4. Oil Refining and Petrochemistry: Use of Zeolites and Opportunities for MOFs

María Ángeles Romero, Jesús Lázaro and Juana Frontela

Cepsa Research Center, Avenida Punto Com, nº 1, 28805 Alcalá de Henares (Madrid), Spain.

Keywords: Refining, petrochemical, oil&gas, process, adsorption, catalysis, shape selectivity

1. Introduction

Compañía Española de Petróleos S.A.U. (Cepsa) is an integrated energy service company that is active along the entire petroleum value chain. Cepsa performs commercial activities in the field of exploration and production of crude petroleum, refinery, petrochemical processes, gas and electricity, and is also present in the distribution and commercialization of all its products. Cepsa has actively participated in the energy service sector since 1929, when it was constituted as the first privately owned petroleum company in Spain. Since then, it has focused on research activities related to production processes, as well as developing innovative products. In August 2011, the International Petroleum Investment Company (IPIC), an investment group established by the Abu Dhabi government in 1984 – which had been a stakeholder for 26 years – completely acquired Cepsa. At present, Cepsa has a worldwide international presence in Europe, America, Africa and Asia, and has over 10,700 employees.

Cepsa refining activity is centred in Spain, where we own three refineries that account for 34 % of our total refining capacity of 27 million tons per year. Our refining operation is presently concentrated in three refineries focused on delivering fuel and petrochemical commodities, as well as a fourth one (co-owned at 50 %), which, produces asphalts. On the other hand, our petrochemical business is based on aromatics. Most of Cepsa's chemical products start from BTX (Benzene, Toluene and Xylenes). Cepsa carries out the basic petrochemicals operations at the refineries, obtaining raw materials, intermediate and final products. These have a multitude of

uses. For instance, the raw materials are used to produce detergents, polyesters, resins, electronic components, insecticides, synthetic fibres, and pharmaceutical products.

In this chapter, we will survey the roles that zeolites and metal-organic frameworks have in these sectors today and the ones they could play in the years to come, from our viewpoint of a research-intensive industrial company. Zeolites, as analysed in previous chapters, are defined as crystalline aluminosilicates with porous structure and ion exchange capability whilst they have been widely used as adsorbents and catalysts in the refining and petrochemical industry for the last 50 years. The international zeolite market was assessed at around USD 3.5 billion and a volume over 3000 kt. The compound annual growth rate (CAGR) is predicted to grow at around 3.5 % from 2015 to 2020 [1–3]. Metal-organic frameworks (MOFs) are also crystalline porous materials, but their three-dimensional framework is composed of metal ions (clusters) linked to multidentate organic molecules. Thus, they are coordination polymers. MOFs can have very high specific surface areas, up to $5900 \text{ m}^2 \text{ g}^{-1}$, and specific volumes, up to $2 \text{ cm}^3 \text{ g}^{-1}$ [3–4].

Most of the refining and petrochemical processes require a high temperature at several steps due to thermodynamic or kinetic limitations. Some processes, like cracking, hydrotreating, etc., operate at temperatures higher than 400°C . This high severity prevents the extensive use of MOFs in such operations due to their limited thermal stability. Moreover, several streams of the refining and petrochemical industry are highly polar, and MOFs are not as stable as desired either. Acid and polluted streams from industrial operations need to be treated or purified for downstream units or to fulfil legal specifications. In these cases, chemical stability is a limitation for the industrial application of MOFs, too [3–6]. As a result, there are no important industrial processes based on MOFs in the current refining and petrochemical industry at present. Zeolites, however, are extensively used in many applications in this industry, as demonstrated in the following sections. These are divided into adsorbents, refining catalysts, and petrochemical catalysts. Table 1 at the end of the chapter provides an overview of the different catalytic refining and petrochemical processes in which zeolites participate.

2. Zeolites as adsorbents in the refining and petrochemical industry

The use of zeolites as adsorbents in the refining and petrochemical industry is mainly linked to the production of lineal paraffins and aromatics, in

which *shape selectivity* plays a key role [7]. The operating temperature for adsorption processes is normally below 200 °C. Adsorption processes in the refining and petrochemical industry are made possible by the development of adsorbents exhibiting very specific selectivity, in particular, synthetic zeolites. Thus, shape selectivity of zeolites becomes crucial in many separation steps. Adsorption is usually applied in two cases: in the ultrapurification of feed to other processes, and in the fractionating of mixtures that are very difficult to separate by distillation [8].

2.1. Linear paraffin production

One of the most widely used tensioactives in the detergent industry is the LABSA (sulphonated linear alkylbenzene). This LABSA precursor, the linear alkylbenzene or LAB, is produced by alkylation of benzene with long chain olefins (C_9 to C_{14}). LAB's current global demand exceeds 3000 kt per year. These olefins are produced through dehydrogenation of linear paraffins from kerosene. Straight run kerosene contains not only linear paraffins but also isoparaffins, naphthenes, and aromatics. After a hydrotreating step to remove impurities, kerosene is sent to a separation process. This step uses a 5A zeolite molecular sieve to produce a kerosene raffinate with very few linear paraffins and a kerosene extract containing mostly linear paraffins.

In 1945, Barrer et al. discovered the adsorption capacity of linear paraffins over natural zeolites. They conducted a deep study on molecule sizes and operating conditions of the adsorption phenomena. Since then, the importance of the use of zeolites as adsorbents in separations processes has continued to grow until today [9].

There are two industrial processes employing molecular sieves: MolexTM (UOP) and EluxylTM (IFP) [8]. The world global demand of normal paraffins in 2016 exceeded 3000 kt and it is expected to increase growth by about 4 % in the coming years. MolexTM is the process most used for this application. It was developed in the sixties by Universal Oil Products (UOP). The process consists of three steps: feed pretreatment, adsorption, and *n*-paraffin recovery. During the feed pretreatment, a hydrotreatment process takes place in order to remove mainly sulphur, nitrogen, olefins and oxygen from the kerosene, which are poisons to the molecular sieve. The adsorption step mimics a countercurrent flow between the feed and the *n*-paraffins, while the zeolite remains packed (simulated moving bed). This simulation occurs thanks to a rotary valve that feeds kerosene and desorbent and yields raffinate and extract at different points in the adsorption column. EluxylTM is

also based on a simulated moving bed but it employs several valves instead of the rotary valve of the UOP system [8].

2.2. Xylenes production: *m*-xylene and *p*-xylene

There is another application of zeolites in separation processes closely related to the *n*-paraffins separation process. In this case, the desired molecule is the *p*-xylene, which is the raw material for the production of PET (polyethylene terephthalate). Shape selectivity in this case allows the separation of *p*-xylene from a mixture of *p*-, *o*- and, *m*-xylenes.

In 1964 Eberly and Arey used 13X molecular sieves for xylenes separation [10]. In 1981 Rosback proposed the used of Ba- and K-faujasite type zeolites for the same process [11]. In 1969, UOP launched the ParexTM process, which consists of a simulated moving bed, while in 1997 IFP introduced the EluxylTM technology for this same application [8]. UOP has introduced MX SorbexTM for the separation of *m*-xylene, a process very similar to ParexTM but with a different molecular sieve, more selective towards adsorption of *m*-xylene.

