

Review

Production of Gasolines and Monocyclic Aromatic Hydrocarbons: From Fossil Raw Materials to Green Processes

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Abstract: The properties and the applications of the main monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, styrene, and the three xylene isomers) and the industrial processes for their manufacture from fossil raw materials are summarized. Potential ways for their production from renewable sources with thermo-catalytic processes are described and discussed in detail. The perspectives of the future industrial organic chemistry in relation to the production of high-octane bio-gasolines and monocyclic aromatic hydrocarbons as renewable chemical intermediates are discussed.

Keywords: bio-gasoline; pyrolysis; hydrodeoxygenation; hydrocarbons; aromatics from renewables; renewable intermediates; green chemistry



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1. Introduction

Monocyclic aromatic hydrocarbons, i.e., benzene, toluene, ethylbenzene, and the three xylene isomers, comprehensively denoted with the acronym BTEX, are highly anti-knocking components of high-octane number gasolines [1]. Even if in the near future, full electric mobility and hydrogen fuel-cell based electric vehicles will maybe become predominant, it seems likely that the use of liquid fuels will remain the best solution at least for some specific applications [2,3]. Although ligno-cellulosic bioethanol is (or will be) a good bio-gasoline component, its use as a pure or highly concentrated fuel has several drawbacks [4] and is actually forbidden in the European Union. Thus, the development of hydrocarbon-based renewable gasolines is desirable to fuel vehicles powered by conventional Otto-type engines limiting greenhouse gas emissions.

BTEX also represent key intermediates in industrial petrochemistry [5,6]. In fact, benzene, toluene, and xylenes, and their derivative styrene, are among the top 15 petrochemicals in terms of market [7] and are applied as building blocks for producing a large number of secondary intermediates and final products [8]. As we review in the next sections, these compounds are produced today in large amounts from fossil raw materials. As we will remark, some of these compounds are or may be cancerogenic. On the other hand, they are present in the environment also as products of (auto)combustion or heating of biomass and in oil seepages. They are also formed spontaneously by cooking food [9], smoking tobacco [10], and burning wood for heating, cooking, and garden care.

The concerns related to global warming and the expected progressively limited availability of fossil raw materials in the next fifty years push for the use of renewable raw materials for the production of fuels and chemicals. The development of new “green” processes is needed to convert biomasses into commodity and specialty products. However, this does not imply a complete revolution of industrial chemistry and products. In fact, the production of primary “petrochemical” intermediates using alternative green and sustainable processes can allow the use of already well-developed technologies for the manufacture of secondary intermediates and final chemical products.

In this paper, the conventional industrial chemistry of gasolines production and monocyclic aromatic hydrocarbons manufacture is reviewed together with emerging green

technologies which in the future could allow the production green hydrocarbon-based gasolines and of the same BTEX intermediates.

2. Applications of Monocyclic Aromatic Hydrocarbons

As previously said, in addition to their role as components of gasolines, monocyclic aromatic hydrocarbons also represent very important petrochemical intermediates. In Figure 1, the structures of the most relevant monocyclic aromatic hydrocarbons are reported. In Table 1, properties of such compounds are summarized.

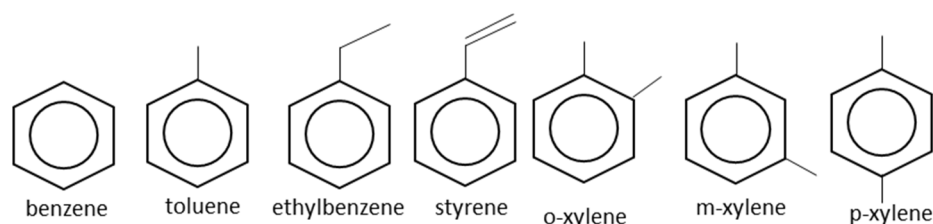


Figure 1. Structures of main monocyclic aromatic hydrocarbons present in oil and its primary transformation products (reformate and pyrolysis gasoline).

Table 1. Properties of main monocyclic aromatic hydrocarbons present in oil and its primary transformation products (reformate and pyrolysis gasoline).

Monocyclic Aromatic Molecule	T_{eb} °C	T_m °C	Vp kPa	d g/mL	\varnothing_c nm	RON	MON	Fp °C	IARC Classification
Benzene	80.1	+5.5	12.70	0.879	0.67	101.0	93.0	−11	Group 1
Toluene	110.6	−59.4	3.79	0.867	0.67	121.0	103.0	4	Group 3
Ethylbenzene	136.2	−95.0	1.28	0.867	0.67	108.3	97.9	15	Group 2b
Styrene	145.2	−30.0	0.81	0.906	0.67	103.0	100.2	31	Group 2a
Para-xylene	138.3	+13.3	1.18	0.861	0.67	146.0	101.2	25	Group 3
Meta-xylene	139.1	−47.9	1.12	0.864	0.71	145.0	102.8	23	Group 3
Ortho-xylene	144.4	−25.2	0.89	0.880	0.74	120.0	100.0	17	Group 3

T_{eb} = boiling point; T_m = melting point; Vp = vapor pressure at 25 °C; d = density at 20 °C; \varnothing_c = critical radius; RON = research octane number; MON = motor octane number; Fp = flash point; IARC = classification of International Agency for Research on Cancer.

