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PROCESS INTEGRATION FOR INDUSTRIAL WATER REUSE: A CASE STUDY FROM A BRAZILIAN BIODIESEL COMMERCIAL PLANT

ABSTRACT

This paper presents a case study of process integration for a Brazilian biodiesel commercial plant water reuse by using the P+WATER method coupled with Water Sources Diagram (WSD). The process flow diagram of biodiesel plant was simulated considering different operation conditions for transesterification unit, the biodiesel refining unit, and the glycerol recovery unit. WSD was employed to select the main scenarios of waste stream reuse. Statistical techniques were applied to assess the operation cost of each scenario and the respective opportunity to reduce the water consumption by water reuse. The most promising scenarios of waste stream reuse were compared using the P+WATER method to evaluate the opportunity of being really introduced in the industrial plant.

KEYWORDS: Process Integration; Water Reuse; Biodiesel; P+Water.

INTEGRAÇÃO DE PROCESSOS PARA A REUTILIZAÇÃO DA ÁGUA INDUSTRIAL: UM ESTUDO DE CASO DE UMA PLANTA COMERCIAL DE BIODIESEL NO BRASIL

RESUMO

Este artigo apresenta um estudo de caso de um processo de integração para reuso de água de uma planta comercial brasileira de produção de biodiesel através da aplicação da metodologia P+Água associada ao Diagrama de Fonte de Água (DFA). O diagrama de fluxo de água de uma planta de biodiesel foi simulado considerando diferentes condições de operação para as unidades de transesterificação, refino do biodiesel e recuperação do glycerol. DFA foi aplicado para selecionar os cenários mais promissores para reduzir o consume de água através do seu reuso. O cenário mais promissor para reuso da corrente será definido através da comparação entre as correntes dos melhores cenários através da metodologia P + Água para avaliar qual realmente pode ser introduzida na planta industrial.

PALAVRAS-CHAVES: Processo de Integração; Reuso de Água; Biodiesel; P+água.

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INTRODUCTION

The biodiesel industrial production is growing fast in order to supply the demand for an alternative diesel fuel. Many countries around the world are adopting biodiesel blends for their vehicles and Brazil is one of them. Indeed, Brazil is the third producer of biodiesel in the world with potential to become the first one. However, factors such as a large territory for agriculture and the diversity of feedstock are not enough to assure a high and constant production of biodiesel (CASTANHEIRA et al., 2014).

Transesterification of soybean oil using methanol and homogeneous alkaline catalysis is the traditional process for biodiesel commercial production in Brazil, although new routes have been also investigated. This process usually provides a conversion efficiency of more than 98%. However, it has the disadvantage of demanding large amount of water for the pre-treatment of the raw material and wet washing to remove the salt produced from the neutralization process, besides the residual acid or base catalyst (JANAUN and ELLIS, 2010). Particularly, the pre-treatment of raw material evolves several steps where the use and reuse of water should be evaluated. In this context, industrial water reuse is a major issue.

Technical and environmental aspects of the transesterification process have constituted a real challenge to the sustainable development of the biodiesel industry. An efficient use of resources is one of the primary tasks in the chemical process industry and several strategies have been reported for the optimization of material recycle and reuse. According to Ponce-Ortega et al. (2010), mass integration is an effective, holistic framework for optimization of the allocation, generation and separation of streams and species throughout a process. Martins et al. (2010), for example, implemented water balances associated to data reconciliation based on attributing degrees of reliability to the aqueous flow rate accordingly to empirical knowledge about the plant. They developed a method that enables the construction of water balances with any available data without initially worrying about the unknown streams.