2.3. Olefins production

Zeolites exhibit an adsorption selectivity towards olefins over paraffins of approximately 10:1. Based on this, there are several industrial applications with this objective [8,12–13]:

- UOP Olex Process: for separation of C₁₀-C₁₄ olefins on a modified X zeolite
- UOP Sorbutene process: for 1-butene separation from a C₄ cut
- Union Carbide Olefinsiv process: for separation of *n*-C₄/isobutene on a 5A zeolite

2.4. Liquid and gas purification

Other applications of zeolites in the petrochemical industry are related to stream purification by adsorption, as in the LAB production for detergents. Along the LAB production scheme, the *n*-paraffins obtained through the MolexTM process are dehydrogenated to produce *n*-olefins. This is done in the UOP PacolTM process (paraffin conversion to olefins), which produces

not only olefins but also a small amount of undesired alkylaromatics as these can be dialkylated in subsequent steps producing a further loss of yields. UOP PEP™ (Pacol™ Enhanced Process) uses an adsorbent to remove these aromatics [14].

Zeolites are also used in the refining and petrochemical industry for PSA (pressure swing adsorption). This technology is widely used for hydrogen (H_2) purification. Hydrogen is produced and consumed in many processes in the oil and gas industry. Depending on the process, several contaminants can be present along with H_2 , such as N_2 , CH_4 , C_2H_6 , CO , CO_2 , H_2S , H_2O and NH_3 . When H_2 purity is over 60 vol.%, PSA is the best option for H_2 purification compared to cryogenic or gaseous permeation processes. PSA technology is based on the use of activated carbon and/or zeolitic molecular sieve and alternating pressure to effect the H_2 separation from the impurities [8].

3. Zeolites as catalysts in the refining industry

Current refining processes have three main objectives:

- Separating the lighter and more valuable fractions (gasoline, kerosene, diesel) from the crude oil.
- Converting the remaining heavy fractions into lighter ones through conversion processes. These processes require severe conditions (temperature and/or pressure).
- Fine-tuning the obtained light fractions in order to fulfil the legal requirements for fuels and petrochemical needs.

As shown in Figure 1, zeolites are key elements of refinery operations due to their excellent properties for the selective chemical conversion of several hydrocarbons families into more valuable ones.

3.1. Fluid catalytic cracking

Cracking units are used to convert vacuum gasoil and other low valuable cuts into more valuable ones such as gasoline, jet fuel or diesel. The fluid catalytic cracking (FCC) process involves a series of simultaneous reactions, both exothermic and endothermic. Nevertheless, the overall process is endothermic and therefore requires a continuous energy supply in order to reach reaction temperatures above 450 °C [15–16]. Catalytic cracking is

Figure 1. Refinery scheme (zeolite-based processes are highlighted).

Figure 2. The evolution of FCC catalysts [15–19].

the second-largest zeolite consumer, representing more than 95 % of the total volume of zeolites used as catalysts. The highest consumption of zeolites is as detergent builders, which accounts for more than two thirds of the total market [17].

Regarding the catalysts used in the FCC, Figure 2 shows its historic evolution. Since the first developments, when amorphous catalysts were used

(selective active matrix or SAM), to the 60s, when Mobil invented a spray-dried catalyst based on ultra-stable Y zeolite (USY), there has been a clear evolution aligned with product requirements. Since then, zeolite Y with different modifications and additives has been the base of FCC catalyst. Nowadays, the incorporation of ZSM-5 into the catalyst in order to increase light olefin yields and to boost gasoline octane is widespread [15–19].

The Resid FCC process (RFCC) converts heavier feedstock compared to the conventional FCC, with a residue content between 1 to 6 wt.%. This feedstock contains more organic nitrogen and organic metals (vanadium, iron, nickel, sodium and calcium) than those of the conventional FCC. The two most common technologies are Axens RFCC (R2R™ technology) and UOP RFCC. In both cases, a two-stage catalyst regeneration is used in order to minimize catalyst deactivation due to vanadium [15]. The USY requires a balanced concentration of acid sites of proper acid strength in order to minimize coke formation and maximize yields [18].

There are several commercial suppliers which commercialize FCC catalysts, such as GRACE, BASF, Albemarle, SINOPEC and Rive in partnership with GRACE. A review of the latest patents demonstrates that relevant research is developing in this area, in particular in catalyst additives [20] and new zeolite preparation methods for improved stability and mesoporosity [21].

3.2. Hydrocracking

The hydrocracking process allows the transformation of certain heavy streams (vacuum gas oil, deasphalted oils (DAO), coker gas oil) and low-value aromatic streams (such as light cycle oil (LCO) from FCC unit and residues from the vacuum tower) into lighter and higher added value products (such as gasoline or diesel) through a catalytic cracking process in the presence of hydrogen. The reaction system requires high pressures between 80–200 bar and temperatures between 350–450 °C [19]. There are several possible configurations for the hydrocracking process comprising one or two catalytic fixed beds, depending on the conversion requirements. The general scheme is shown in Figure 3.

In both configurations, there is a pretreatment step to remove metals, heterocompounds (sulphur, nitrogen, oxygenates), and some aromatics. The main catalyst for the first reactor is usually nickel-molybdenum supported on alumina ($\text{NiMo}/\text{Al}_2\text{O}_3$). The second step, in which the cracking process takes place, uses an acid catalyst. Several reactions to the same

Figure 3. Hydrocracker configurations [22].

catalyst occur at the same time (aromatics hydrogenation, ring opening and isomerization).

The first hydrocracking supports were amorphous silica-alumina (ASA). Subsequently, Y zeolite-based catalyst was developed. Zeolites show higher cracking activity but lower NH_3 and organic nitrogen tolerance. The zeolite can be exchanged with rare earth or dealuminated. The catalyst is bifunctional, containing a zeolite-based acid function and a metallic phase. Depending on the situation different metals can be used: NiW mixed sulphides provide hydrogenation activity, NiMo mixed sulphides favour nitrogen removal. Even, in some two-stage configurations, noble metals such as platinum or palladium are used if sulphur concentrations are low [19,23]. The modification of a Y zeolite via dealumination has a marked influence on the product's distribution obtained from hydrocracking. The reduction of the unit cell size and the modification of the strength of the acid centres and their distribution improves the selectivity to middle distillates [22,24].

In addition to the standard hydrocracking process, there are two different variations:

- Mild hydrocracking (MHC), which works under much less severe conditions than hydrocracking (30–70 bar, 350–440 °C) and is used to convert vacuum gas oil into medium distillates and low sulphur fuel [25]. Depending on the nitrogen content of the feedstock, loading amorphous or zeolite-based catalysts may not provide a gain of conversion compared to the conventional Co-Mo supported on alumina.

- Resid hydrocracker for vacuum residue gas oils (boiling point $>560^{\circ}\text{C}$), which works at maximum pressures of 200 bar and temperatures up to 450°C . Y zeolite can be used for this purpose. There are several industrial technologies [26]:
 - Fixed bed processes licensed by Chevron Lummus Global, UOP, Axens and ExxonMobil.
 - Ebullated bed licensed by Axens/IFP (H-OilTM) and Chevron Lummus Global (LC-FiningTM and LC-MAXTM).
 - Hybrid/moving bed licensed by Chevron Lummus Global (called On Stream Catalyst Replacement, OCR) and Shell technology.