2.1. Benzene

Global benzene production is forecasted to rise 51 mton/y in 2022 [11]. Benzene is one of the most toxic among common molecules [12,13], being classified by the International Agency for Research on Cancer (IARC) as Group 1 molecules, carcinogenic for humans. Its presence in gasoline, according to its relatively high volatility, creates very toxic gasoline vapors. For this reason, its amount is limited in commercial motor gasoline by law to 1% vol in the European Union. Nevertheless, benzene is a very relevant intermediate for today's production of a large number of household commodities. The main industrial chemistry of benzene is summarized in Figure 2. Even if this chemistry also contributes to some environmental problems [14], its role in developing materials and molecules for our common life is enormous [15]. On the other hand, dangerous amounts of this molecule are also simply formed, e.g., by cooking food [9], and cigarette smoking is still the main source of human exposure to benzene [16].

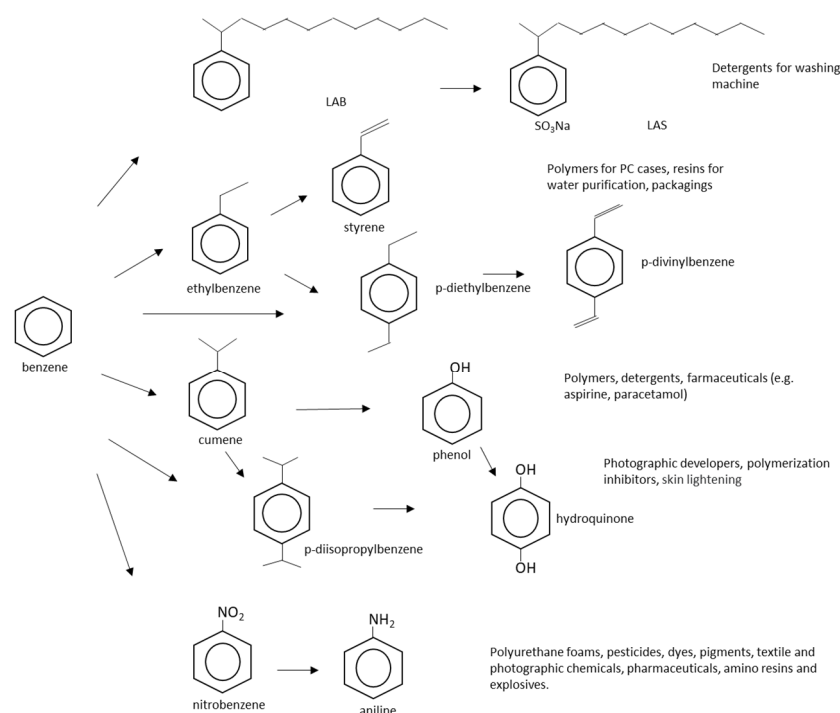


Figure 2. Structures of main secondary products obtained from benzene.

More than half of benzene production today is devoted to the synthesis of ethylbenzene by alkylation with ethylene, which is almost completely converted into styrene. The final product is polystyrene, which is a very common plastic material in daily life, as detailed below.

More than 20% of benzene is converted by alkylation with propylene into cumene, to be later converted into acetone and phenol. Phenol is also a key intermediate for the production of a number of compounds. Among many others, polycarbonate plastics which are used, e.g., for the production of the external cover of laptop computers, and anti-inflammatory drugs, such as aspirin and paracetamol.

More than 10% of benzene is hydrogenated to cyclohexane as a key intermediate to produce nylon 6 (via caprolactam) and nylon 6,6 (via adipic acid and adiponitrile), the two predominant polyamide plastics and fibers. Nylons find a number of applications such as in toothbrushes, wear pads, wheels, gloves, guitar strings and pics, tennis racket strings, medical implants, electrical connectors, fishing line, tents, gears, etc. [17].

Around 10% of benzene is nitrated to nitrobenzene, manufactured in order to produce aniline, which may be transformed into methylene diphenyl diisocyanate (MDI), which is the monomer for producing polyurethane plastics and fibers and other specialty applications. Around 3% is converted into linear alkyl benzenes (LABs) to produce sulfonates (LASs), which are the most common detergents for laundry machines.

2.2. Toluene

Toluene global production capacities are reported to be around 30 million metric tons per year [18]. Toluene is far less toxic than benzene, due to its higher reactivity at the methyl group. It is classified by IARC as Group 3 molecules, not classifiable as to its carcinogenicity to humans, although recent studies do not exclude carcinogenicity [19].

Toluene is a common solvent, e.g., for paints, paint thinners, silicone sealants, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners, and disinfectants. It can be also used as an octane booster in gasolines and is a main component of aviation gasolines (see below).

