucose

Components	Input			Output		
	MI	EI (Mv)	EI (Mult)	MI	EI (Mv)	EI (Mult)
Biomass	0.00	0.0000	0.00	0.16	0.01	0.21
Glucose	0.83	0.0000	0.8299	0.00	0.00	0.00
Oxygen	0.50	0.0000	0.50	-	-	-
Whey	1.60	0.0000	1.60	-	-	-
Acid Citric Loss	-	-	-	0.061	0.009	0.102
Carbon Dioxide	-	-	-	0.41	0.03	0.53
Ammonium Nitrate	0.02	0.0089	0.17	-	-	-
Salts, Acids and Bases	0.00	0.00	0.01	0.00	0.00	0.00
Ash	-	-	-	0.128	0.00	0.167
Fats	-	-	-	0.192	0.01	0.250
Galactose	-	-	-	0.559	0.045	0.726
Proteins	-	-	-	0.162	0.013	0.211
Water	12.62	0.0000	12.62	11.55	0.00	11.55
Sum	15.57	0.0094	15.72	13.23	0.12	13.76

The relative importance of different components is shown in Figs. 1 – 3. Glucose, oxygen and ammonium nitrate are three dominating components in the input EF_{Mult}. The EI_{Mv} does not consider substances with a very low environmental relevance, even if they are consumed in high amount. Whey and oxygen (EI_{Mv} = 0) are not included in the input EI_{Mv} and ammonium nitrate is the unique component, besides small amounts of acids and bases (HCl, NaOH). Carbon dioxide and organic compounds (product loss, glucose, fats, etc.) are dominating output components for both indices.

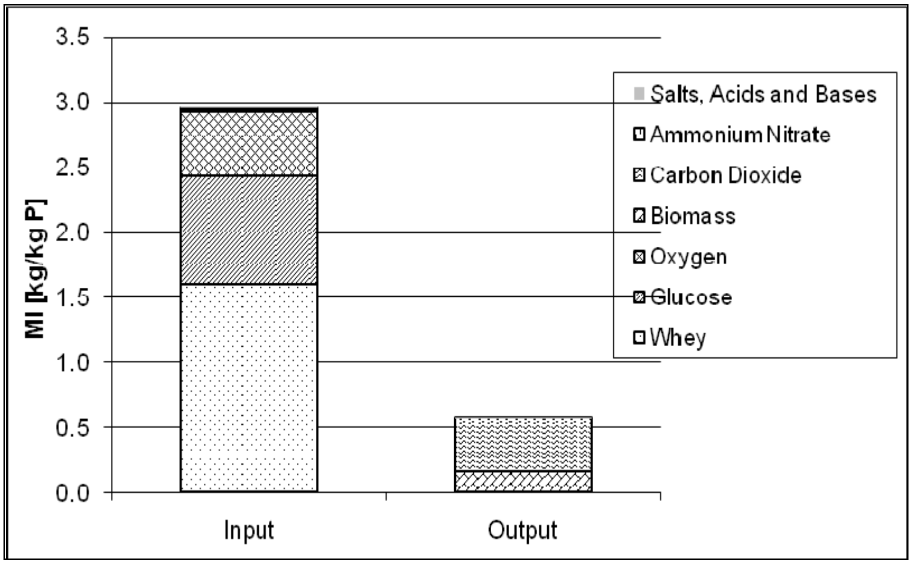

Fig. 1. Mass index (MI) of citric acid production from whey and glucose.

