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Environmental Assessment of HF Alkylation Process Using WAR Algorithm

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Abstract

Alkylation process is essential for fuel upgrading via alkylate production from olefins and isobutane, improving quality of fuels, economics and environmental performance of refinery configuration. For this reason, it is necessary to understand parameter relations in order to improve technical performance and compare total potential environmental impacts of parameter variation.

In this work, computer aided tools as process simulation and graphical user interfase environmental evaluation were used for analysis of an alkylation unit using hydrofluoric acid (HF) as acidic catalyst towards process assessment and improvement, the methodology include waste reduction algorithm was performed for 4 different case studies taking into account energy source and products under 8 categories.

Keywords: Alkylate, Environmental evaluation, Olefins

1. Introduction

The alkylation of light olefins with isobutene is an important process in oil refineries; the products are used as blending feedstock for premium gasoline formulation since they have high octane number (RON), low content of aromatics and Sulphur [1]. The final product of this process is a mixture of isoparaffins used as an additive for the pool blending of gasoline called alkylate [2]; currently, the only processes of commercial importance use either sulfuric acid or hydrofluoric acid [3]. The WAR algorithm was developed by the US Environmental Protection Agency (EPA) and allows quantifying the flow and generation of potential environmental impacts resulting from the activities of the chemical industry [4]. The WAR algorithm introduces the concept of Potential Environmental Impact (PEI) Balance, which is similar to a mass or energy balance [5]. Gasoline components are mixed to meet the required octane specifications, oxygen, sulfur, Reid vapor pressure (RVP), final boiling point, aromatic compounds, olefins and benzene [6,7]. The new rules will require lower content of sulfur, aromatic compounds, and benzene but maintaining a high value of octane and low RVP [8]. Despite the importance of alkylation processes, relatively little quantitative information about applicable kinetics models to large scale process has been published, This is due mostly to the complex system of reactions that occur, this restrict the development of a rigorous model that allows to describe and predict the relations among process variables such as isobutane and olefins consumption, space velocity, pressure etc. In this work, a simple conversion reaction system was used in the order to emulate the real behavior of process variables and its interactions.

2. Materials and methods

2.1 Process simulation

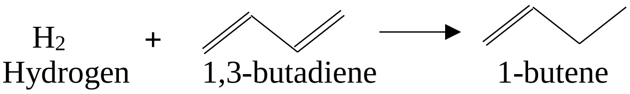
The process modeling was performed using a commercial software taking into account real data from a Latin American configuration plant. Peng Robinson Stryjek Vera was used as thermodynamic model; it has the potential to more accurately predict the phase behavior of hydrocarbon systems [9], particularly for systems composed of dissimilar components. The global mass balance from model summary is shown below in table 1.

Table 1. General mass balance

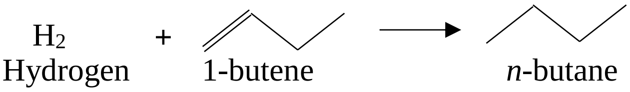
Inlet streams	Mass flow (lb/h)	Outlet streams	Mass flow (lb/h)
Hydrogen	42.34	Alkylate	87962.76
Olefins	83688.14	Propane product	619.85
Make-up isobutane	54082.01	n-butane product	18241.61
Make-up HF	1387279.25	Off-gas	121.15
		Oil water	343.291
		HF waste	1387963.73
		Isobutane purge	3325.23

The main process reactions occurs in three stages: selective hydrogenation, alkylation section and butane product treatment. For simulation, those stages was carried out in simple conversion reactors, the following reactions system [10] was taken into account. The reaction yield was determined based on actual plant conversion data.

Selective hydrogenation section



(1)



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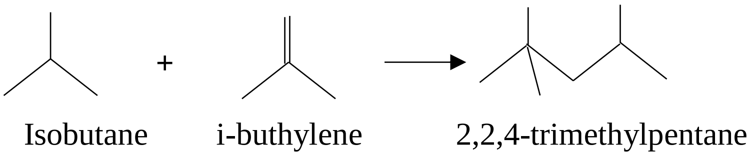
Alkylation section

Desired reactions and adverse reactions were considered, using butyl fluoride as reference organic fluoride.