Toluene is used as a petrochemical intermediate (Figure 3 [20]) to make the diisocyanate (TDI), which is combined with polyols in the manufacture of polyurethanes

plastics. In turn, polyurethanes are used in a wide variety of consumer goods, such as foams for furniture and bedding, coatings for floors and furniture, artificial sports tracks, ski suits, and waterproof leisure wear. It is also used in the production of benzoic acid to be later converted into phenol, to produce explosives (trinitrotoluene, TNT), and by nitration and sulfonation, to produce dyes. Among other smaller applications, toluene is a starting compound for the synthesis of the anti-inflammatory drug ibuprofen, by producing the intermediate isobutylbenzene by side chain alkylation with propene.

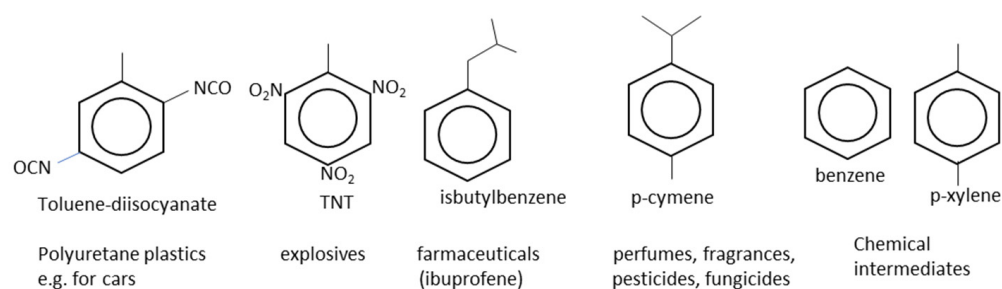


Figure 3. Structures of main secondary products obtained from toluene.

Over 50% of produced toluene, however, is converted to benzene and xylenes by hydrodealkylation and disproportionation/transalkylation (see below). Recently, toluene selective methylation to paraxylene using methanol has also been developed [21].

2.3. Ethylbenzene

Ethylbenzene is present in moderate to small amounts in gasolines. It is classified by IARC in Group 2b molecules, as a possibly carcinogenic molecule [22]. Most of it is produced ex novo by liquid-phase alkylation of benzene with ethylene over zeolite catalysts [23]. Most of ethylbenzene is later converted into styrene by gas-phase dehydrogenation over iron oxide based catalysts at 500–600 °C [24]. Ethylbenzene is also used as a solvent for treatment of other aromatics, such as in the styrene radical polymerization process [25].

2.4. Styrene

Styrene is present in significant amounts in pyrolysis gasoline, from which it can be separated by extractive distillation [26] usually after previous hydrogenation of phenylacetylene impurities [27], and in small amounts in coke oven benzole. However, most styrene is produced by catalytic dehydrogenation of ethylbenzene [24]. Styrene is the monomer for the different forms of polystyrene (PS) [28,29]. General purpose PS (GPPS), characterized by good mechanical properties but is relatively brittle, is a very common material for packaging, particularly for foods. High impact PS (HIPS), which contains an elastomer, usually polybutadiene rubber, to improve impact strength and has a milky or opaque appearance, is commonly used for housings of apparatuses such as TV, copying machines, printers, air conditioners, etc. Expandable PS (EPS), made of tiny spheres of GPPS impregnated by a blowing agent that expands in further processing (molding, extrusion) to produce the characteristic beaded nature, is also mainly used in packaging and building insulation. It is also applied in the manufacture of important copolymers such as SAN (styrene-acrylonitrile) and ABS (acrylonitrile-butadiene-styrene) plastics, or manufacturing toys, small appliances, computers, mobile phones, electrical components and medical devices, and SBR (styrene butadiene rubber) elastomeric material for the manufacture of tires, hoses, toys, shoe soles, or asphalt sheets. Styrene is included in the list of probable carcinogenic molecules. The International Agency for Research on Cancer (IARC) classified styrene into Group 2a, being possibly carcinogenic to humans [30].

2.5. Mixed Xylenes

Mixed xylene, which is usually composed of m-xylene (40–65%), p-xylene (20%), o-xylene (20%), and ethyl benzene (6–20%), is used for various applications [31,32]. For instance, it is used to enhance the octane number of gasoline. Mixed xylene is also used as a solvent in various end-use industries and as a thinner in paints, inks, etc. It is a common component of adhesives and a cleaning agent, e.g., for steel, silicon wafers, and integrated circuits. Additionally, single xylene isomers have some important applications (Figure 4). There is no conclusive evidence of carcinogenicity for xylenes [33], which are classified by the IARC as Group 3 molecules, not classifiable as to its carcinogenicity to humans.

