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Selective oxidation of hydrocarbons and the global warming problem

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Abstract

Based on recently published studies on the life cycle analysis of several chemicals, and the CO_2 emissions associated with their production, a new approach to the selective oxidation of light hydrocarbons is discussed. By nature, selective oxidations are also producing CO_2 as the end product, much preferred by the thermodynamics. New technologies such as the circulating fluid bed reactor in selective oxidation, could be considered to propose a solution to reduce the CO_2 emissions both with respect to the yield improvement, but also as a solution to recover CO_2 from a high partial pressure recycling loop.

Keywords: Selective oxidation; Propane; Acrylic acid; Process; Global warming; CO_2 emissions

1. Introduction

Due to thermodynamic considerations, in selective oxidation reactions carbon dioxide is the common by-product. Recently, due to the global warming and its impact on the environment a lot of attention was put on more environmental friendly processes. However, for industrial chemists, this is not new. We only found a new name for it. In usual industrial processes, engineers and researchers are focussing on the improvement of yields and on energy savings. If the target is to make the process more and more economically viable, it also means that energy and feedstock consumptions have to be reduced per kilogram of product. Many processes have reached very high yields, and further improvement will require a deeper modification of the process. Reduction of global warming potential emissions and improvement of the overall economics of a process becomes more and more linked together, since a CO_2 taxation has been or will be introduced in some countries. With a value of €20–25 marginal t^{-1} of CO_2 it may affect significantly some process routes and promote the research on new synthesis routes. At €100 t^{-1} CO_2, this ecotax would add about \$50 bl^{-1} to the current oil price.

In the past, many changes in selective oxidation processes have found their way to the commercial plants. For example: benzene oxidation to maleic anhydride, and naphthalene oxidation to phthalic anhydride were replaced by butane oxidation and orthoxylene oxidation. One of the significant gain is made on the number of carbon atoms in the starting molecule, which in the latter cases is the same than in the targeted molecules. Other gain is made on the energy, and this is of course strongly linked to the selectivity. As the commercial plant is designed for a given productivity, in case of a strongly exothermic reaction such as benzene and naphthalene oxidations, a lot of reaction heat has to be withdrawn, and if there is no direct use for it, it is lost. Improvement of selectivity, or an alternative feedstock contributes to the reduction of the loss of energy. Of course, there is a further incentive to shift to new processes: the cost of the raw material, which in both cases was about half of the existing processes.

All these changes in raw materials have been possible when taking also into account possible changes in processes. For example, butane oxidation to maleic anhydride is now done in various processes such as multitubular fixed bed reactors, fluid bed reactors and even in a circulating fluid bed reactor.

In this paper, we will first use the life cycle assessment data available to review the synthesis of some of the basic chemicals used in the industry. From these data it is possible to

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derive the amount of CO_2 produced from cradle to grave for a given chemical (or well to wheel, when discussing of transportation fuels). In the present case, we are more interested to the values that we can call the ''cradle to gate'' of the chemicals (or well to tank, for fuels), i.e. the amount of CO_2 that was released in the atmosphere at the many steps through the chemical synthesis: oil or gas production, transportation, refining, steam cracking and so on. Since 1997, the simple inventory of emissions has been replaced by the international standards ISO 14040 series. As a consequence, many companies are now releasing an annual environmental report and collaborate in the processing of data to get meaningful interpretations. However, most of the precise data remain the property of companies and are hardly opened to the public.

From the data available, it is possible to estimate what should be the selectivity for a new process design in order to remain competitive on the CO_2 emission basis. Some examples will be treated here after. In this paper, we will discuss on the propane activation with a special focus on the direct oxidation of propane to acrylic acid. Any contribution to the decrease in CO_2 emissions is in some way a contribution to the sustainable development.

2. CO_2 emissions and global warming potential

2.1. Carbon dioxide equivalents

In addition to CO_2 industrial processes can contribute to the emission in the air of other compounds having a global warming potential (GWP). For each compound a global warming potential in terms of equivalent CO_2 can be estimated. As the effect of the different gases is time dependant, as they are reacting at different rates in the atmosphere, their potential can be either given for 20, 100 or 500 years period [1] or averaged [2]. As the calculated value depends on the references we can find in the literature, in the present report we will take into account the 100 year GWP values which are the most common data found in the literature (Tables 1 and 2).