Depending on each case the active phase can be Mo, Co-Mo, Ni-Mo or Ni-V. The catalysts have a large specific surface area with a low metal retention capacity and low acidity.

Nowadays the main suppliers that commercialize hydrocracking catalysts are UOP, Criterion, ART-Grace, Albemarle, Haldor-Topsoe, Axens, and SINOPEC.

3.3. Linear paraffin isomerization

The stream commonly called “light naphtha” comes from the atmospheric distillation tower and is composed of linear and branched hydrocarbons with five and six carbon atoms. The isomerization of this stream is intended to maximize the octane number by increasing its branching degree. This isomerized stream is then added to the gasoline pool [15,27].

The catalysts used in this process are chlorinated aluminas, zeolites, and sulphated zirconias. Chlorinated aluminas work at a lower temperature (180°C) than zeolites (250°C) because of their higher acidity. However, the need for a continuous chlorine input to maintain activity produces an effluent with small amounts of HCl, which results in corrosion problems. In this regard, chlorinated aluminas also have low water tolerance. As for zeolites, the most commonly used is Mordenite, which is dealuminated to obtain the required acidity. It is also impregnated with a noble metal (mainly platinum), which prevents coke formation by hydrogenating coke precursors. The first zeolitic process was developed by Shell in the 1960s under the name of Hysomer using Pt-Mordenite as a catalyst. Subsequently, UOP introduced the PenexTM process, similar to the previous one, in which the isomerization was integrated with a separation over a molecular

sieve and subsequent recycling [15]. In the late 1980s, Cepsa developed its own version of the isomerization catalyst, which Süd-Chemie commercializes under the name Hysopar. This catalyst is based on a Mordenite with better sulphur and coke resistance than the conventional Mordenite [27–29].

Subsequently, Süd-Chemie launched a new catalyst version, called HYSOPAR-SA (super acid SA). The introduction of superacid catalysts based on sulphated zirconias, which allow working at lower temperatures (around 60 °C), suggests that zeolites could be displaced by this type of catalysts if zirconia resistance to poisons like water and sulphur is improved in the future [28]. There are other suppliers that commercialize these catalysts, namely Shell and UOP.

3.4. Post-treatment of reformat

The octane number of naphtha (from six to ten carbon atoms) produced in the reforming process can be further increased by converting the residual linear paraffins (with very low octane numbers) to aromatics and branched alkanes through a zeolite-based hydrocracking process. ZSM-5 catalysts are preferred because their shape selectivity only allows linear paraffins to access their active sites.

In the 1960s Mobil introduced the Selectoforming process, using an erionite-based catalyst, which was modified in the 70s by the M-forming process, employing a more shape selective ZSM-5 type zeolite. Gulf also commercialized a similar process using Ferrierite as a catalyst. The commercial success of these processes is limited by the loss of gasoline yield compared to the octane gain and the by the low added value of the products. After that, Mobil developed a process named Mobil Reformat Upgrading (MRU), in which the zeolite is located at the bottom of the last fixed-bed reactor of the reforming process. In 1996 ExxonMobil commercialized a process based on the old Selectoforming called BTXtraTM, in which zeolite is used in the last reactor of a semi-regenerative catalytic reforming plant to increase the production of toluene and xylenes [15,24,27–28,30].

3.5. Naphtha post-treatment

Heavy stream naphtha produced in the FCC unit requires a deep hydro-treating step in order to fulfil sulphur requirements while minimizing

the loss of the gasoline octane number and avoiding olefin hydrogenation. The current industrial processes include: Axens Prime G+TM, Exxon-Mobil SCANfiningTM, CD Tech CD HydroTM and CD HDSTM, UOP ISALTM, ExxonMobil OCTgainTM, and Phillips S Zorb SRTTM. Although almost all these processes use catalysts based on Ni or Co-Mo on alumina, ISALTM and OCTgainTM use zeolite due to its reactant shape selectivity. In the case of the ISALTM process, it uses a CoMo-P/Al₂O₃ associated to a Ga-Cr/HZSM-5 zeolite [28,31–32].

3.6. Non-conventional reforming

Conventional catalytic reforming process has limitations in the aromatization of molecules with six and seven carbon atoms. Other catalysts based on zeolites appear to cover these deficiencies. Zeolite L exchanged with Ba and K and impregnated with Pt shows a very high selectivity to aromatics compared to the conventional reforming catalyst (Pt-Re on chlorinated alumina), although it exhibits extreme sensitivity to sulphur in the feed [33]. The current industrial process' that use L zeolite are Chevron Aromax[®] and UOP RZ-PlatformingTM, both operating at temperatures up to around 500 °C [34–35].

3.7. Dewaxing and isodewaxing of middle distillates and lubricants

Dewaxing and isodewaxing processes can be applied to both medium distillates (kerosene and diesel) and lubricants. These processes operate at high temperatures (280–400 °C) and pressures (20–110 bar). They are intended to improve “cold properties” such as pour point, cloud point, cold filter clogging point, etc. by eliminating or modifying linear paraffins. This dewaxing process can be carried out in several ways: extraction with solvents, selective cracking of paraffins or isomerization of paraffins. In the case of distillates, the latter two are most commonly used [1].

ZSM-5 is the catalyst most widely used in dewaxing by catalytic cracking. It was introduced by Mobil (MDDWTM, Mobil Distillate Dewaxing) in 1978. In the late 1980s, Akzo-Fina improved the process by adding a desulphurising function to the ZSM-5. In 1992, an alliance between Mobil, Akzo and Kellogg, (MAK) improved desulphurization catalyst properties in a new process called MDDW-CFITM (Mobil Distillate Dewaxing Process). This process is able to treat middle distillate feedstock with

Figure 4. Lube oils production scheme (zeolite-based processes are highlighted) [37].

higher *n*-paraffins content in order to produce better quality kerosene [1,28,36].

Dewaxing by isomerization employs a bifunctional catalyst of a metal supported on a ZSM-5 zeolite or SAPO-11. The first process of this type was introduced in 1990 and commercially tested by ExxonMobil in 1996 (MIDW-Mobil Isomerization Dewaxing) to produce low pour point and very low sulphur diesel. The use of Beta zeolite in a first step followed by a medium pore zeolite (like zeolite ZSM-22 or ZSM-23) is described for this process with benefits in shape selectivity for linear paraffins [28].

As for dewaxing and isodewaxing of lubricants, the process scheme is illustrated in Figure 4. The different cuts of vacuum gas oil from the vacuum distillation tower are subjected to a furfural extraction process to extract the aromatics. The raffinate, from which the aromatics have been removed, requires a dewaxing or isodewaxing process to improve its cold flow properties. Subsequently, the dewaxed stream can be treated in the hydrofinishing unit to improve the colour (removal of aromatics) and remove sulphur [37].