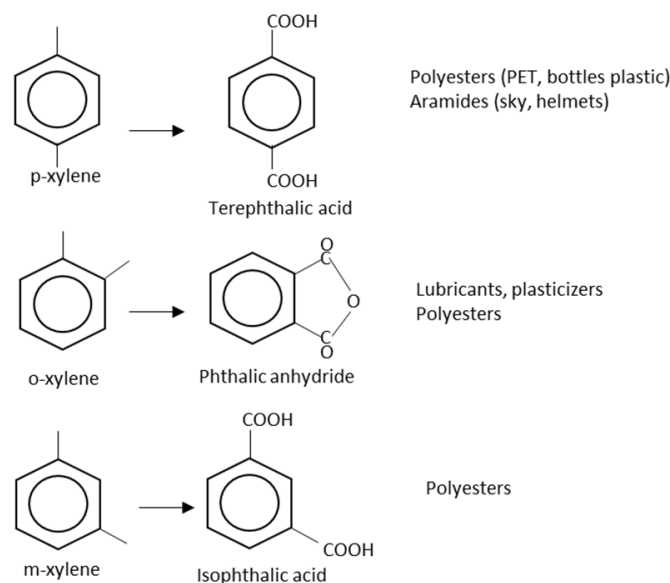


Figure 4. Structures of main secondary products obtained from xylenes.

2.6. Ortho-Xylene

Most ortho-xylene is devoted to the manufacture of phthalic anhydride [31] by gas-phase catalytic oxidation [34]. Phthalic anhydride is mostly converted to phthalate esters which have significant applications as plasticizers (mainly for PVC) as well as lubricants. Phthalic acid is also used for the manufacture of alkyd resins and polyesters.

2.7. Para-Xylene

Para-xylene global world production is of the order of 50 million tonnes per year, and accounts for 85–90% of global xylenes demand. Para-xylene is mostly converted by liquid-phase partial oxidation into terephthalic acid [31,35], or by oxy-esterification to dimethyl-terephthalate, which are the monomers for the manufacture of polyethylene terephthalate (PET) by poly-esterification or poly-transesterification processes. PET is the constituent of beverage bottles, and is also a synthetic fiber. Terephthalic acid is also used to produce other polyesters as well as aramides such as Kevlar [36], widely-used as a friction material in the automotive industry and a combustion protection material in the aerospace industry.

2.8. Meta-Xylene

Although m-xylene is the most stable and usually the most abundant among xylene isomers, it is the least useful. Meta-xylene is used mostly to produce isophthalic acid [31,37] by liquid-phase oxidation, useful to produce polyesters and, mainly, as a modifier in the production of polyethylene terephthalate (PET). However, most of it is converted to meta- and ortho-xylene in the xylene isomerization process (see below).

2.9. Other Industrially Relevant Monocyclic Aromatic Hydrocarbons

There are a number of other industrially relevant monocyclic aromatic hydrocarbons with an important market.

Cumene (isopropyl benzene). The intermediates for producing phenol and acetone in the so-called Hock processes. It is produced by liquid-phase benzene alkylation with propylene over zeolite catalysts [38]. It was first produced as an octane booster for aviation gasoline during the Second World War.

Linear alkylbenzenes (LAB). They are the intermediates for producing the very relevant family of linear alkylbenzene sulfonate detergents (LAS). They are produced by alkylation of benzene with linear higher olefins either using HF liquid catalysts or with more modern solid acid catalysts [39].

Diethylbenzene and divinylbenzene. Para-diethylbenzene is a byproduct of ethylbenzene synthesis and is used as a solvent, e.g., for para-/meta-xylene separation in the Parex selective adsorption process [40]. However, most p-diethylbenzene is used to produce p-divinylbenzene by dehydrogenation over iron oxide catalysts. Para-divinylbenzene is a co-monomer for producing the network Polystyrene-Polydivinylbenzene (PS-PDV) based cation exchange resins, applied, e.g., to water purification, and catalysts for liquid phase reactions.

4-ethyltoluene and 4-methylstyrene. The former can be produced by alkylation of toluene with ethylene. It is a valuable intermediate in the production of 4-methylstyrene via catalytic dehydrogenation is used as a comonomer in the production of specialized polystyrenes as well other copolymers.

4- and 3-di-iso-propylbenzenes. These compounds are currently used industrially for the production hydroquinone (para-dihydroxybenzene) and resorcinol (meta-dihydroxybenzene), via Hock-type processes [41]. They are produced by alkylation of either benzene or cumene with propylene [42].

Para-cymene (p-isopropyl-toluene). Para-cymene is naturally present on a number of vegetable materials but is also conventionally produced by alkylation of toluene with propene [43] or isopropanol [44]. Para-cymene is a key compound in the synthesis of pesticides, fungicides, perfumes, fragrances, and as a starting material for the synthesis of p-cresol, which is in turn used in the production of antioxidants such as butylated hydroxytoluene (BHT) [45].

Isobutyl-benzene (IBB) is synthesized by side chain alkylation of toluene with propylene in the presence of alkali metals [46]. It is the starting molecule for producing the common anti-inflammatory drug ibuprofen [47].