2.2. Reported CO_2 emissions for chemical productions

In this paper, CO_2 emission and global warming potential values were taken from various open sources [1–7], see also the references included [8–16]. Most of the time, these data are only available directly from the plant, and are considered as confidential information, as it contains informations that could be used by a competitor to grasp an idea on process details. Other sources of information, are the reports of consulting groups, but these also cannot be disclosed to third parties. A lot of attention has been paid to find data that are accepted by the industry to get meaningful information.

Table 1
Carbon dioxide equivalents of selected chemicals [1]

Species	20 Year GWP	100 Year GWP	500 Year GWP
Carbon dioxide	1	1	1
Chloroform	14	4	1
Methylene chloride	31	9	3
Sulphur hexafluoride	16300	23900	34900
Methane	56	21	6.5
Nitrous oxide	280	310	170

Table 2
Global warming effect at 100 years of selected chemicals [2]

Species	Coefficient IPCC, 2002 (g equiv. CO_2)
CO_2	1
Biomass CO_2	0
Fossil CH_4	23
Biomass CH_4	23
N_2O	296

The collection of data is presented here (Tables 3–6) to illustrate the need of more selective processes but also to promote the proposal of new synthesis route for oxygenated compounds. Throughout the collection of data reported here, there might be some difference in values for a given product. It reflects also the difficulty in this kind of exercise as the data may differ significantly from one plant to another. When taking into account the electrolysis, the country in which it is done is very important as the source of electricity is not the same. For example, most of the French electricity is made from nuclear energy, and Norway has Hydroelectricity, both of them having low CO_2 emissions. However, Poland's electricity is based on coal burning, Italy has a lot of oil- and gas-based electricity.

Recently a large study involving companies and official agencies in France, analysed the energy balance and the global warming potential of conventional road fuels and of biofuels [2]. The study is based on statistical data of actual production, but also includes some prospective case study. From all the data reported, the values derived from the existing technologies are reported in Table 6. The data also account for biomass CO_2 co-production, in biofuels. But as this CO_2 production was first taken from the atmosphere, it does not have a global warming potential. Of course, as this study is based on the French industry it also means that when electricity is needed, the allocated CO_2 equivalents correspond to the French electricity network mainly based on nuclear power. In the GWP values, the production of methane and N_2O during the biomass growth and processing can have a significant impact (Table 6).

In case of fuels, the CO_2 allocated side production is given before and after combustion as the end-usage of the fuel is to be burned. In this case, we can observe that the biofuels are not so good in terms of GWP if they are not burned, but are superior to the conventional fuels on this criteria after combustion (complete life cycle analysis).

From the data that were gathered in this report, we can also estimate the values for some other products.

Table 3
Raw materials and associated CO_2 allocation

Fuel or material	CO_2 (g/unit)	GWP (g equiv. CO_2/unit)	Comments
Electricity (MJ)	34.9	36.5	Data for the electricity produced in France
Natural gas (MJ)	62.8	64.5	See also Ref. [8] cited in the report
Steam (2.6 MJ/kg) (kg)	226	232	
Naphtha (kg)	621	738	See also Ref. [9] cited in the report
Straw (kg)	96.7	182	
Isobutylene cut (kg)	500	506	Data provided by TOTAL
Hexane (kg)	299	313	
Soda (NaOH 50%) (kg)	550	587	Produced by electrolysis of sodium chloride. See also [10]
Phosphoric acid (H_3PO_4 52%) (kg)	1372	1424	Process route reaction of sulphuric acid on calcium phosphate. See also [11]
Methanol (CH_3OH) (kg)	475	521	Production of methanol through steam reforming of natural gas. Distribution from Middle East, 3500 km by boat and 400 km by road
Ammonium sulphate ($SO_4(NH_4)_2$) (kg)	650	751	Stoichiometric reaction
Ammonium phosphate ($(NH_4)_2HPO_4$) (kg)	1426	1580	Distance between production site and field: 400 km by truck [12]
Sulphuric acid (H_2SO_4) (kg)	147	148	Process route [13]: $S + 3/2O_2 + H_2O \rightarrow H_2SO_4$
Chlorhydric acid (100% HCl) (kg)	1198	1199	Process route: $H_2 + Cl_2 \rightarrow 2HCl$
Coke (kg)	655	958	Coal carbonization. See also Ref. given in the report [14]
Limestone (CaO) (kg)	1039	1049	Process included extraction, crushing calcination: $CaCO_3 \rightarrow CaO + CO_2$
Polyethylene (kg)	1100		All grades [15]
Polyurethane (kg)	3737	4194	Rigid foam [16]

Data are taken from Ref. [3]. References included in it are also given.