Desired:



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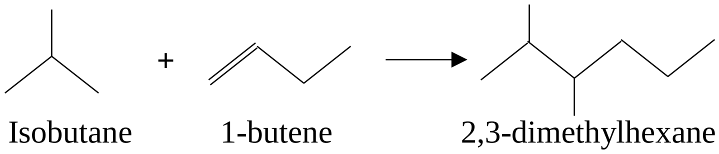

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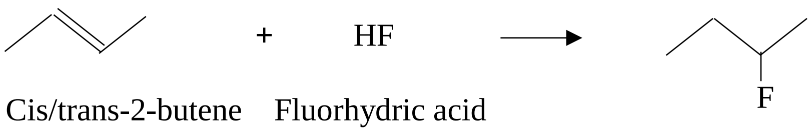
Undesired:



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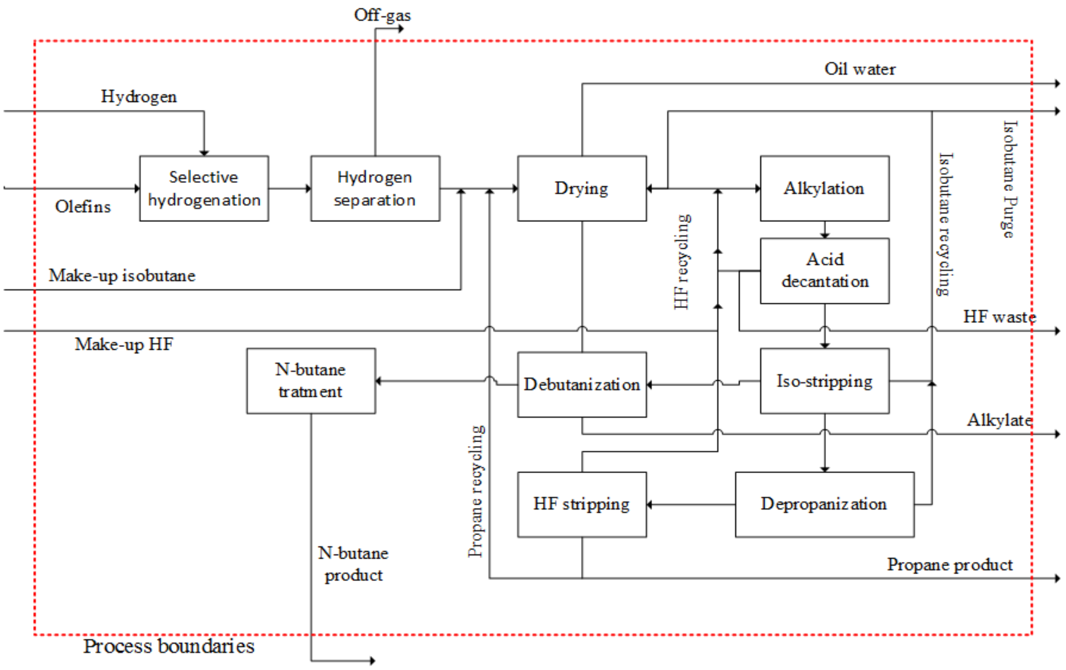

Figure 1. Block diagram of HF alkylation process

2.2. Environmental impacts assessment using WAR algorithm

The WAR methodology was implemented through graphical user interphase environmental evaluation for analysis of an alkylation unit towards process assessment and improvement. The WAR algorithm evaluates processes in terms of potential environmental impacts (PEI). The potential environmental impacts of a chemical can be defined, as the effect that a chemical compounds would have on the environment if it were emitted into the environment [11]. The impact categories evaluated by the WAR algorithm [12] are divided into major two groups: global atmospheric and global toxicological. The categories of global atmospheric impact are global warming potential (GWP), ozone depletion potential (ODP), acidification potential or acid rain (AP) and photochemical oxidation or smog potential (PCOP). The categories of global toxicological impact are human toxicity potential by ingestion (HTPI), human toxicity potential by exposure (HTPE), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP). In this work, in order to carry out a global analysis of the process, this was considered as a single block or stage, taking into account only the overall inputs and outputs of the process (see figure 1) and was evaluated under 4 conditions, a base case taking into account all energy sources present in the process (Case 1), and 3 cases where was considered the product stream (Case 2), the energy process (Case 3), and the amount of energy-product stream (Case 4).