Catalytic dewaxing for lube oils uses the following zeolites [1,28,36–39]:

- British Petroleum (BP) developed the first catalytic dewaxing process in 1972. The catalyst was Pt on Mordenite. However, the relatively large pore size of this zeolite also caused cracking on some of the isoparaffins, causing a bad viscosity index (VI) in the final lubricant.
- In the 1980s Mobil introduced the most widely used lubricant dewaxing process: MLDWTM (Mobil Lube Dewaxing). This process is based on a modified ZSM-5 that presents a greater selectivity to the cracking of

linear paraffins. However, it also presents some problems regarding the VI when it is compared to products obtained by solvent dewaxing.

Catalytic dewaxing by isomerization for lube oils uses the following zeolites [1,28,36–39]:

- Exxon Mobil has a lubricant dewaxing process MSDWTM (Mobil Selective Dewaxing) based on a medium pore zeolite with a metal function that compensates the cracking activity of the zeolite (for example Pt on SAPO-11).
- Chevron developed its process using SAPO-11 zeolite. The one-dimensional nature of SAPO-11 and its pore size makes it very selective in producing highly branched products so the pour point is also improved.

4. Zeolites as catalysts in the petrochemical industry

The use of zeolites as catalysts in petrochemistry is closely connected to aromatic hydrocarbons. Many schemes have been proposed to optimise the production of aromatics depending on the products that one wants to maximize. Some technology licensors offer comprehensive solutions known as the ‘xylenes loop’, in which technologies from several companies can be combined. ParamaX™ from Axens is an example of this [40]. Figure 5 shows a possible scheme of a petrochemical complex, highlighting those processes that use zeolites.

Commercial sources of aromatics include catalytic reforming, pyrolysis gasoline, and coal pyrolysis. In crude oil refining, reforming naphtha

Figure 5. Petrochemical scheme (zeolite-based processes are highlighted).

or reformat is the product obtained from the catalytic reforming process, in which a low octane naphtha is converted to high octane aromatics including benzene, toluene and xylenes. The amount of aromatics contained in the reforming naphtha is typically in the range of 18 to 33 vol.%. Pyrolysis gasoline is a co-product of steam cracking of a hydrocarbon feed, whereas light oil from coal pyrolysis is a co-product of the manufacture of coke for the steel industry, and both processes produce certain amounts of aromatics.

4.1. Benzene alkylation with light olefins: cumene and ethylbenzene

Approximately 90 % of all ethylbenzene consumed in the styrene-polystyrene industry is produced by the alkylation of benzene with ethylene. This reaction is carried out by acid catalysis over AlCl_3 , $\text{BF}_3/\text{Al}_2\text{O}_3$ or zeolites. The usual temperature range for these reactions is between 100–180 °C. The Mobil-Badger process, marketed in the 1970s, was the first commercial process that employed zeolite (ZSM-5) as a catalyst. The shape selectivity of the zeolite allowed a reduction of coke formation by condensation and hydrogen transfer reactions (transition state shape selectivity). Substantial amounts of diethylbenzene were produced in the process. These were recycled to the reactor and converted to ethylbenzene via transalkylation with benzene. The process had an overall yield of 99 % to ethylbenzene. The Mobil-Badger EBMax (1995) process employs a zeolite, which produces fewer polyalkylates and oligomers, thanks to its particular porous system, which is capable of carrying out the alkylation reaction in liquid phase, thanks to its higher intrinsic activity [41]. Lummus/UOP has developed the EBone process, also a liquid phase alkylation process using a zeolite catalyst, which according to the supplier, can work during long cycles [42].

The alkylation of benzene with propylene yields cumene (isopropylbenzene), is another important product in petrochemistry as it is the precursor of phenol. For this process, larger pore zeolites such as Mordenite, Beta or HY are usually used, since the narrower ZSM-5 leads to higher yields of undesired *n*-propylbenzene. The process developed by Mobil/Badger has also been applied to the cumene process and is actually the most commonly used today. UOP developed the QMaxTM process using an internally developed zeolitic catalyst, which allows (always according to the manufacturer) high cumene yields and a longer lifetime [43].

Other reactions related to the alkylation of aromatics with short olefins using proprietary zeolites are the alkylation of toluene with methanol to yield xylenes [44], and the synthesis of *p*-ethyltoluene in the production of *p*-methylstyrene [45].

4.2. Benzene alkylation with heavy olefins: linear alkylbenzene (LAB)

Long chain alkylaromatic compounds are used as raw materials in many industrial fields. Among the most important applications is the production of surfactants for detergency and enhanced oil recovery. The usual process to produce these compounds in industry is the dehydrogenation of linear paraffins in the range C_9 to C_{16} (see section 2.1) and the alkylation with benzene of these olefins. Linear alkylbenzene sulphonate (LABSA) is produced by sulphonation of the linear alkylbenzene (LAB) and subsequent neutralization of the corresponding sulphonic acids. The range of temperatures for the alkylation process is around 120–170 °C. For the alkylation reaction, acid catalysts such as hydrofluoric acid are usually employed [46]. The use of hydrofluoric acid has the disadvantage of being a corrosive, difficult to handle with a lot of health and environment concerns.

Solid catalysts such as fluorinated silica-alumina and zeolites have been successfully developed in recent decades to replace hydrofluoric acid. Regarding zeolites, the use of zeolite Y, Beta, ZSM-5, ZSM-18, ZSM-20, Mordenite and offretite have been described as valid for this process. In practice, when the aromatic compound is alkylated over acid catalysts, undesired dialkylated products are formed in addition to the monoalkylated species, especially when the reaction proceeds at a high conversion and low benzene/olefin ratio. Thanks to the shape selectivity of the zeolites, the formation of these compounds is greatly minimised. This effect is very beneficial since decreasing the production of by-products greatly improves the economy of the process at the same time. Regarding the use of zeolite Y, it is possible to modify its acidic properties and stability by an exchange with rare earth cations (La, Ce, Nd, Pr) giving rise to zeolites called rare earth Y zeolite (REY) which have shown their ability to work in this reaction at very low temperatures [46–47].

The key point of this process is to control the amount of 2-phenyl isomer in the final alkylate. Depending on the zeolite type it is possible to obtain different percentages of this isomer in the product. Large-pore zeolites with moderate shape selectivity allow the production of LABs with a

low 2-phenyl content, similar to the distribution from a non-selective catalyst such as HF. However, zeolites with monodimensional channels such as Mordenite allow production of alkylates with a high amount of this isomer, thus increasing versatility in the process. The combination of these zeolites allows the desired amount of the isomer to be obtained [45].

The DETALTM process launched by Cepsa and UOP in 1995 supposed a breakthrough in the state of the art, being the first benzene alkylation process to produce LAB with a solid bed configuration [48–49]. As an upgrade to this process, the DETAL PlusTM process employs an improved catalyst that allows to production of fewer by-products and a lower benzene/olefin ratio [50].

4.3. Xylenes isomerization

The target of this process is mainly to maximize the production of *p*-xylene by isomerizing the xylenes to thermodynamic equilibrium. This also implies in some cases the transformation of ethylbenzene (as the reforming streams and pyrolysis gasoline contain from 15–55 % of ethylbenzene, which is very expensive to separate). Typical temperatures for this process are between 200 and 500 °C.