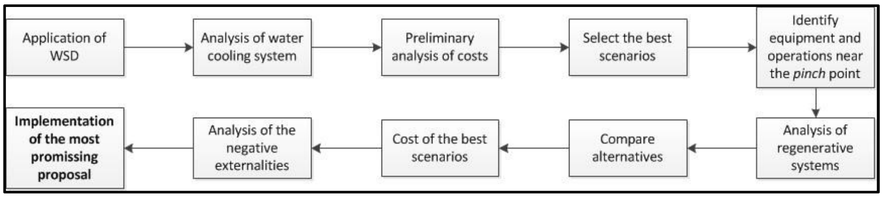
Once the intensive use of water in the biodiesel industry is a requirement, the reuse, regeneration and recycle of water currents have being strongly investigated to develop procedures for the design of water systems. Basically, the literature mentions two classes of methods for synthesis of water systems: (i) mathematical programming and (ii) graphical, heuristic, or algorithmic methods. The first one lies on the use of engineering knowledge, and the successive refinement and generation of design alternatives. Its weakness is due to the lack of a systematic framework for process modelling and to the need of adequate initial conditions, besides its reliance on heuristics which may not always be valid (ALVA-ARGÁEZ et al., 1998; ALVAREZ-VAZQUEZ et al., 2008; KARUPPIAH and GROSSMANN, 2006). The second class provides a simple procedure that allows an immediate understanding of the entire process, although its limitations to achieve optimal solutions.

The Water Sources Diagram (WSD) is classified in the second class mentioned and was developed by means of a heuristic procedure to synthesize water mass exchange network for a single contaminant (GOMES et al., 2007). However, real processes usually deal with multiple contaminants and for this reason further development of WSD algorithm has been done. Recently, the P+WATER method has been coupled with Water Sources Diagram (WSD) for multiple contaminants (GOMES et al., 2013). It constitutes a powerful tool for process integration towards industrial water reuse but it has not been applied to several processes such as biodiesel production yet. In this paper a case study of process integration for Brazilian biodiesel commercial plant water reuse is done for the first time by using the P+WATER method coupled with Water Sources Diagram (WSD).

THEORETICAL REVISION

Process Integration for industrial Water Reuse

The methodology P+WATER for process integration is based on the philosophy of pollution prevention that is cleaner production using Water Source Diagram as a supporting tool, as shown in Graphical 1. The purpose of this method is to consolidate the scenarios of industrial plants with minimal water consumption and wastewater generation through reuse of chains (MIRRE, 2012).

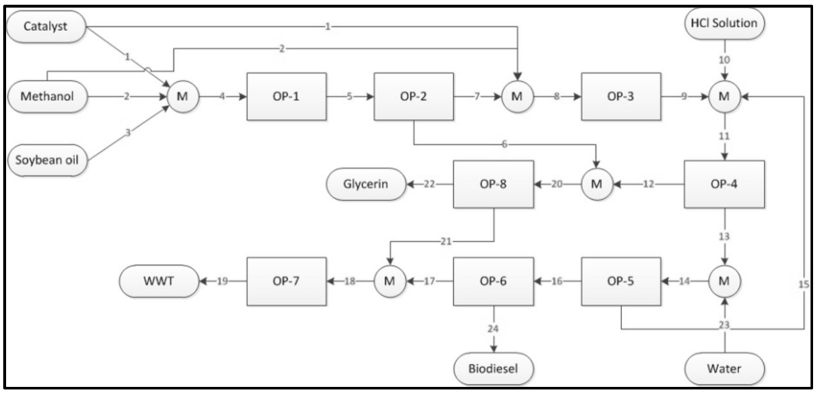


Graphical 1: P+WATER methodology.

The WSD step is performed after the survey data of water consumption and wastewater generation of the industrial plant. This is a critical stage, precisely because of the difficulty of gathering relevant fieldwork information. It should be said that information about industrial water consumption in Brazil is scarce because water is still a cheap feedstock. The algorithm used here to generate the water source diagram for the water allocation problem with the multiple contaminants is based on that proposed by Gomes et al. (2013), which identifies a reference contaminant as a basis to describe the mass transfer of all other contaminants, adopting a linear mass transfer relationship.

Case study: Biodiesel Commercial Plant

The Biodiesel commercial plant investigated has been processing vegetable oils, particularly soybean oil, and animal tallow as raw materials, which are produced outside of the industrial complex. The production of biodiesel is carried out through a transesterification reaction promoted by homogeneous catalysis using a methyl source. Graphical 2 shows the process flow diagram of the biodiesel commercial plant. There are eight basic operations: OP1 – first reactor where the transesterification reaction occurs; OP2 – first settler vessel used to separate biodiesel from glycerol; OP3 – second reactor used to convert the remaining oil into biodiesel; OP4 – second settler vessel used to separate biodiesel from glycerol; OP5 - third settler vessel used to separate biodiesel from water and impurities; OP6 – stripper responsible for separating methanol from biodiesel; OP7 – rectifier used to separate methanol from water; OP8 - stripper used to separate methanol from glycerol



Graphical 2: Biodiesel process flow diagram.