3. Results and discussion

3.1 Total Potential Environmental Impact

Figure 3 shows generated PEI with negative values for all four cases; output PEI has high values for all four cases, which may be due to the acid wastes in the process. In the other hands, the in output PEI/hr, both case 2 and case 4 have similar values (approximately 1.43 x 10^6), consequently, this is due to the relative low energy consumption, which is reflected in the low temperatures at which the alkylation reactions are carried out (100 ° F), unlike the processes that use sulfuric acid as catalyst that are carried out at higher temperatures, which is an advantage in terms of environmental and economic performance. On the other hand, we can see that for the simulated process the energy consumption is relatively low (9.76 MJ / lb alkylate), this is because the only energy requirements are in preheating stages, and in the distillation column reboilers in the stages of separation (hydrogen separation, iso-stripping, depropanization, debutanization and HF stripping). However, the heating requirements in the simulated process were supplied by industrial services, however in practice the processes are integrated using energy available in some streams.

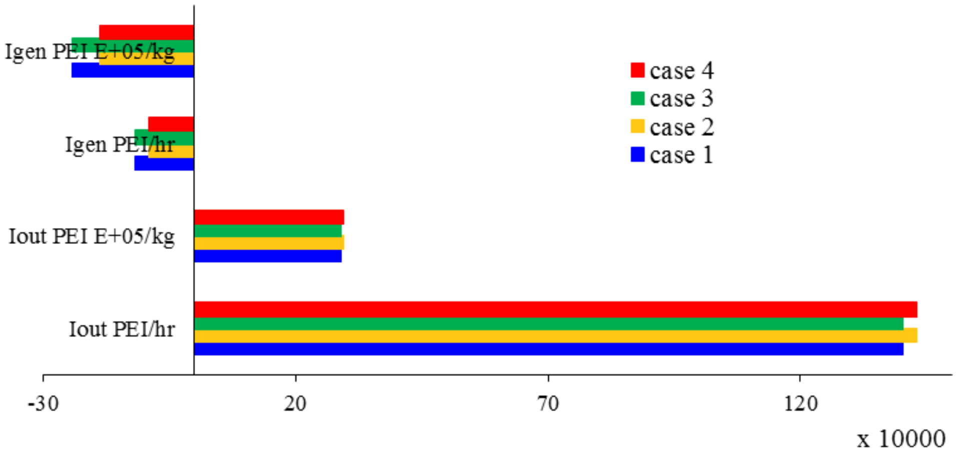

Figure 2. Total PEI generated and output of the system for an HF alkylation process

3.2 Local toxicological impacts

Figure 3 shows the local toxicological impacts generated and output of the process, which includes humans (HTPI y HTPE) and ecological (ATP y TTP) impacts. Figure 3 shows for most of toxicological impacts categories PEI consumption, $-1,35x10^4$, -21.2 and $-1.35x10^4$ for HTPI, HTPE and TTP (in PEI/h) respectively; however, the values of PEI shown ($5.5x10^5$, $7.75x10^4$ and $5.54x10^5$ PEI/h, respectively) are high this can be due to the large amount of volatile components present in streams such as off-gas, and waste HF, which are mainly composed of propane, hydrogen and hydrofluoric acid, these components have a great toxicological potential.