Mobil launched two processes based on ZSM-5. The MVPI (Mobil Vapor Phase Isomerization), besides isomerising xylenes, converts ethylbenzene via transalkylation to benzene and diethylbenzene. The small pore diameter of the ZSM-5 facilitates the formation of *p*-xylene, which tends to diffuse rapidly minimising disproportionation reactions of xylenes (product and transition state shape selectivity). The process MHTI (Mobil High-Temperature Isomerization) works at higher temperatures with a catalyst based on a noble metal on ZSM-5. Under these conditions, ethylbenzene is dealkylated to yield benzene and ethane. Currently, ExxonMobil offers the XyMaxSM and the Advanced MHAI (Mobil High-Activity Isomerization) processes that use a double catalytic bed system to optimize conversion of ethylbenzene, cracking of non-aromatics and isomerization of *o*-xylene and *m*-xylene to *p*-xylene [51]. The UOP ISOMARTM process is also used to convert mixtures of xylenes. Two different types of catalysts can be used, one that converts the ethylbenzene to xylenes, and another one that converts the ethylbenzene to benzene [52]. AXENS also has a new generation catalyst for the isomerization of xylenes and ethylbenzene with the name OPARISTM (Optimized Aromatics Isomerization), which minimizes the production of benzene [53].

4.4. Toluene disproportionation

The purpose of this process is to convert toluene to xylenes, particularly to *p*-xylene. The processes that maximize the production of *p*-xylene normally use ZSM-5, whose selectivity is increased by partial coking or by silanization. Mobil Selective Toluene Disproportionation (MSTDP) and Mobil Toluene Paraxylene (MTP) are two examples in which the catalysts combine the catalytic activity with the diffusional characteristics of the zeolite used. The catalyst can achieve 80 % *p*-xylene selectivity, whereas a mixture in equilibrium would result in 24 % [54]. ExxonMobil has recently launched the Mobil Toluene Disproportionation Process (MTDP-3). Their third generation catalyst is based on a more selective and stable ZSM-5 zeolite, which allows cycles of more than seven years. The catalyst minimizes the production of C₉ aromatics, which is one of the current limitations of this process [55]. UOP proposes for this process its PX-Plus™ technology, which selectively disproportionates toluene to xylenes and benzene [56]. Typical temperatures for this process are between 350 and 500 °C.

4.5. Heavy aromatics and toluene transalkylation

When the feeds are rich in aromatics of nine or more carbon atoms (pseudocumene, durene, etc.), disproportionation of toluene to benzene and xylenes can be combined with transalkylation reactions between toluene and higher aromatics to yield xylenes. Three types of reactions take place: transalkylation of C₉ with toluene, toluene disproportionation, and alkylbenzene dealkylation. Typical temperatures for this process are between 350 and 500 °C.

Two types of catalysts are employed in this process, those having no shape selectivity and those, which increase selectivity to *p*-xylene. The former are based on Mordenite. The use of a large pore zeolite allows the disproportionation of toluene to benzene and xylenes and also the transalkylation reactions between toluene and other alkylaromatics. The latter are based on ZSM-5, which can be used in combination with the Mordenite-based catalyst [57]. In some patents, the use of metals such as Ni or Pd is described as improving the dealkylation of the heavy aromatics [58].

There are several processes used for this purpose, one example being the Toray Advanced Catalyst (TAC-9*) process. The process can work with

mixtures of toluene and aromatics C_{9+} or with pure C_{9+} . Ethyltoluene (one of the most abundant compounds in the C_{9+} fraction) is converted to toluene by dealkylation and can be further transalkylated to give xylenes [59]. Other industrial processes for the conversion of heavy aromatics are Tatoray* launched by UOP [60] or TransPlusSM from ExxonMobil. The latter has been developed by the Chinese Petroleum Corporation (CPC) of Taiwan and uses a catalyst developed jointly with ExxonMobil. The great challenge of this process is to increase the selectivity to xylenes and to extend the catalyst lifetime. Licensors of all these processes claim to have significantly improved these drawbacks over the previous generations of catalysts [61].

5. Zeolites in other processes related to the refining and petrochemical industry

This section includes some processes related to the refining and petrochemical industry. The products of these processes are raw materials for the refining and petrochemical industry or materials derived from them. In Figure 6, gas conversion processes are shown.

Figure 6. Gas conversion processes (zeolite-based processes are highlighted).

5.1. Conversion of light olefins

Light olefin conversion to gasoline and middle distillates

Olefins from FCC, from the coker or from LPG dehydrogenation can be raw materials for gasoline production. ExxonMobil MOG process (Mobil Olefins to Gasoline) produces high octane gasoline through oligomerization, aromatization, and isomerization over ZSM-5 zeolite. Shell has developed a similar process called SPGK (Shell PolyGasoline and Kerosene) with Ni-Mordenite for the gasoline production from C_2 - C_5 olefins [62]. Ethylene, propylene and butene oligomerization are highly exothermic reactions. The reactions can be carried out with catalysts able to activate the olefin: in the homogeneous phase with metals (Ni or Ti) or in the heterogeneous phase with acidic supports (such as zeolites or Al_2O_3). Operating temperature varies from 100 to 250 °C in heterogeneous reactors or below 100 °C in homogeneous ones. Secondary reactions can occur on zeolites, (cracking and skeletal isomerization) and the reactivity of the different olefins increases with their molecular weight [63].

Light olefin isomerization

Isobutene is the raw material for the production of methyl *tert*-butyl ether (MTBE) and for poly-isobutylene. Several processes produce the skeletal isomerization of butenes to isobutylene. Mobil-BP-Kellogg developed ISOFINTM, which uses a medium pore zeolite, while the Texaco (ISOTEX, Texaco olefin skeletal isomerization process) and the Shell processes use Ferrierite zeolite [64].

5.2. Syngas to fuels through gas to liquids technology (GTL)

Synthetic gas or syngas can be produced from many sources, including natural gas, coal, biomass, or virtually any hydrocarbon feedstock, by a reaction with steam or oxygen. Syngas is a crucial intermediate raw material for the production of hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels. The syngas conversion to gasoline or other fuels or heavy streams constitutes the well-known Fischer-Tropsch (FT) process. The active phase is a composite of conventional catalysts and zeolites (ZSM-5 and/or SAPO-11 and/or SAPO-12), which is used in a two-step process [65]. Shell Middle Distillates Synthesis (SMDS) is the world's first commercial project to employ gas to liquids (GTL) technology, which can be used to produce petroleum-like products, chemical products, waxes, and other materials

from natural gas. The technology seems to have huge potential as an effective way to utilize natural gas. Mobil is another licensor that developed a two-stage slurry FT with ZSM-5 especially designed to produce high octane gasoline [66].

5.3. Other processes

From LPG

The most important process is the conversion of light paraffin (C_3 and C_4) to aromatics using Ga on ZSM-5. This BP/UOP process is called CYCLARTM. The resulting gasoline has high octane due to the high benzene, toluene and xylenes (BTX) content [67].