Only five of these eight operations use water directly in the process to wash the biodiesel and remove contaminants. After assessing the process flow diagram and the water balance, some operations that need make up of water balance were chosen and a quantitative characterization of the main parameters and contaminants of their streams was done.

Water Sources Diagram (WSD)

The WSD for multiple contaminants starts calculating the maximum water mass flowrates (f_k) in each operation (*k*) and the corresponding maximum inlet and outlet concentrations ($C_{ik,max}$; $C_{fk,\,max}$) of each contaminant (*j*). The amount of contaminant *j* transferred in operation *k* (*Δmkj*) is calculated by Eq (1) and the corresponding results are shown in Table 1.

$$\Delta m_{kj} = f_k (C^k_{fi,\max} - C^k_{ij,\max}) \tag{1}$$

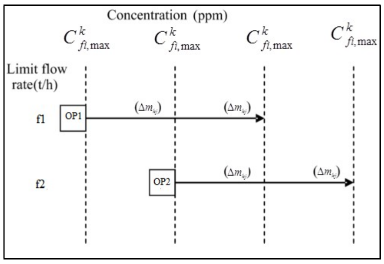
After calculating the maximum concentration of contaminants, it is necessary to construct the diagram to assess the mass transfer, as shown in Graphical 3 and 4, as well as to start calculating of the minimum flow of water for each concentration range before inserting the use of raw water. The respective flow rates are calculated with Eqs (2) and (3):

$$f^e_{ew,k,i} = \frac{\Delta m_{ki}}{(C_{fi} - C^*_{ew})} \tag{2}$$

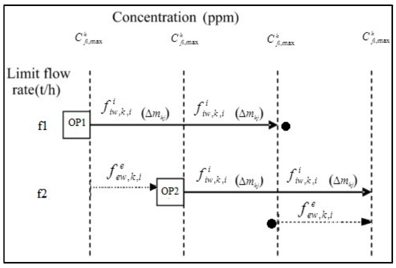
$$f^i_{iw,k,i} = \frac{\Delta m_{ki}}{(C_{fi} - C^*_{i,iw})} \tag{3}$$

Where $f^e_{ew,k,i}$ is the flow rate of the external water source (ew), allocated to the operation k in the concentration interval i and C^*_{ew} is the concentration of the external water source (ew). The $f^i_{iw,k,i}$

is the flow rate of the internal water source (iw), allocated to the operation k in the concentration interval i and c^{*}_{iw} is the concentration of the internal water source (iw).



Graphical 3: WSD with operations and respective mass transfer



Graphical 4: WSD for a reference contaminant

All steps of WSD methodology were followed and other factors of the process were also considered such as replacement of cooling towers, steam ejectors, and so on, which are subject to restriction of flow. Flows considered low, that is less than 1 t/h, were neglected. Another important point to observe is the process limits such as corrosion, maximum solubility and simulation.

Operation Cost of Each Scenario

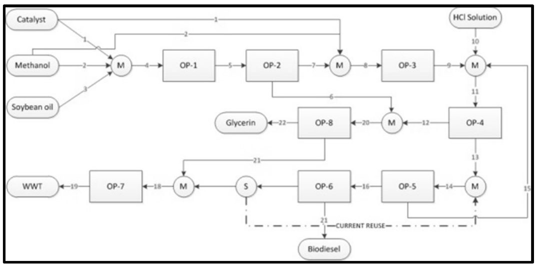
Three scenarios of water streams reuse were generated from data shown in Table 1, using the methodology described based on the contaminant methanol. The three possibilities of reuse were: reuse OP 7 chain on OP 6; Reuse OP 7 chain in OP 4 and reuse of Op 6 chain in OP 4. The first scenario cannot be applied due to the presence of impurities such as glycerin, which must not be inserted into the OP 6. In the second scenario, the reuse would cause acidification of the product beyond the presence of various impurities that would reduce the quality of the final product, so its reuse would require a prior regeneration. Therefore, only the third scenario is acceptable due to the contaminants in the process that do not exert negative influence on the performance of the OP 4, offering the possibility of adding a new stream reuse, as shown in Figure 3, which provides current utilization without troubling the process.