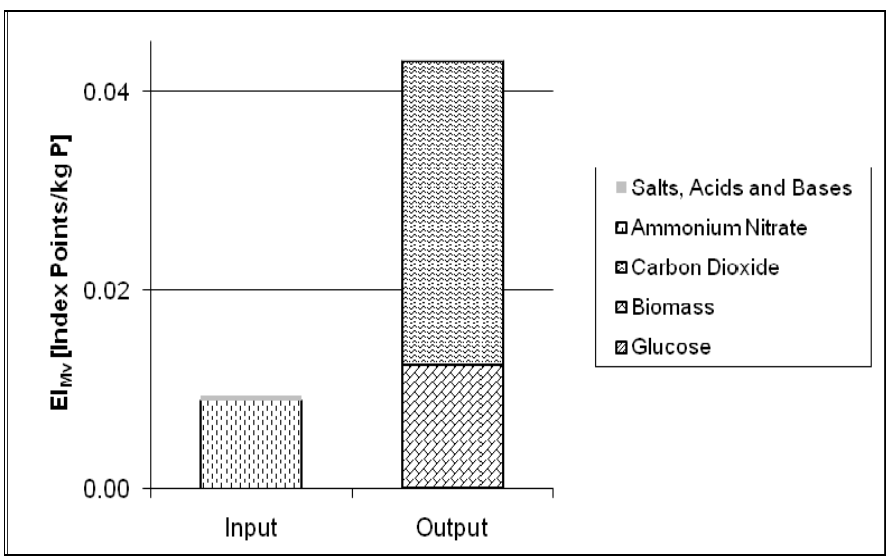

Fig. 2. Environmental index (EI_{MW}) of citric acid production from whey and glucose.

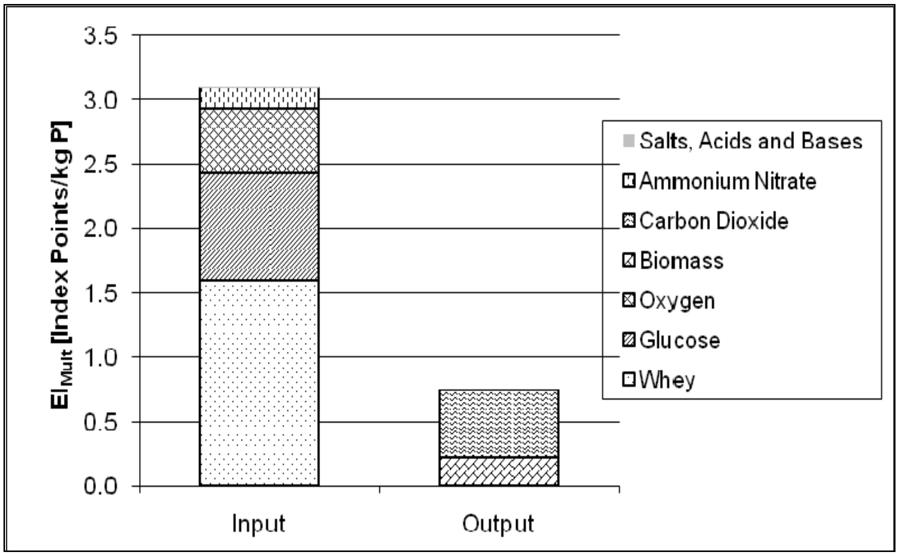

Fig. 3. Environmental index (EI_{Mult}) of citric acid production from whey and glucose.

4. Environmental assessment of citric acid production from starch

The ABC classifications of the input and output involved in acid citric production from starch were made similarly as in the previous case.

The environmental indices are summarized in Table 4.

Table 4

Environmental assessment parameters of citric acid production from whey and glucose

Components	Input			Output		
	MI	EI (Mv)	EI (Mult)	MI	EI (Mv)	EI (Mult)
Starch	1.27	0.0000	1.27	-	-	-
Organic Compounds	-	-	-	0.08	0.01	0.13
Oxygen	0.51	0.0000	0.51	-	-	-
Biomass	0.00	0.0000	0.00	0.16	0.01	0.21
Carbon Dioxide	-	-	-	0.41	0.03	0.53
Ammonium Nitrate	0.02	0.0089	0.17	-	-	-
Salts, Acids and Bases	0.01	0.00	0.01	0.00	0.00	0.00
Water	14.97	0.0000	14.97	15.12	0.00	15.12
Sum	16.78	0.0097	16.93	15.77	0.05	15.99

The overall mass index of input is 16.78 kg /kg product, excluding water. The amount of carbon dioxide produced is low, with only 0.41 kg/kg product. The overall EI_{Mult} of input is 16.93 Index Point/kg Product. The overall mass index MI of output is 15.77 kg /kg product. The overall EI_{Mult} of output is 15.99 Index Point/kg Product. When using the EF_{mult}, the weighting factor for class C is 1. This mean the minimal possible EF_{Mult} = MI. When calculating EF_{Mv}, class C is set to 0. Here, the minimal possible EF_{Mv} is 0. The environmental indices, both for input and output, are all quite close to their minimum possible values (see Table 4) and this indicates a generally low environmental relevance of the substances involved in the process. The input materials includes mainly carbon source (starch), ammonia nitrate used as nitrogen sources, hydrogen chloride need for pH control in fermentator, and used in ion-exchange column to elute anions and product, sodium hydroxide added to prevent the evaporation of hydrogen chloride during crystallization, and water. The most important output components are unused carbon sources, dioxide carbon and biomass.