Table 4
Raw materials and associated CO_2 allocation

Fuel or material	Number of plants supplying data	Year period	Comments/process considered	CO_2 (g/kg)	GWP (g equiv. CO_2/kg)	Publication date
ABS copolymer	5	1995	Acrylonitrile–butadiene–styrene copolymerisation	3100		1999
Acetone	3	1996	Benzene + propylene → cumene, cumene oxidation to phenol and acetone	2000		1999
Acetone cyanohydrin	4	1992–1993	Acetone + HCN	2700		1999
Acrylonitrile	4	1990–1996	Propylene ammoxidation	2800		1999
Ammonia	3	1992–1996	Through natural gas steam reforming and water gas shift	4300		1999
Benzene	14	1989–1995	Steam cracking of naphtha and catalytic reforming	1400		1999
Butadiene			Steam cracking dehydrogenation of butanes	1100	1100	2003
Butenes mixed			Steam Cracking	1200	1300	2003
Crude oil			Crude oil extraction and transportation to Europe	130	170	2003
Electricity	56	1989–1998	On-site average	150 g/MJ		1999
Ethylene	15		Steam cracking	1100	1300	2003
Hydrogen			Cracker hydrogen	1300	1400	2003
Hydrogen cyanide	3	1992–1993	Reaction of methane with ammonia	4400		1999
Naphtha			Refining	280	340	2003
Natural gas			Natural gas production	230	480	2003
Pentane	3	1990–1996	Extracted and purified during refinery operation	1200		1999
PMMA	5	1992–1993	Through acetone cyanohydrine	5600		1999
Polyols	12	1995	Various processes	3100		1999
Propylene			Steam cracking	1200		2003
Pyrolysis gasoline			Steam cracking	1200	1300	2003
Steam	215	1989–1997	On-site production (average)	270		1999
Styrene	11	1990–1994	Dehydrogenation of ethylbenzene	2400		1999
Toluene	10	1990–1996	Catalytic reforming	1500		1999
Vinyl chloride monomer	12	1992–1995	Direct chlorination and oxychlorination	1700		1999
Xylenes (mixed)	8	1990–1996	Catalytic reforming	1300		1999

Year period: year to which data refers. Data are taken from eco-profiles of the European plastics industry [4].

Table 5
Raw materials and associated CO_2 allocation

Material	Comment	CO_2 (g/kg)	Plant location	Reference
Methanol, at plant	One reference plant in Siberia	610		[5]
Chlorine gaseous (Cl_2)	Hg cell electrolysis	930	Europe	[6]
NaOH, 50% in H_2O	Hg cell electrolysis	920	Europe	
H_2 liquid	Hg cell electrolysis	930	Europe	
Chlorine gaseous (Cl_2)	Diaphragma cell	800	Europe	
Chlorine gaseous (Cl_2)	Membrane cell	780	Europe	
Chlorine liquid (Cl_2)	Production mix	900	Europe	
Propylene oxide		3800	Europe	
Propylene glycol	Through hydrolysis of propylene oxide	3500	Europe	
Ethylene, at plant	Through steam cracker	1200	Europe	[7]
Propylene, at plant	Through steam cracker	1200	Europe	
Styrene, at plant	Through steam cracker	2400	Europe	
Vinyl chloride, at plant		1500	Europe	
Purified terephthalic acid, at plant	From paraxylene	1500	Europe	
PET, amorphous at plant	Through terephthalic acid production	2300	Europe	

Data are taken from EcoInvent Zentrum. Life cycle inventory (cumulated data).

Table 6
Associated CO_2 productions and global warming potential with several fuels issued from the conventional oil refining and from biomass [2]

Fuel	Before combustion		After combustion	
	g Fossil CO_2/kg fuel	GWP (g equiv. CO_2/kg fuel)	Contribution of CO_2 to the GWP (%)	GWP (kg equiv. CO_2/kg fuel)
Gasoline	443	444	99.97	3653
Ethanol (wheat)	739	922	80.2	922
Ethanol (beet)	818	902	90.8	902
MTBE	611	631	99.4	3131
ETBE (wheat)	765	860	96.3	2531
ETBE (beet)	802	851	98.1	2522
Diesel fuel	276	277	99.96	3394
Colza oil	354	660	53.5	660
Sunflower oil	367	498	73.7	498
Methylester of colza oil	470	755	67.9	888
Methylester of sunflower oil	486	612	83.0	745

Data correspond to the French refining industry as well as to the French agriculture.