Table 1: Limit Operational Data

Operation (*k*)	*f*(kg/h)	Contaminant (*i*)	$C_{ik,max}$ (ppm)	$C_{fk,\,max}$ (ppm)	Δm (kg/H)
		HCl	0.75	14.18	172.11
		Methanol	57.84	357.22	3,836.93
		Soybean Oil	1.98	2.08	1.27
4	12,816.45	Biodiesel	794.32	834.07	509.54
		Glycerin	3.91	82.15	1,002.78
		Sodium methoxide	1.09	20.68	251.11
		Sodium chloride	0.00	2.48	31.87
		HCl	0.00	0.02	0.32
		Methanol	41.54	252.33	2,553.71
		Soybean Oil	2.01	2.09	1.04
5	12,114.67	Biodiesel	907.08	841.58	-793.50
		Glycerin	0.00	0.00	0.00
		Sodium methoxide	0.00	0.00	0.00
		Sodium chloride	0.13	3.26	37.93
		HCl	0.00	0.00	0.00
		Methanol	32.48	0.00	-373.91
		Soybean Oil	2.09	2.17	0.86
6	11,509.41	Biodiesel	841.58	871.78	347.56
		Glycerin	0.00	0.00	0.00
		Sodium methoxide	0.00	0.00	0.00
		Sodium chloride	0.00	0.00	0.00

7	4,057.79	HCl	0.00	0.01	0.05
		Methanol	1.04	0.00	-4.23
		Soybean Oil	0.00	0.00	0.00
		Biodiesel	0.10	36.57	147.98
		Glycerin	0.05	18.93	76.60
		Sodium methoxide	0.00	0.00	0.00
		Sodium chloride	0.00	1.54	6.24
8	2,452.79	HCl	0.00	0.32	0.78
		Methanol	4.80	1.04	-9.23
		Soybean Oil	0.00	0.00	0.00
		Biodiesel	0.00	0.00	0.00
		Glycerin	7.88	426.41	1,026.55
		Sodium methoxide	0.00	0.00	0.00
		Sodium chloride	0.64	34.74	83.63

The current available for reuse from OP6 to OP4 was 3,293.53 kg/h whose characteristics were critical absence of the contaminant methanol and some impurities that will not reduce the efficiency of OP4. This reuse current allows to exclude the chain 23 of fresh water showed in Graphical 2, that has 463 kg/h, and only replace with the current reuse without making any modification in the production process of biodiesel, Graphical 5.



Graphical 5: Biodiesel process flow diagram.

Assessing the economic aspect of P+water, one should take in account the investment in new facilities and equipment operating costs required to make feasible water reuse. For this reason payback period has been reported to evaluate the opportunity of this change being really introduced in the industrial plant in comparison to the current process flow diagram. The payback period (PBP) refers to the length of time within which the benefits received from an investment can repay the costs incurred during the time in question while ignoring the remaining time periods in the planning horizon. Economically, the replacement of 463kg/h of fresh water by reuse current represents a reduction in turnaround time and a reduction in the consumption of inputs. Table 2 shows the BPP for the current process and the proposed process using P+water.

Table 2: Economic evaluation.

Plant	*payback period (years)*
Current process	1.39
P+water	1.25

CONCLUSIONS

The sustainability of water use in biodiesel production process is at the beginning. In this work preliminary results showed that P+WATER method coupled with Water Sources Diagram (WSD) consists in a powerful tool to identify opportunities of water reuse and recycling in the biodiesel industry towards a sustainable process. However, this study only focused on the identification of opportunities for reuse of aqueous streams. For recycling water many process parameters need to be analyzed, such as intermittent flow or streams sent to final treatment, that were not considered in this study. For future work, further simulations should be done to take in account the regenerative unit in order to recycle the water from the sewage treatment, as well as, additional sources of water will also be considered such as the water used in boilers and cooling towers station processes.

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