The relative importance of different components is shown in Figs. 4 – 6. Starch, Oxygen and ammonium nitrate are three dominating components in the input EF_{Mult}. The EI_{Mv} does not consider substances with a very low environmental relevance, even if they are consumed in high amount. Starch and oxygen (EI_{Mv} = 0) are not included in the input EI_{Mv} and ammonium nitrate is the unique component, besides small amounts of acids and bases (HCl, NaOH). Carbon dioxide and organic compounds (product loss, glucose, fats, etc.) are dominating output components for both indices.

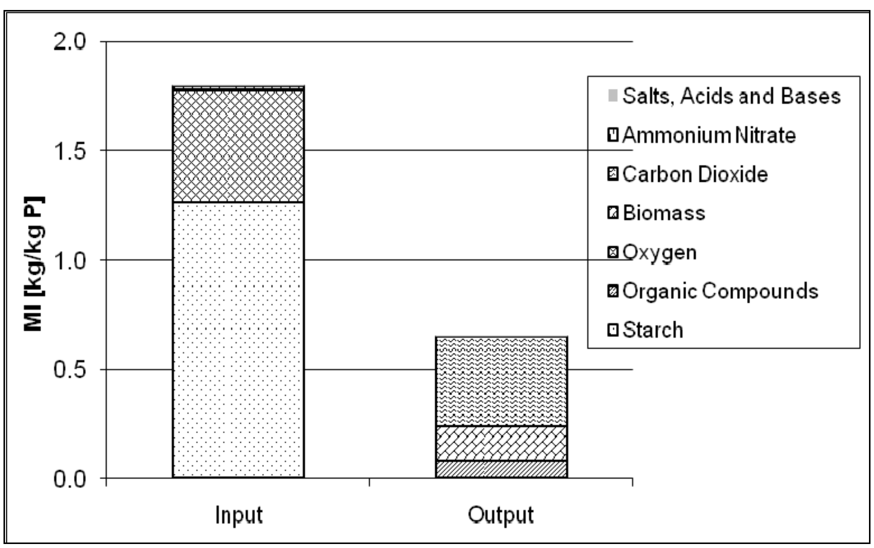

Fig. 4. Mass index (MI) of citric acid production from starch

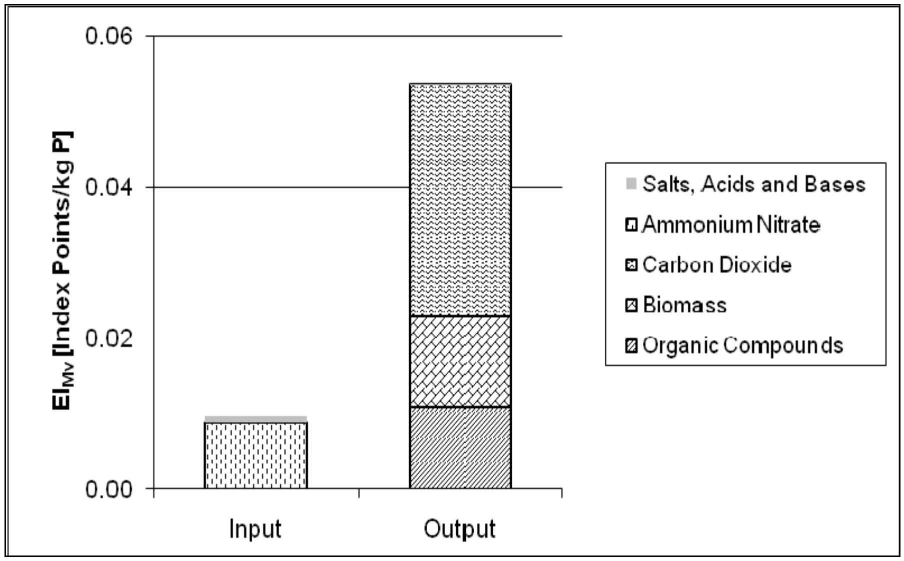

Fig. 5. Environmental index (EI_{MW}) of citric acid production from starch

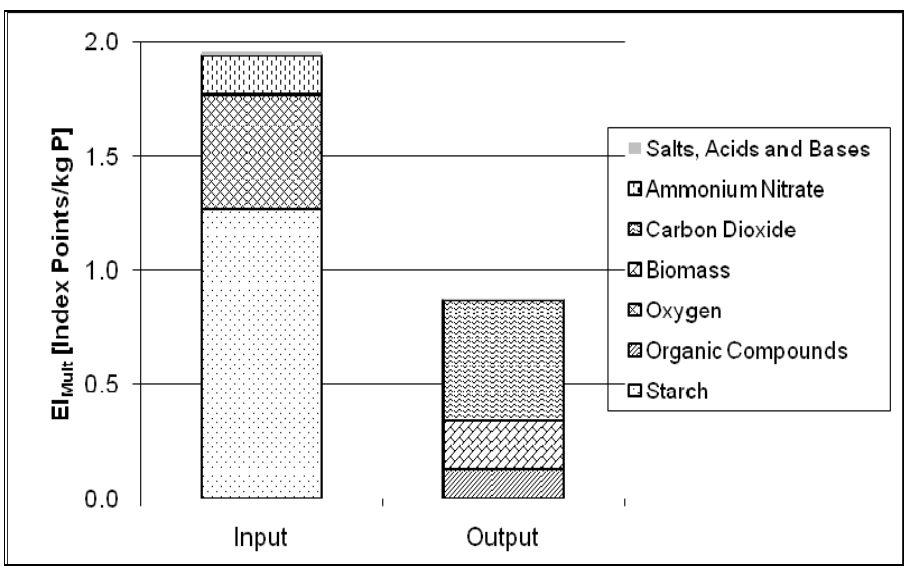

Fig. 6. Environmental index (EI_{Mult}) of citric acid production from starch

5. Comparison between the two processes

In Table 5 it is compared the Mass Index (MI) and the Environmental Index (EI_{Mult}) of both processes. A difference of the values of the Environmental Index EI_{Mult} between the two alternatives can be observed. This difference is in the favor of the process using whey.

Table 5

Comparison between the two proceses

Case study	I/O	Whey	Starch
MI	I	15.57	16.78
EI (Mult)	I	15.72	16.93
MI	O	13.23	15.77
EI (Mult)	O	13.76	15.99

I-Input ; O-Output

6. Conclusions