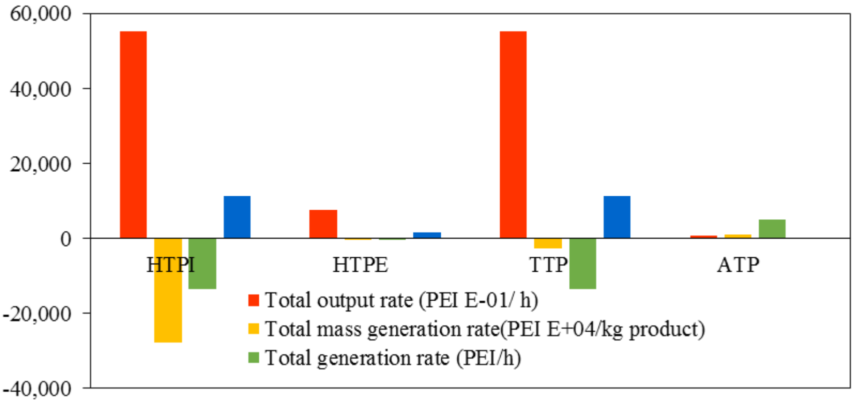

Figure 3. Local output and generated toxicological impacts for the process

3.3 Global Atmospheric impacts

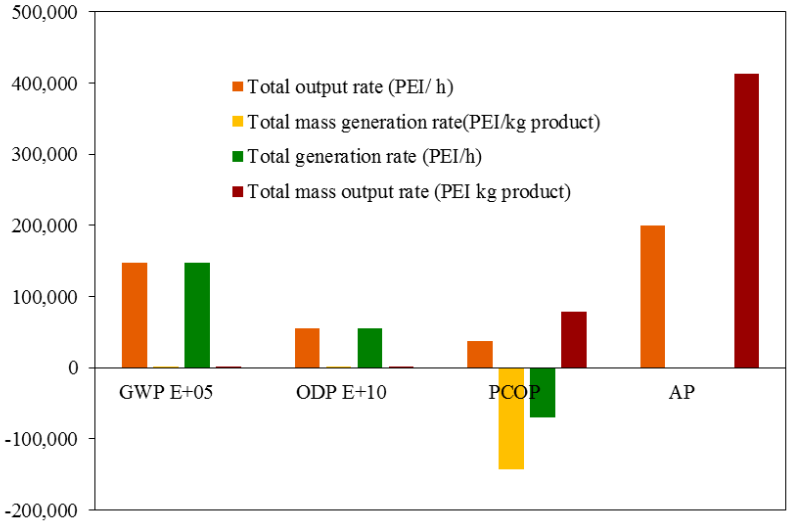

Figure 4. Output and generated atmospheric impacts of a HF alkylation process

Figure 4 shows that atmospheric impacts are composed for global (GWP y ODP) and regional (AP y PCOP). The results show that the contribution of the process to environmental problems such as global warming and the decrease of the ozone layer are minimal, which are reflected in relatively low values in the impact categories GWP and ODP (1.47 and $5.59x10^{-6}$).

3.4 Effect of energy source

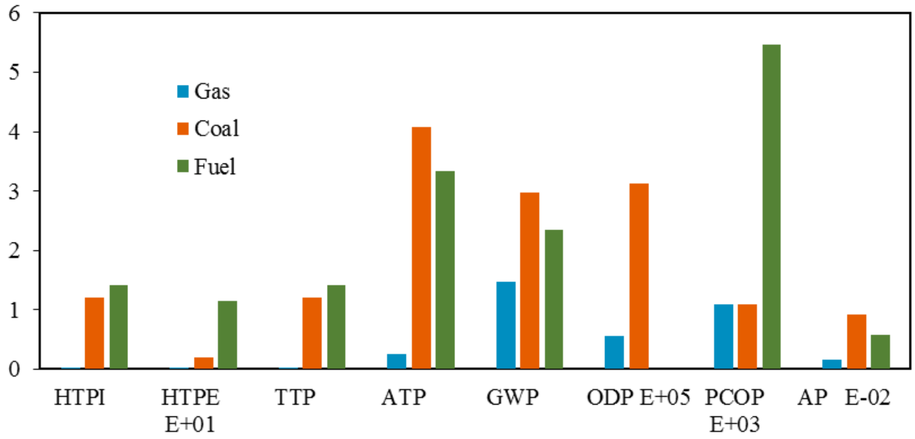

Figure 5. Effect of energy source on output rate from energy usage for a HF alkylation process

Under this scenario, three types of fuel (gas, coal and oil) were evaluated for each impact category, including the energy and excluding the product stream. Figure 5 shows the best energy source for this process are based-gas fuels, oil and coal sources increases all impact categories, coal has the highest values for some global impacts such as ozone depletion potential (ODP), global warming potential (GWP), acidification potential or acid rain (AP) and aquatic toxicity potential (ATP).

4. Conclusions

The environmental evaluation shows a negative PEI generation ratio which indicates consumption of the same within the process. Major sources of potential environmental impacts are the waste streams of hydrofluoric this means the total outgoing PEIs are due to the large amount of acid waste from the main reaction section, the alkylation process mainly two acid catalyst, both HF and H_2SO_4 are hazardous materials, and however, HF is considerably more dangerous. In the United States, HF has been identified as a hazardous air pollutant in current federal and state legislation. The above shows that from the environmental point of view, alkylation with H_2SO_4 would be less polluting. Although the energy consumptions are not very high compared to other processes, the type of fuel chosen to meet the requirements must be taken into account. In this sense, the results show that the best fuel for this process is natural gas, given the available energy savings present in the process, an integrated heat exchange network can be implemented, reducing the environmental effects associated with energy consumption.

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