3. Manufacture of Monocyclic Aromatic Hydrocarbons and Gasolines from Fossil Raw Materials

3.1. Monocyclic Aromatics in Crude Oil and in Commercial Gasolines

Monocyclic aromatic hydrocarbons are present in crude oil to a limited extent (Table 2). They may represent about 10% of full range straight-run naphtha and up to 20–26 wt% of the straight-run heavy naphtha fraction (boiling point range 370–430 K). Due to their strong anti-knocking power, monocyclic aromatic hydrocarbons are further produced mainly by catalytic reforming processes. The addition of other aromatic-rich gasolines such as pyrolysis gasoline and coke oven gas oil, but also gasoline coming from the fluid catalytic cracking process (FCC gasoline) which usually contains about 30% aromatics, allows for finally obtaining the required concentration in commercial gasolines. In the European Union, the maximum content of aromatics in MoGas (Motor Gasoline) is 35 vol% with a maximum benzene content of 1 vol% (due to its toxicity), and minimum RON and MON being 95 and 85, respectively (Table 3).

In the case of the most common aviation gasoline (AvGas 100LL), the minimum MON is 99.5. However, for technical reasons, aromatics content is practically limited to less than about 25%. In fact, the maximum freezing point of $-58\text{ }^{\circ}\text{C}$ excludes the presence of important amounts of benzene and the xylenes, while the minimum heating value allows

the presence of up to near 25% toluene. Thus, the starting lead-free distillate has a MON around 91. To obtain the needed minimum RON of 99.5, commercial AvGas 100LL currently contains the additive tetraethyl lead (TEL), in amounts up to 0.53 mL/L or 0.56 gPb/L, which are increased to 1.06 mL/L and 1.12 gPb/L for AvGas 100 [48].

Table 2. Typical monocyclic aromatics content in different hydrocarbon cuts [5,6,49].

Component	Crude Oil	Full Straight Run Gasoline	Reformate Gasoline	Light Reformate Gasoline	Pyrolysis Gasoline	Coke Oven Light Oil
Benzene	0.1–0.3	1–3	3–12	20–30	25–34	60–80
Toluene	0.3–2	2–8	12–25	40–50	15–22	9–18
Xylenes	0.5–3	2–8	15–30	<0.5	5–15	1–6
Ethylbenzene			2–8	<0.5	2–5	1–2
Styrene	0	0	tr	tr	2–6	1–2
C ₉₊ aromatics	0.3–2	2–8	10–20	0	2–5	5–10
Total monocyclic aromatics	1–7	7–20	35–65	60–80	45–65	95–98

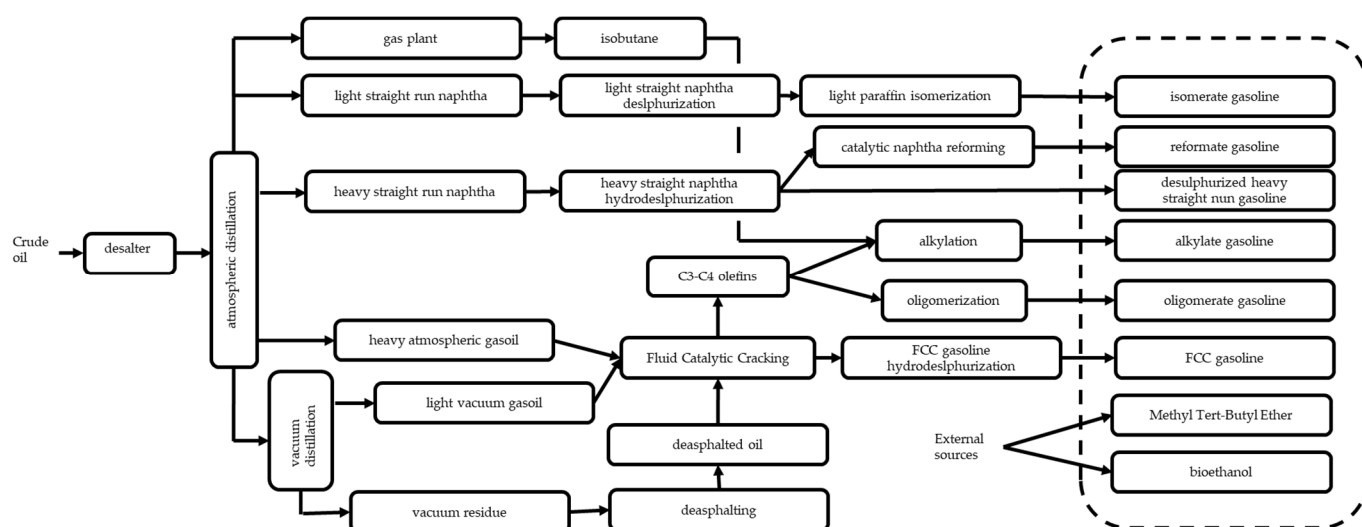
Table 3. Specifications for commercial gasolines in Europe (Euro VI legislation).

		Mogas [50]	Avgas100LL [51]
Sulfur	ppm wt max	10	500
Benzene	% v/v max	1	-
Olefins	% v/v max	18	-
Aromatics	% v/v max	35	-
Oxygen	% w/w max	3.7	-
Lead	mg/L max	5	560
Manganese	mg/L max	2	-
Biofuel (Bioethanol)	% w/w min	1	-
Density	kg/m ³ range	720–775	720 *
Vapor pressure **	kPa range	45–60	38–49 ***
RON	min	95	99.5
MON	min	85	-
Freezing point	°C max	-	−58
Distillation end point	°C	210	170

* typical; ** summer period; *** range at 38 °C.