For example, when seeds oil is processed to make the methylester (diester), glycerol is the main co-product. For colza and sunflower, 88% of the consumptions were attributed to the ester produced by methanolysis. The remaining 12% are attributed to the glycerol (CH_2OH–$CHOH$–CH_2OH). The calculated values are listed in Table 7. Of course these values should remain the same after combustion if it was used as a fuel.

Some discrepancies can appear between the data sets. But they might also reflect the efficiency of different processes. For example, in the comparison of processes, small differences can be seen between the different types of electrolysers (Table 5). However, on chlorine production the mercury cell seems to have a higher impact. In comparison of the data on isobutylene, it appears that the isobutylene produced in a refinery leads to lower emissions than the isobutylene produced from steam crackers. This reflects the superiority of catalytic processes over thermal processes. Unfortunately, it is not that easy to recover the isobutylene from a C_4 cut.

Table 7
Estimated data for glycerol production

Glycerol source	g Fossil CO_2/kg glycerol	GWP (g equiv. CO_2/kg glycerol)
From colza oil	470	755
From sunflower oil	486	612

Methanol may become a popular feedstock in the future if large oil companies decide to implement their plans to build large units, in an effort to reduce their emissions while flaring or burning associated gas. These large units will find their way only if valuable applications can be found downstream. Methanol production plants would be built were natural gas is available: in Siberia, Middle East, West Africa, etc. that means far from the consumers. It will be necessary either to ship methanol to chemical plants, or to build chemical plants near the methanol production sites.

Then, depending on the application, methanol associated emissions will include or not the emissions related to transportation from the production site to the consumption site. Methanol associated emissions can also reflect the kind of technology selected: steam reforming, combined reforming or autothermal reforming. Corresponding values for the process only are 470, 310 and 330 g/kg [5]. For new plants, the most efficient, and economic process should be selected; however older plants should continue to operate with lower efficiencies.

3. Alternative processes based on other raw materials

3.1. Hydrogen production

Some units in the refining industry such as the hydrodesulphurization unit is consuming hydrogen. It has to be considered as the other components in the calculations, and then it is necessary to add the CO_2 emissions corresponding to the hydrogen production. Conventional units for H_2 production include partial oxidation of residues (POX units), steam reforming of natural gas or naphtha. When a steam cracker is located nearby, the refinery can also use the hydrogen production from steam cracking. The refinery itself is producing hydrogen in the reforming unit. Basically in the reforming unit the C_6–C_8 cut is dehydrogenated to produce aromatics. The reaction is endothermic and energy input is necessary. Of course the weight of hydrogen produced is very small compared to the weight of reformate produced. If mass allocation rules are followed, the amount of CO_2 that will be allocated to hydrogen can be calculated as follows:

To make it simple lets assume that the feedstock to the reforming unit is like a naphtha (621 g CO_2/kg naphtha (Table 3)), and whatever the hydrogen yield, the CO_2 allocated to the hydrogen production is at least 621 g CO_2/kg hydrogen, by using the simple mass allocation rules.

If CO_2 is produced through steam reforming and water gas shift reactions of methane, according to the following equations:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad CO + H_2O \rightarrow CO_2 + H_2$$

About 4 moles of hydrogen (8 g) are produced for 1 mol of CO_2 (44 g), only based on the stoichiometric calculation. This gives an allocated CO_2 emission of 5500 g CO_2/kg hydrogen. Of course, in addition to that we should add the energy needed in the process. The reported value in the literature goes up to 9780 g CO_2/kg hydrogen [3].

In order to make hydrogen a more environment friendly fuel, one has to find other ways. Electrolysis of water can be a solution if the electricity is produced from hydroelectric power (renewable source) or from nuclear energy. Other possibilities are to produce hydrogen from biomass. If steam reforming of glycerol (taken here as a representative biomass product) is used to produce hydrogen, then the amount CO_2 associated would be limited to the CO_2 emissions associated to glycerol production. In this case, the CO_2 produced by the reaction itself was first atmospheric CO_2, transformed into vegetable oil during the growth of the plant, and is going back to the atmosphere after the steam reforming–water gas shift reactions. Then it does not contribute to the global warming. By this way, the CO_2 allocation is limited to the emissions associated to the glycerol production (Table 7) + the energy needed for the steam reforming–water gas shift reactions.

Other possible ways to produce hydrogen would involve carbon-exclusion. Examples of carbon-exclusion reactions are the reforming reaction, cyclohexane to benzene, methane to benzene, methane to carbon black, hydrocarbons to carbon fibers and so on. As no carbon dioxide is produced by the reaction itself, the balance is more favourable to hydrogen. Another example, of importance for the following discussion is the dehydrogenation of light hydrocarbons such as propane and isobutane, to propylene and isobutylene. There are now commercial processes available for these reactions and if the hydrogen produced can be economically recovered, there are additional incentives for these processes compared to the direct oxidative dehydrogenation.