The method described in this paper can be use to compare different processes and to design more sustainable process. The purpose of this environmental assessment is to identify the environmental "hot spot" of the process. This means that it should draw attention to those materials or process steps that cause most of the potential environmental burden. Since the method can be applied from early phases of the process development, these environmental burdens can be reduced from the beginning. Thus, costs for waste treatment or possible regulatory penalties can be avoided or least reduced [6].

Most compounds used are from biological origin, e.g. glucose, starch, whey, biomass. Sodium hydroxide, hydrogen chloride, and ammonium nitrate are hazardous chemicals involved in acid citric production.

Water used in large amounts and primarily converted to wastewater, which has to be treated before release to a receiving water body. There are no organic wastes produced in citric acid process. As in almost bioprocess, water is dominating. Incomplete consumption of substrate is much less significant.

The major mass flow in this process is caused by aeration. However, only a very small fraction of the oxygen supplied to the fermentator is actually consumed. The very large air flow does not directly cause any environmental pollution, but the necessary electric energy consumption by the compressor is very high, causing increased costs and indirect environmental pollution during production of electric energy.

Acknowledgments

Financial support from National University Research Council, Ministry of Education, Research, Youth and Sports, Grant ID 1727, Multilevel Optimization of Sustainable Bioprocesses is gratefully acknowledged.

R E F E R E N C E S

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