3.2. Conventional Production of Commercial Gasolines and Monocyclic Aromatics from Oil

Motor gasoline (MoGas) is, together with diesel fuel, a main product of oil refineries. Refineries may also produce other types of gasoline products such as aviation gasoline (AvGas), gasoline for agriculture, etc. These liquid fuels are the result of blending different naphtha flows produced in the refinery, which constitute the so-called “gasoline pool”. A simplified schematics of the manufacture of the different main components of gasoline pool is reported in Scheme 1 [49], where the gasoline pool is in the broken line.



Scheme 1. Simplified flowsheet of the production of the gasoline pool components in a conventional oil refinery.

The main target of the refinery is to maximize the manufacture of the most remunerative oil products, i.e., the automotive fuels mogas and diesel fuel, and to consume the entire crude oil to useful products. A number of other products or byproducts are or may be also manufactured, such as aviation fuels (aviation gasolines and jet fuel), liquified petroleum gas (LPG), lubricants, asphalts, solvents, pet-coke, sulfur, and feeds for petrochemicals production processes.

Some of these processes upgrade straight run gasolines to better environmental and technical properties: they are desulfurizations, isomerization, and reforming processes treating naphthas directly obtained by crude oil atmospheric distillation (straight run naphthas). Some gasolines come from cracking of heavy oils (mainly from the fluid catalytic cracking process) while others come from the recombination of gaseous molecules (oligomerization of olefins and liquid phase alkylation processes). The goal is to obtain the largest possible amounts of commercial fuels with the specifications allowing their commercialization, as summarized in Table 3. Together with hydrocarbons coming from oil refining, oxygenated compounds can be added up to a 3.7 wt% oxygen limit in MoGas in the European Union (Euro 6 legislation). This is because molecules such as ethers (most usually MTBE, methyl tert-butyl ether) and alcohols (usually bioethanol and some methanol) have high anti-knocking properties, allowing them to obtain the minimum Research Octane Number (RON) of 95, or up to 98–101 for the more expensive “premium gasolines”. In the European Union, a minimum 1% of biofuel is also mandatory. This is usually bioethanol, which is added from a minimum 1% to a maximum 10% (E10 gasoline) to fulfill oxygen limits.

As it can be seen from Table 3, commercial motor gasolines usually contain significant amounts of BTEX hydrocarbons. These molecules improve the technical quality of gasolines because of their high anti-knocking properties. However, due to the strong toxicity of benzene and to improve the combustion process and the environmental quality of the waste gases, the total amount of aromatics is also limited in mogas by law to 35 vol%. As seen below, for technical reasons, the amount of aromatics in AvGas is also practically limited.

3.3. The Naphtha Catalytic Reforming Process

Catalytic naphtha reforming is the main process producing aromatic gasolines. “Ox-tanizing” catalytic reforming processes are carried out in oil refineries to convert desulfurized and usually dehexanized straight-run naphtha into high-octane number aromatic-rich gasoline (the reformate, RON 98–103) [52–55]. The increase in antiknocking properties is obtained mainly through aromatization of naphthenes such as (alkyl)cyclohexanes, with production of (alkyl)benzenes and coproduction of hydrogen to be used in hydrotreat-

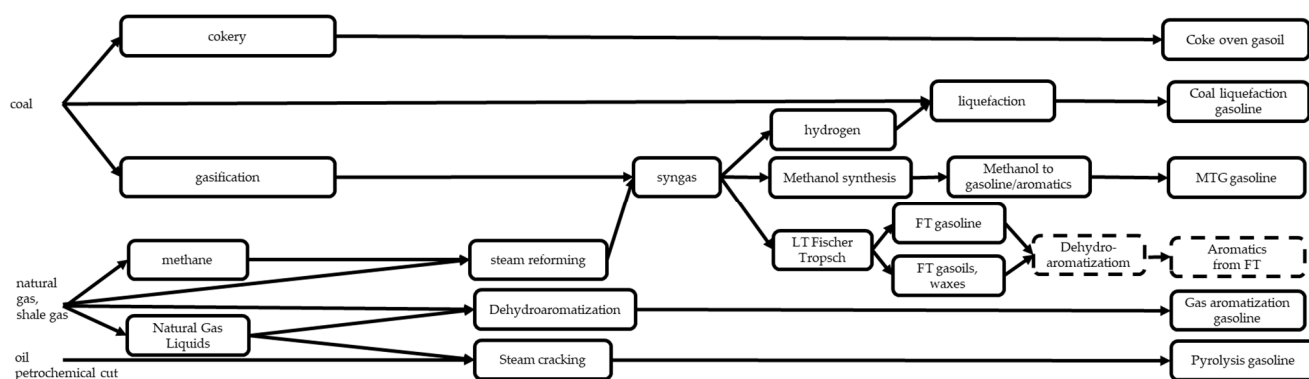
ings. Additionally, branching and cyclization of paraffins is obtained to provide further cyclohexanes for aromatization. The process is realized in multiple fixed bed reactors with intermediate reheating at around 500 °C and 15–35 bar in the presence of hydrogen with Pt-Re-Sn alloy catalysts supported on chlorided alumina.