3.2. Selective oxidations

In addition to the now well-known direct oxidation of butane to maleic anhydride, there are nowadays several substitutions processes that are being investigated, to produce base chemicals such as:

- direct oxidation of methane to methanol or formaldehyde;
- ethane oxidation to acetic acid;
- propane ammoxidation to acrylonitrile;
- propane oxidation to acrylic acid;
- isobutane oxidation to methacrylic acid.

Based on the CO_2 emissions associated to the various chemicals it is possible to calculate, what should be the minimum yield (or selectivity as we have to assume 100% conversion) for the new process routes in order to be competitive on the CO_2 emissions basis.

3.3. Methylmethacrylate

Polymethylmethacrylate is now a common polymer, much more known under the commercial brand names of Altuglas^{TM} and Plexiglas^{TM}. For methylmethacrylate synthesis there are several processes now in use over the world. It is not the objective of this paper to review all of these processes. The most common process is the so-called acetone cyanohydrine process. The popular process in Japan is the selective oxidation of isobutylene or tertiobutanol to methacroleine, followed by the oxidation of methacroleine to methacrylic acid, which is further esterified with methanol to lead to methylmethacrylate. Over the past 15 years a lot of research has been devoted to develop a new process for the direct oxidation of isobutane to methacrylic acid, due to the lower cost of the raw material.

When one look at the statistical data collected on the acetone cyanohydrine process, and the related CO_2 emissions: 5600 g CO_2/kg PMMA (Table 4), it becomes obvious that there is room for an improvement. In this process, acetone is reacted with hydrogen cyanide to produce acetone cyanhydrine. This is further reacted with sulphuric acid to lead to methacrylamide sulphate, further reacted with methanol to form methylmethacrylate and ammonium sulphate. The later is recovered to regenerate sulphuric acid. Acetone is the common co-product of the phenol synthesis, and hydrogen cyanide is obtained either as a by-product of the acrylonitrile synthesis or by reacting methane with ammonia. Ammonia was obtained by reacting nitrogen and hydrogen, obtained itself from steam reforming and water gas shift of methane. There are many sources of emissions in this process, but there is one that is not necessary when one look at the overall stoichiometry: the ammonia production, as no nitrogen atom remains in the methylmethacrylate.

The other commercial process route is from isobutylene. Unfortunately, the detailed CO_2 emissions statistical values have not been found. However, as the production of methacrylic acid by selective oxidation is an exothermic process, lets consider that a well optimised process should be self sufficient in energy. Most of the time, at first we have to consider that a new plant is isolated, and later on when it is time to decide whether to build it, some synergies can be found. Here, especially because we do not take into account process considerations, we assume that there are no consumers for extra energy produced and that if the new process needs to import energy (fuel, electricity, etc.), it is contributing to increase its global emissions. Then what we are looking for is to determine the minimum yield required in order to have the same CO_2 emissions than for the existing process.

Isobutylene can be extracted from the butene mixed cut from the steam cracker of from the C_4 cut of a refinery stream. The later process is quite common for the MTBE synthesis. Isobutylene can be extracted either through the hydration process to form tertiobutanol or through the MTBE process, followed by the back-cracking of MTBE. From the data listed in the table above we can obtain two different values for isobutylene: 500 g CO_2/kg C_4 cut from the refining operation (Table 3), and 1200 g CO_2/kg C_4 cut from the steam cracker operation (Table 4).

Isobutane is available from natural gas as well as from refinery streams. The precise value for isobutane is not available, so lets consider the value for natural gas: 230 g CO_2/kg. The oxidation of isobutane to methacrylic acid can be done either directly or through isobutylene. For the later, two routes can be considered: dehydrogenation of isobutane to isobutylene and hydrogen, or oxydehydrogenation of isobutane to isobutylene and water.

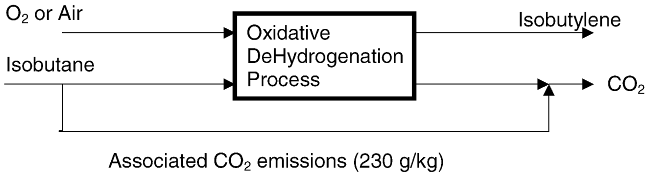

Fig. 1. General scheme to estimate the minimum yield required.