Methanol to olefins (MTO) and to gasoline (MTG)

Methanol is produced from syngas, oil, coal or, increasingly, biomass. The methanol to hydrocarbons process was discovered by Mobil in 1977. This process is used to convert methanol to products such as olefins and gasoline. In the methanol to olefins (MTO) process, methanol is converted to olefins such as ethylene and propylene. The main catalysts applied are ZSM-5 and SAPO-34. The light olefins obtained can be used to produce polyolefins, which constitute many plastic materials. ZSM-5 is used at temperatures of around 400 °C in the methanol to gasoline (MTG) process, [68].

6. Perspectives

6.1. The future of the refining and petrochemical industry

Refining and petrochemistry are both mature sectors. The technologies we use today are the result of decades of operations and millions of processed tons. Any new technology aimed to overcome the mature ones will have to be proven not only technically but also in economic, sustainability and safety terms. So, what are the drivers for opportunities today? There are Three challenges:

- First of all, the oil and gas sector is facing the introduction of *non-conventional crude oils*. Today's operations are optimized for conventional crudes. Catalysts for refining are prepared to cope with some poisons at certain concentration levels. Non-conventional crudes are sour, dense, and present high levels of heavy metals, including unusual metals. This

Figure 7. Evolution of the content of sulphur in diesel fuel.

is forcing a huge effort in R&D in pre-treatment processes – not only in catalysts but also in metal traps and guard beds.

- Secondly, *legislation* in Europe is posing more and more stringent specifications on fuels and emissions. The oil and gas industry has to implement and improve the finishing processes. A clear example is the new specification for marine fuel in terms of maximum sulphur. IMO's MARPOL Annex VI regulation will globally cap sulphur content to max. 0.5 % in 2020 [69], thus posing a challenge for fuel oil manufacturers. Another example is sulphur in automotive fuels: in 21 years (from 1996 to 2017) sulphur in diesel has suffered a huge decrease due to European Regulations, Figure 7.

In the case of automotive fuels the European Commission is also putting pressure on refiners to include biofuels in the market [70]. Biofuels are liquid or gaseous transport fuels, such as biodiesel and bioethanol, which are made from biomass (see Chapter 6). By 2020, the EU aims to have 10 % of the transport fuel in every country coming from renewable sources, such as biofuels. Fuel suppliers are also required to reduce the greenhouse gas intensity of the EU fuel mix by 6 % by 2020 in comparison to 2010. Refining companies are coping with this in two different ways. It is possible to maintain the oil business as it is and acquire the biofuel for blending from third parties, or it could be possible to go towards the concept of *biorefinery*. That is, to introduce biomass in the production sites to co-process it along with the mineral feed. Cepso's approach is the introduction of biomass in the current operations. This is another example of pressure on refiners.

Figure 8. Biofuels R&D Projects at Cepsa [71].

- *Efficiency.* Combustion motors are nowadays much more efficient than in the past. Less fuel is now required to cover the same distance. Refineries are facing this challenge by diversifying or looking at other markets or products in order to remain competitive. In the case of Cepsa, the integration of refining and petrochemical businesses is helping the company to face this challenge. Production schemes have to be flexible enough to optimize fuels or chemicals production depending on both demands.

There are other challenges but these three are certainly key in the oil and gas sector. What is Cepsa doing to face them? In relation to zeolites, in addition to refining and petrochemical projects dedicated to improving the present industrial operation, new materials and products are researched. These include the development of advanced fuel and biofuels. As can be seen in Figure 8, regarding the biofuels area, the technology readiness level (TRL) of the different studies range from lab-scale to industrial research, evidencing that there is room for improvement at every level.

6.2. The future of zeolite and MOF materials in refining and petrochemistry

As has been shown throughout this chapter, the fact that most relevant catalytic processes within refining and petrochemical industry are intended for conversion of certain crude oil fractions into higher value ones, future

conversion trends will be aligned by a) optimizing economics of catalytic processes by maximizing the catalytic activity and selectivity under less severe conditions (temperature, LHSV, pressure, H_2 demand, etc.), and b) increasing process flexibility to deal with changes in the economic environment. This aspect implies being able to manage cheaper and more complex raw materials (crude oil basket) while accomplishing newer and or stricter specifications of quality from demanded products (gasoline/diesel).

As for zeolites, the future challenges for each of the process' differ, although common goals include the improvement of selectivity, catalyst lifetime, and possibilities of regeneration. Zeolitic materials combine the advantages of having high specific surface areas (specific surface areas of $300\text{--}800\text{ m}^2\text{ g}^{-1}$) [72] and therefore the possibility of spreading a high number of active sites per unit of mass, with a certain variety of pore and cage sizes and shapes. Apart from that, due to their chemical nature, it is easy to generate acid sites and modify their strength. Finally, zeolites have a high thermochemical resistance.

Sustainable chemistry for the future requires the improvement of catalyst selectivity and the production of fewer waste by-products. An example of this is the catalytic alkylation of aromatics with olefins. In both processes, the alkylation with short chain olefins to obtain cumene and in long chains to give LAB, the production of dialkylated compounds has to be avoided, as these have to be treated as by-products or subjected to processes of transalkylation to recover the desired monoalkylated product. The modification of the textural and catalytic properties of the zeolites making them more selective to the products of interest then becomes crucial [73].

It is desirable to reduce the cracking that produces light compounds and yields losses in transalkylation catalysts. In this case, research should be focused on modulating the acidity to increase the yield to the desired product without producing cracking.

The use of new zeolites, zeotypes or even MOFs could improve the selectivity, although the introduction in the market of new structures is not simple as a result of the strong implantation of the existing zeolites. The majority of the current zeolite catalysts are based on three main structures: Y, ZSM-5 and Mordenite. It is true that other zeolites such as Beta or MCM-22 have been applied, but about 95 % of the volume of the zeolites used in catalysis is accounted for by Y zeolite for the FCC process.

Additionally, some possible new applications for zeolites can be expected, such as:

- a) Methane steam reforming to produce hydrogen. Due to the fact that many refining and petrochemical processes require hydrogen, this conversion

- would be very useful and profitable. In the last few years, Ru–CeO₂/Mordenite and Ni–La₂O₃/5A, have been studied for CH₄ reforming with CO₂ [74–75]. The catalyst with Mordenite as a support resulted in highly dispersed Ru and CeO₂. Low coke formation and high activity were also reported, constituting a promising type of new steam reforming catalysts.
- b) Fine-tuning processes: developing new zeolites that work in a selective way to remove poisons or chemical species that are refractive to conversion. An example could be the removal of 4,6-dimethyldibenzothiophene in hydrotreating processes [76].

In their turn, MOFs have different advantages. Due to the possibility of combining multiple metals with different oxidation levels and almost infinite organic ligands, the possibilities of tri-dimensional porous frameworks are huge compared to new potential zeolitic systems. However, most relevant refining and petrochemical processes require high temperature, making it difficult to envision MOFs as the catalytic phase for reactions like cracking, hydrocracking, etc., because of their low thermal stability [3–6]. The replacement of zeolites in the paraffins and xylenes separation processes seems difficult, too, since these processes are very well established and the adsorption process operates at moderately high temperatures.