Petrochemical versions of the process (e.g., Aromizing reforming from Axens and Rz-platforming from UOP) also exist, to which depentanized naphtha is fed to increase the yield in benzene, and an advanced catalyst formulation is used to promote the production of aromatics. In this case, catalysts are usually based on Pt-KL zeolites. The final aromatics content in reformates may be of the order of 60–80 wt%, with gasoline yields above 80%.

The Chevron Phillips Chemical's Aromax® Process [56] selectively converts light paraffins and naphthenes to hydrogen and aromatic products utilizing conventional fixed-bed reforming equipment, with exceptional selectivity for converting C₆ and C₇ paraffins and naphthenes to benzene, toluene, and hydrogen. The catalyst is based on Pt-K-L-zeolite [57].

3.4. Co-Production of Aromatics in Petrochemical Plants: The Steam Cracking Processes

Aromatic hydrocarbons are also products or byproducts of processes realized out of oil refinery (Scheme 2). Steam cracking (SC) processes [58] are realized in petrochemical complexes to produce light olefins, i.e., ethylene, propylene, 1,3-butadiene, and butenes. It is realized without any catalyst in cracking furnaces at 1000–1250 K, 1–5 bar and low residence times (0.001–1 s) with the presence of large amounts of steam (0.2–1 kg_{steam}/kg_{hydrocarbon}). Several hydrocarbon feeds can be used, the most common being naphtha and ethane, the latter recycled from the same steam cracking processes products or separated from natural gas. “Pyrolysis gasoline” (pygas) is a byproduct of these processes. Pygas yield is few percent from ethane SC, of the order of 20% from naphtha SC and 30% from gasoil SC. Pyrolysis gasoline contains around 60 wt% aromatics.



Scheme 2. Manufacture of aromatics-rich gasolines from fossil sources out of refineries. In broken lines are processes not considered in the literature.

3.5. Recovery from Coal Benzol

Crude benzol [59] is a byproduct of coking, the technology producing coke from coal by pyrolysis. Benzol (also called as benzole or coke oven light gas-oil, COLO) is a mixture of hydrocarbons produced by condensation of coke oven gas, in which benzene itself predominates (65–90%), the total aromatic content being up to 98%.

Benzol fraction produced during the high temperature carbonization of the coal is around 0.7% to 1.1% of dry coal. It is present in the coke oven gas in the range of 25 g per normal cubic meters (g/Nm³) to 40 g/Nm³ of coke oven gas.

3.6. Methanol to Gasoline (MTG) and Methanol to Aromatics (MTA) Processes

The methanol to gasoline (MTG) process [60], first developed by the Mobil company in the 1970s, selectively converts methanol to conventional gasoline (RON 92) with virtually

no sulfur, with 87% yield, and a small LPG stream. Methanol is partly converted to dimethylether over alumina catalyst at 300–350 °C. The mixture is then reacted over a H-ZSM-5-based zeolite catalyst at 400–420 °C. The process is applied today mainly in China using methanol produced from syngases arising from coal gasification. This is consequently a so-called coal-to-liquids (CTL) technology. However, methanol coming from natural gas steam reforming has also been used to produce gasoline in a gas-to-liquid (GTL) technology. MTG gasoline may contain 26% aromatic hydrocarbons, mostly C₈ (10%) and C₉⁺, but including about 1% of benzene and 3% toluene [61]. The process could be modified in order to increase the amount of aromatics using Zn-, Ga-, or Ag-containing ZSM-5 zeolite, where the metals help the dehydrogenation catalysis needed for aromatization, at 400–450 °C with aromatic selectivities up to 65% and xylenes and C₉⁺ aromatics as the main products [62–64]. This process is sometimes called MTA (Methanol to Aromatics).

3.7. Other Processes Producing Gasolines from Coal

Countries with limited oil and large coal availabilities are interested in producing liquid fuels from coal. This occurred in Germany in the first half of the 20th century and in South Africa starting from the Second World War and then in China at the beginning of the 21st century. Direct coal liquefaction (DCL), the catalytic hydrogenation of coal at high temperature and pressure, was realized in Germany in the 1930s and 1940s [65] and was renewed recently in China with two large plants belonging to the Shenhua group [66]. The process [67] utilizes two-stage reactors at about 455 °C and 170 atm, using γ -FeOOH as a catalyst precursor fed together with sulfur so that a ratio of Fe:S = 1:2 and a ratio of Fe/coal = 0.5–1.0%. The hydrogen donor solvent is hydrogenated distillate that boils in the range of 220 to 450 °C. The effluent coal liquids are hydrogenated in a suspended bed reactor with forced recirculation at about 360 °C and 130 atm. The main product of these processes is diesel fuel, but a high-octane number aromatic-rich gasoline (>40% [68]) is also coproduced.