With the data available it is possible to calculate what should be the selectivity of the oxydehydrogenation process in order to be competitive with the isobutylene production from a steam cracker. In Fig. 1, assuming only two products isobutylene and CO_2, a minimum yield of 78% is then necessary [17]. It is important to note here that the selectivity required by this simple calculation is not far from the selectivity needed to make this process economically viable.

The same kind of calculation can be done to compare the direct oxidation of isobutane to methacrylic acid route and the acetone cyanohydrine process to methylmethacrylate. In this case, methylmethacrylate is the end product, then one has to take into account methanol and the allocated CO_2 production of 475 g CO_2/kg methanol (Table 3). Using the same simple calculation as before, we find that the minimum yield required is 26% to compete on the CO_2 emission basis [18]. On this basis, we can see that there is a very favourable ground to find a substitute process. In fact, this process is already existing as the isobutylene oxidation to methacrolein and to methacrylic acid. Because, there is more CO_2 emissions associated to isobutylene (1200 g CO_2/kg isobutylene) than associated to isobutane, we can do the same calculations as before to know what would be the minimum yield required for the isobutylene oxidation. The value obtained: 34% is far below the 65% yield obtained commercially with this process. It also means that the reference process for the development of a new process based on isobutane, is no longer the acetone cyanohydrine process (although this route represents most of the MMA produced worldwide) but the isobutylene oxidation. Combining the results for isobutane oxidative dehydrogenation and isobutylene yield, we find that a minimum yield of 52% is needed to compete on the CO_2 emission basis. Once again, this value is not far from what is necessary for making the isobutane selective oxidation economically viable.

3.4. Methanol and formaldehyde

Methanol is produced by steam reforming of methane to produce syngas. Then syngas is reacted under pressure to produce methanol. The associated CO_2 emissions were estimated to 475 g/kg methanol for a delivery in Europe (Table 3). Again the same calculations, as in the case of methylmethacrylate, can help to estimate the minimum yield required for the direct oxidation of methane to compete with the conventional methanol synthesis process. On the CO_2

emissions basis only, a minimum yield of 80% is calculated [19].

As formaldehyde is produced by the oxidation of methanol in the current processes with a very high yield, it would also be possible to estimate the minimum yield for a direct oxidation of methane to formaldehyde.

The minimum yield that have been calculated here, do not take into account the energy that would be necessary, nor the other streams required in the process, nor the emissions associated with the catalyst production. However, as specified, it is a minimum requirement, and if no catalyst is able to reach these targets, the process is not so environment friendly and its global warming potential has to be taken into account.

3.5. Propane upgrading

As in the case of isobutane, we can consider the oxidative dehydrogenation of propane to produce propylene. The CO_2 emissions associated with propylene production from a steamcracker were evaluated to 1200 g CO_2/kg propylene (Table 4). Once again, the minimum yield required to compete on the CO_2 emission basis: 78% is not far from the value calculated to make the process economically viable [20].

Of course, these criteria are only based on the CO_2 side production and not on the overall economics. But due to the CO_2 taxation that is being implemented, it is becoming important to take it into account, especially when considering selective oxidation reactions. For many reasons, nowadays it would be difficult to develop a process such as the acetone cyanohydrine process for methylmethacrylate production. For a process to be industrialised, it is very important not only to improve the yield but also to reduce the investment cost. For this reason, the next part of this paper will focus on the technology.

Based on the examples given so far, there is a challenge to develop new processes by selective oxidation. In a recent paper, the possible strategies in the selective oxidation of propane to acrylic acid on Mo–V-based oxides was reviewed [21]. It is not the scope of this paper, to explain in details the progress made on the development of these catalysts as it is extensively described in the paper [21]. We will focus here on the development of a new process using the circulating fluidised bed reactor for propane selective oxidation to acrylic acid. The driving force to select a new process may not be the same for all companies and the final choice made depends also on local situation. The driving force for the development of a new process can be the replacement of the feedstock, the use of existing reactors, a new demand from the business side (market opportunity), or to comply with new regulations. The same forces can take to an end a process development, for example the implementation of a new regulation on the use of Arsenic can lead a company to drop the research on a new catalyst; the merging of two companies, promoted by the decrease of the market demand, can lead to an increase of production capacity, and by then postpone the construction of a new unit or the implementation of a new process.