A greater future for MOFs can be predicted in the case of adsorption and gas purification processes that usually work at moderate temperatures [77–78]. MOFs could be used in methane reforming (separation of H₂ from CO₂ stage) and hydrogen stream purification (CO_x removal for vegetable oil co-processing) in gas streams. As for separation processes in a liquid phase, it is noted that several heterocompounds present in oil streams, such as some nitrogen containing molecules (quinolones, indoles...) poison some refining and petrochemical catalysts located downstream. MOF MIL-101 has shown a very good selectivity to remove nitrogen compounds in straight run gas oil or light cycle oil streams at the lab-scale [79]. These experiments could be a good starting point for combining purification units with current refining and petrochemical units [80–82].

In the petrochemical field, there are also oxidation reactions, which are currently carried out at low temperature without a catalyst that could be withstood by MOFs. The literature describes their application to redox reactions involving light molecules [4,72]. These include their use for the direct synthesis of phenol from benzene. In this field, MOFs have been used for cumene oxidation to yield cumene hydroperoxide, a precursor of phenol. This reaction is currently carried out by oxidation with air, without a catalyst, with residence times longer than 12 hours. Being that the

temperatures are not very high (80–90 °C), it could be a possible field of application for these products. In fact, applications of MOFs for this reaction can be found in the literature. In particular, MOF MIL-101 has been applied for hydroxylation-epoxidation reactions and for cumene oxidation to cumene hydroperoxide at the lab-scale [83–85]. The use of highly localized energy supply systems (e.g. microwaves) might be another possibility for temperature-sensitive materials, or to improve the efficiency of the catalysis in general [86–87].

Although there are many recognized and mature industrial applications for zeolites compared to MOFs, both fields have a long way to go in creating and, why not, to combining them for the development of novel, efficient applications. Research and development is a challenging task, in which every achievement will undoubtedly be of great interest to this industry and to our society.

References

- [1] Chen, N.Y., Garwood, W.E., Dwyer, F.G. *Shape Selective Catalysis in Industrial Applications*, Marcel Dekker, 1989.
- [2] *Zeolite (Natural and Synthetic) Market for Catalysts, Adsorbents, Detergent Builders and Other Applications – Global Industry Perspective, Comprehensive Analysis, Size, Share, Growth, Segment, Trends and Forecast, 2014 – 2020* Market Research Store.
- [3] Unnikrishnan, P., Srinivas, D. Heterogeneous Catalysis. In *Industrial Catalytic Processes for Fine and Specialty Chemicals*, p. 41, Joshi, S.S., Ranade, V.V. (Eds.), Elsevier, 2016.
- [4] Corma, A., García, H., Llabrés i Xamena, F.X. *Chem. Rev.* 2010, 110, 4606.
- [5] Isaeva, V.I., Kustov, L.M. Metal-Organic Frameworks and Related Materials: Miles to Go. In *Zeolites and Zeolites-like materials*, p. 33, Sels, B., Kustov, L. (Eds.), Elsevier, 2016.
- [6] Albero, J., García, H. Metal Organic Frameworks as Catalysts for Organic Reactions. In *New Materials for catalytic applications*, p. 13, Parvulescu, V.I., Kemnitz, K. (Eds.), Elsevier, 2016.
- [7] Marcilly, C.R. *Top. Catal.* 2000, 13, 357.
- [8] Wauquier, J.P. *Petroleum Refining, Separation Processes*, IFP Ed. Technip, 2000.
- [9] Barrer, R.M. *J. Soc. Chem. Ind.* 1945, 44, 130.
- [10] Eberly, P.E., Arey, W.F. *US Patent* 3126425, 1964.
- [11] Rosback, D.H., Gillespie, J.M. *US Patent* 4283587 A, 1980.
- [12] Broughton, D.B. Adsorptive separation: liquids. In *Kirk-Othmer Encyclopedia of Chemical Technology* 3rd edition, p. 563, John Wiley, 1978. AICHE Symposium Series.
- [13] Broughton, D.B. AICHE Symposium Series, 1984, 80, 233, 62.
- [14] *Hydrocarbon Process* 1979, 58, 185.
- [15] Sie, S.T. *Stud. Surf. Sci. Catal.* 1994, 85, 587.
- [16] Sadeghbeigi, R. *Fluid Catalytic Cracking Handbook* 3rd edition, Elsevier, 2012.
- [17] Komvokis, V., Xin Lin Tan, L., Clough, M., Shaun Pan, S., Yilmaz, B. Zeolites in fluid catalytic cracking (FCC). In *Zeolites in Sustainable Chemistry*, p. 271, Feng-Shou Xiao, F.S., Meng, X. (Eds.), Springer, 2016.
- [18] Furimsky, E. *Stud. Surf. Sci. Catal.* 2007, 169, 305.

- [19] Rigutto, M. in *Zeolites and Catalysis: Synthesis, Reactions and Applications*, p. 547, Čejka, J., Corma, A., Zones, S. (Eds.), Wiley-VCH, 2010.
- [20] <http://www.dilworthip.com/fluid-catalytic-cracking-patents-2015-catalyst-additives/>
- [21] <http://www.dilworthip.com/review-2015-trends-fluid-catalytic-cracking-patents-part-ii-catalysts-zeolites/>
- [22] Scherzer, J., Gruia, A.J. *Hydrocracking Science and Technology*, p.174, CRC Press, 1996.
- [23] Lloyd, L. in *Handbook of Industrial Catalysts*, p. 211, Springer.
- [24] Degnan, T.F. *Top. Catal.* 2000, 13 349.
- [25] Valavarasu, G., Bhaskar, M., Balaraman, K.S. *J. Petrol. Sci. Eng.* 2003, 21, 1185.
- [26] Morel, F., Kressmann, S., Harlé, V., Kasztelan, S. Processes and catalysts for hydrocracking of heavy oil residues. In *Hydrotreating and Hydrocracking of Heavy Oil Fractions*, p. 1, Froment, G.F., Delmon, D., Grange, P. (Eds.), Elsevier, 1997.
- [27] Primo, A., García, H. *Chem. Soc. Rev.* 2014, 43 7548.
- [28] Čejka, J., Pérez-Pariente, J., Roth, W.J. in *Zeolites: From Model Materials to Industrial Catalysis*, p. 357, Transworld Research Network.
- [29] Lazaro, J., Corma, A., Frontela, J. *US Patent 5057471*, 1991.
- [30] Antos, G.J., Moser, M.D., Lapinski, M.P. The New Generation of Commercial Catalytic Naphtha-Reforming Catalysts. In *Catalytic Naphtha Reforming. Revised and Expanded*, p. 344, Antos, G.J. (Ed.), Marcel Dekker, 2004.
- [31] Babich, I.V., Moulijn, J.A. *Fuel* 2003, 82, 607.
- [32] Bruneta, S., Meya, D., Pérot, G., Bouchy, C. Diehl, F. *Appl. Catal., A* 2005, 278, 143.
- [33] Hughes, T.R., Buss, W.C., Tamm, R.W., Jacobson, R.L. *Stud. Surf. Sci. Catal.* 1986, 28, 725
- [34] <http://www.cpchem.com/en-us/rnt/licensing/aromaxtech/pages/history.aspx>
- [35] Lapinski, M., Baird, L., James, R. Catalytic Reforming. UOP platforming process. In *Handbook of Petroleum Refining Processes*, 3rd edition, p. 4, Meyers, R.A. (Ed.) Mc Graw Hill, 2006.
- [36] Perego, C., Calenma, V., Pollesel, P. Naphtha Reforming and Upgrading of Diesel Fractions. In *Zeolites and Catalysis: Synthesis, Reactions and Applications*, p. 585, Čejka, J., Corma, A., Zones, S. (Eds.), Wiley-VCH, 2010.
- [37] Sequeira Jr. A. *Lubricant Base Oil and Wax Processing*, Marcel Decker, 1994.
- [38] Blauwhoff, P.M.M., Gosselink, J.W., Kieffer, E.P., Sie, S.T., Stork, Zeolites as catalysts in industrial processes. In *Catalysis and zeolites: fundamentals and applications*, p. 437, Weitkamp, J., Puppe, L. (Eds.), Springer, 1999.
- [39] Lynch, T.R. in *Chemical industries*. Vol. 16, p.141, CRC Press, 2008.
- [40] Chemical Week, vol. 169, issue 8, p. 17.
- [41] Abichandani, J.S., Breckenridge, L.L., Chaya Rao Venkat, C.R. *WO Patent 1994013603 A1*, 1994.
- [42] Meyers, R.A. *Handbook of Petrochemicals Production Processes*, McGraw-Hill, 2005.
- [43] Jeanneret, J.J., Greer, D., Ho, P., McGeehee, J., Shakir, H. *The Q-Max Process: Setting the Pace for Cumene Production*, DeWitt Petrochemical Review, 1997.
- [44] Engelhardt, J., Szanyi, J., Valyon, J.J. *Catal.* 1987, 107, 296.
- [45] Young, L.B. *EP Patent 0026030 A1*, 1981.
- [46] Venua, P.B. *J. Catal.* 1966, 4, 81, 98.
- [47] Berna Tejero, J.L., Danvila, A.M. *US Patent 5157158*, *BR Patent PI 9204326-7*, 1992.
- [48] Vora, B.V. *US Patent 4467128*, 1984.
- [49] Vora, B.V. *US Patent 4523048*, 1985.
- [50] <https://www.uop.com>
- [51] *Hydrocarbon Process*, International Edition, 2001, 80 (7), 32, 2002, 81 (7) 75.
- [52] Otani, S. *Chem. Eng.* 1973, 80, 106.
- [53] <http://www.axens.net/product/technology-licensing/10038/oparis.html>
- [54] <http://www.exxonmobilchemical.com>