4. Circulating fluid bed reactor (CFBR)

In our previous paper [21] we compared several technologies, multitubular fixed bed reactor, fluid bed reactor, and the circulating fluid bed reactor. Such a process is quite common in the refining industry with the fluid catalytic cracking (FCC) units, and has been developed by DuPont for the butane oxidation for maleic anhydride production [22–25]. In this process, the catalyst is circulating from a reactor where the hydrocarbon reacts with the catalyst to the regenerator where it is re-oxidised with air before returning to the reactor. The CFBR technology can be considered if the catalyst operates according to the Mars–Van Krevelen mechanism, i.e. catalyst reduction and re-oxidation are decoupled in time. In such a case, they can be decoupled in space, and reduction and re-oxidation take place in different vessels. Patents have been applied for both acrylic acid and acrylonitrile using this redox process [26].

4.1. Advantages of the CFBR process

The advantages of this process for the selective oxidation of light hydrocarbons can be summarised as follows:

- *Flammability limits*: higher hydrocarbon partial pressures can be used.
- *Productivity*: higher flowrates.
- *Heat transfer*: better management of the heat of reaction and more homogeneous temperature.
- *Gas recycle*: gas recycle process allows to work with a lower conversion in the hope to maximize the selectivity.
- *Environment and CO_2*: purge gas thus obtained is very rich in propane and has a high heating value. It is possible to eliminate the catalytic incinerator and use a conventional incinerator. CO_2 recovery can be considered to avoid taxation on the CO_2 emissions.
- *Pressure drop and diffusion limitations*: no diffusion limitations due to the small particle size.
- *Reduction of the catalyst*: careful control of the catalyst oxidation state.

For all these reasons, the capital cost and operating expenses should be smaller for a circulating fluid bed. It is possible to consider this technology, even with catalysts having lower conversions and selectivities than in other processes.

4.2. Propane oxidation to acrylic acid

A catalyst used in this process has to operate according to the well-known Mars–Van Krevelen mechanism. This means that the molecular oxygen is not participating directly in the rate-limiting step of the hydrocarbon activation, and that reduction of the catalyst by the hydrocarbon and re-oxidation by molecular oxygen are separated on time. The lattice oxygens are the active species.

At the lab scale level, on a few grams of catalyst, it is difficult to build a test equipment working according to this process. Then it is more convenient to operate with pulses of reactants.

5. Experimental

5.1. Catalyst preparation

The MoVTeNbO mixed oxide catalyst used in this study was prepared according to the recipe described in the patent [27]. Since the discovery of the MoVTeNbO mixed oxide catalysts by Mitsubishi Chemical researchers, selective oxidation of propane is attracting a lot of attention from both the industry and the academics. The early work of Ushikubo et al. was designed to develop a direct route for the ammoxidation of propane [28]. Later theses oxides were found to be able to catalyse the direct oxidation of propane to acrylic acid [29]. Although, MoVSbNbO mixed oxides were found to catalyse the propane ammoxidation, they were also patented for the selective oxidation to acrylic acid by ToaGosei's researchers [30].

5.2. Catalyst testing

The testing procedure involves alternating pulses of propane and oxygen in an inert gas stream. The inert gas stream is a mixture of He/Kr and steam. About 1% Kr is included in the helium gas as it serves as in internal standard. A constant flow is maintained with mass flow controllers. Water is pumped, at a 3.46 g/h rate, from a tank and pushed by the helium stream to a vaporiser.

Propane and oxygen pulses are generated by mass flow controllers. Square pulses are generated with a pulse duration of 9.5 s for propane and 20 s for oxygen. Flowrates of propane and oxygen during the pulses were respectively 0.863 and 1.726 nl/h. The He/Kr gas flowrate was 4.281 nl/h. Detailed testing procedure is described in Ref. [27].

6. Results and discussion

The CFBR reactor is not a common type of reactor, as only one commercial plant is using it for the butane oxidation to maleic anhydride. We will then introduce some definitions to make the understanding of the results easier.

Oxygen consumed: When summing all the products, and according to the stoichiometry required it is possible to calculate the amount of oxygen that was pumped from the catalyst (units: g of oxygen/kg of catalyst, or moles of oxygen/kg of catalyst).