- [55] Cheng, N.Y., Kaeding, W.W., Dwyer, F.G. *J. Am. Chem. Soc.* 1979, 101, 6783.
- [56] *Eur. Chem. News* 1997, 67, 23.
- [57] Levin, D., Ross, A.D., Beech, J.H. *US Patent 8481443 B2*, 2013.
- [58] Nacamuli, G.J., Vogel, R.F., Zones, S.I. *US Patent 5952536*, 1999.
- [59] *Oil Gas Journal* 1998, 96 (48), 35.
- [60] Hydrocarbon Processing International Edition, 1975, 54 (11), 115.
- [61] *Eur. Chem. News* 1997, 68, 33.
- [62] Blauwhoff, P.M.M., Gosselink, J.W., Kieffer, E.P., Sie, S.T., Stork, W.H.J. Zeolites as Catalysts in Industrial Processes. In *Catalysis and Zeolites*, p. 437, Weitkamp, J., Puppe, L. (Eds.), Springer, 1999.
- [63] Martínez, C., Corma, A. *Coord. Chem. Rev.* 2011, 255, 1558.
- [64] Sawicki, R.A. NPRA, vol 95, issue 45 of A.M: National Petroleum Refiners Association.
- [65] Zwart, J., Vink, J. *Appl. Catal.* 1987, 33, 383.
- [66] Kuo, J.C.W. *Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline*, Final Report, DOE Contract No. DE-AC22-80PC30022, 1983.
- [67] Zhou, L. Base aromatics production processes. In *Handbook of Petroleum Refining Processes*, 3rd edition, 2.29, Meyers, R.A (Ed.), McGraw-Hill, 2003.
- [68] Stöcker, M. Methanol to Olefins (MTO) and Methanol to Gasoline (MTG). In *Zeolites and Catalysis: Synthesis, Reactions and Applications*, p. 687, Čejka, J., Corma, A., Zones, S. (Eds.), Wiley-VCH, 2010.
- [69] <http://www.imo.org/en/OurWork/environment/pollutionprevention/airpollution/pages/air-pollution.aspx>
- [70] *Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC* Official Journal of the European Union, June, 5, 2009.
- [71] Frontela, J. Cepsa Strategy for implementing *Biofeedstocks into Downstream Operation*, European Refining Technology Conference (ERTC), Lisbon, 2016.
- [72] Czaja, U.A., Trukhanb, N., Muller, U. *Chem. Soc. Rev.*, 2009, 38, 1284.
- [73] Ceña-López, C., Peláez, J., Márquez-Álvarez, C., Franco, M.J., Lázaro, J.J., Sastre, E., XXV Congreso iberoamericano de catálisis, Montevideo (Uruguay).
- [74] Luo, J., Gao, L., Ng, C., Au, C.T. *Catal. Lett.* 1999, 62, 153.
- [75] Hashimoto, K., Watase, S., Toukai, N. *Catal. Lett.* 2002, 80, 147.
- [76] Bej, S.K., Maity, S.K. Turaga, U.T. *Energy Fuels* 2004, 18, 1227.
- [77] Yilmaz, B., Trukhan, N., Müller, U. *Chinese J. Catal.* 2012, 33, 1.
- [78] Rangnekar, N., Mittal, N., Elyassi, B., Caro, J., Tsapatsis, M. *Chem. Soc. Rev.* 2015, 44 7128.
- [79] Laredo, G.C., Vega-Merino, P.M., Trejo-Zárrega, F., Castillo, J. *Fuel Process. Technol.* 2013, 106, 21.
- [80] Achmann, S., Hagen, G., Hämmeler, M., Malkowsky, I., Kiener, C., Moos, R. *Chem. Eng. Technol.* 2010, 33, 275.
- [81] Richter, I., Kiener, C., Malkowsky, I.M., Achmann, S., Hagen, G., Haemmerle, M., Moos, R. *US Patent 2010138781 A1*, 2011.
- [82] Mora, R.J., Montoya J.A., Laredo, G.C., Meneses, E., Castillo, J.J., Zapata, B. *US Patent 20160332138 A1*, 2016.
- [83] Santiago-Portillo, A., Navalón, S., Cirujano, F.G., Llabrés i Xamena, F.X., Alvaro, M. García, H. *ACS Catal.* 2015, 5, 3216.
- [84] Yang, H., Li, J., Wang, L., Dai, W., Lv, Y., Gao, S. *Catal. Commun.* 2013, 35, 101.
- [85] Luz, I., León, A., Boronat, M., Llabrés I Xamena, F.X., Corma, A. *Catal. Sci. Technol.* 2013, 3, 371.
- [86] Kustov, L.M., Sinev, I.M. *Russ. J. Phys. Chem. A* 2010, 84, 1676.
- [87] Hakek, M. *Chem. Commun.* 1997, 62, 347.