Table 8
Evaluation of the catalyst at 380 °C

Product	Yield (%)	Selectivity (%)
Acrylic acid	10.5	59.6
Acetic acid	1.05	5.96
Acrolein	0	0
Acetone	0.17	0.98
Propionic acid	0.08	0.45
Allylic alcohol	0	0
Allyl acrylate	0	0
Propanaldehyde	0	0
Acetaldehyde	0	0
CO	1.37	7.78
CO_2	1.27	7.22
Propylene	3.17	18.0
Propane conversion (%)	17.6	
Oxygen consumption from the catalyst (g/kg catalyst)	0.23	

Contact time: The contact time is probably the most difficult parameter to define. In fixed bed reactors or even in fluid bed reactors, the catalyst is remaining in the reactor, then the contact time can be defined as a ratio between the volume of catalyst and the gas flow rate. In a transported bed reactor, the gas is moving up in the riser and the catalyst also, however not at the same speed. It is possible to introduce a slip factor, but even though two different time constants are appearing: the time the gas remained in the reactor, and the time the catalyst remained in the reactor. The problem is even more complicated when the tests are done in fixed bed with pulses. Two different parameters are calculated, the usual contact time (volume of catalyst divided by the gas flow rate, here 1.6 s) that reflects the time taken by the gas to flow through the reactor, and the pulse duration that reflects the time during which the catalyst is reacting while flying in the reactor.

The example presented here (Table 8) illustrates that the catalyst is indeed working selectively according to the Mars–Van Krevelen mechanism. At a reasonable conversion a selectivity of nearly 60% to acrylic acid and 18% to propylene was achieved. At 380 °C, about 0.23 g of oxygen was pumped from the catalyst, within about 10 s. As explained before, in this recycle process, the selectivity (which is the most important parameter) is nearly equivalent to the yield as the propane is going to be recycled to extinction. As the gases are recycled, the CO_2 will accumulate in the loop, and will become easier to recover, making the whole process more environment friendly.

7. Conclusion

Alkane selective oxidation is a 'hot topic' for many companies including Atofina. In the past, the chemical industry was built first on coal mining, then on oil (Petrochemistry) and the future should be on gas. The huge amount of research being done in various fields such as the Fischer–Tropsch synthesis, methanol to olefins, and alkane activation illustrate the trend in the industry. As alkanes are more difficult to activate than their corresponding olefin, those working on selective oxidation of alkanes, are not expecting to reach the same selectivity at the same high conversion. Then the main by-product would be CO_2, and with global warming considerations, we have to face questions on CO_2 emissions.

In the catalyst development for selective oxidations, our target is always to reduce the CO_2 production, as it means lower selectivity to the desired product, loss of energy, higher production cost, etc. So, far before people heard of life cycle analysis and global warming, catalyst researchers and process engineers were trying to reduce the CO_2 emissions associated to the production of chemicals. Now, these data are available, and they can help the researchers to focus on the chemical productions where the highest gain is possible, and when detailed studies are published, it is even possible to focus on the precise step of the process.

On the CO_2 emissions basis, the required minimum yield can be calculated. Quite likely, these targets were found near what is accepted as the economic target. In fact, it is not so surprising as excessive CO_2 emissions also means energy loss, higher feedstock consumption and higher production cost. To reach these targets, it is now necessary to develop new processes. Process intensification is necessary to lower the production cost, but also to reduce global warming emissions.

In that sense, the circulating fluid bed reactor might also offer a solution to reduce the CO_2 emissions in selective oxidation processes.

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[17] With the steam cracker isobutylene a 1200 g CO2/1000 g isobutylene emission value is obtained. Taking into account the 230 g CO2/kg i-sobutane, we find that it is necessary to feed 1330 g isobutane to obtain 1000 g isobutylene, and 893 g or CO2 by the oxidative dehydrogenation process. For 1000 g isobutylene, a mass of 1000/56 × 58 = 1036 g of isobutane is necessary. Solving the equations, leads to the mass of CO2 produced: 893 g, and by then to the selectivity required: (1000/56)/(1330/58) = 78%.

[18] In this case we assume that the esterification is stoichiometric and that methanol is not contributing to the CO2 production. Then the amount of methanol needed is stoichiometric to the MMA produced: 1000/100 × 32 = 320 g. The amount of CO2 associated to methanol production is then 475/1000 × 320 = 152 g. We find that it is necessary to feed 2208 g of isobutane, leading to 4940 g of CO2. The amount of CO2 emissions associated to the isobutane is 2208 × 230/1000 = 508 g. Then the overall CO2 emissions are 5600 g for 1 kg of MMA, and the minimum yield required is 26%.

[19] To produce 1000 g of methanol a CO2 emission of 475 g is allocated. Then the amount of methane needed is 621 g having an associated CO2 emission of 230 × 621/1000 = 143 g and leading to a CO2 production of 332 g. Then the minimum yield required is 80%.

[20] To produce 1000 g of propylene by oxidative dehydrogenation of propane, 1345 g of propane are needed, leading to an associated CO2 emission of 309 g, and a direct production of 891 g of CO2. The minimum yield required is then 78%.

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