Alternative to DCL processes are indirect coal liquefaction technologies. Syngas produced by coal gasification can be used to produce methanol and later hydrocarbons (as described above, MTG process) or directly hydrocarbons through the Low Temperature Fischer–Tropsch (LTFT) process. This process [69], realized at 200–250 °C and 20–50 bar over cobalt-based catalysts, produces linear hydrocarbons (paraffins and terminal olefins) both in the diesel and in the gasoline ranges, together with gases and waxes. Thus, the gasoline obtained by this process is definitely low-octane and aromatic-free. However, cracking/reforming processes of LTFT products could allow, in principle, the production of monocyclic aromatic compounds. The alternative High temperature Fischer–Tropsch process (HTFT) carried out mainly with iron catalysts at 300 °C also produces aromatic hydrocarbons, along with large amounts of olefins and oxygenated compounds [67].

3.8. Aromatics from Other Sources

Monocyclic aromatic hydrocarbons can also be produced by dehydrocyclization of light hydrocarbons such as natural gas (NG) and natural gas liquids (NGL, i.e., C₂–C₄ hydrocarbons from NG), shale gas (SG), and liquefied petroleum gas (LPG). These processes are similar to catalytic reforming processes, applied to lighter hydrocarbons.

The so-called Cyclar process (BP-UOP) consists of the conversion of LPG (C₃ and C₄ hydrocarbons) at temperatures higher than 700 K on a series of catalytic reactors with intermediate reheating of the feed. The aromatics yield (55–65%) depends on pressure. Toluene is the main product (40–45% among aromatics) with benzene at 20–30%, Xylenes at 20–25%, and C₉⁺ aromatics < 10% [70,71]. Catalysts are very likely based on Ga-H-ZSM-5 zeolite [72,73]. In a similar way, AromatizationSM technology from GTC-Sulzer converts C₄–C₈ olefins into aromatics [74].

Benzene and aromatics can be obtained by DeHydroAromatization of methane (Methane DehydroAromatization, MDA) and of methane-rich gases such as natural gas and shale

gas [75]. The reaction occurs at very high temperatures in the presence of zeolite catalysts such as Mo-ZSM-5. The aromatics yield is increased if hydrogen, which is the coproduct of the reaction, is continuously subtracted, e.g., using membrane reactors.

4. Separation of Monocyclic Aromatic Hydrocarbons from Naphthas

4.1. Distillation

Aromatic hydrocarbons usually have intermediate volatility and boiling points with respect to aliphatics with the same number of carbon atoms and those having one carbon atom more. However, due to the presence of many isomers and of azeotropes, pure distillation can be used only to produce quite concentrated solutions of the aromatics, not pure compounds. This is the case of benzene, whose boiling point is intermediate between that of all C₆ aliphatics (but very near to that of cyclohexane) and lower than that of most C₇ hydrocarbons. In refineries, a benzene-rich C₆ cut (up to 80–90%) can be removed from straight-run or reformat gasoline in a de-hexanizer as a heart cut fraction. Both head fraction (light gasoline) and the bottom fraction (heavy gasoline) will have less than 1% benzene, as required by law for commercial mogas (motor gasoline). Similar aromatic-rich heart cuts can be separated for toluene and C₈ aromatics from reformat, pyrolysis gasoline, or COLO [76].

4.2. Liquid-Liquid Extraction (LLE)

According to their polarizability, aromatic hydrocarbons have higher solubilities in polar organic molecules than aliphatics. Liquid-liquid extraction (LLE) processes exploit this property to allow separation of aromatic hydrocarbons from aliphatic ones. In Table 4, typical solvents allowing liquid-liquid extraction of aromatics from gasoline fractions are reported. These molecules are denser than gasolines and do not form azeotropes with hydrocarbons. Thus, liquid-liquid extraction is followed by distillation to recover aromatics and regenerating the solvent to be recycled to the extraction column. Techtiv 100 and 500 are blended systems developed by the GTC Technology company, containing sulfolane solvent, co-solvent, and additives to provide improved performance [77].

Table 4. Solvents used for aromatics extraction processes.

Solvent	Acronym	T _b °C	d g/cm ³	Rv	Process Name		Companies
					LLE	ED	
Diethylene Glycol	DEG	244	1.12	-	Udex [78]	-	Dow, UOP
Triethylene Glycol	TEG	285	1.12	1.44	-	-	
Tetraethylene Glycol	Tetra	327	1.12	1.39	Tetra [78]	-	Union Carbide/UOP
Mixed Glycol Ethers	CAROM	-	-	1.35	Carom [79]	-	UOP
N-formyl-morpholine	NFM	244	1.15	1.89	Morphylex [80]	Morphylane [80,81]	Uhde
N-methyl-pyrrolidone	NMP	206	1.03	1.95	Aerosolvan [78]	Distapex [82]	Lurgi
Dimethylsulfoxide	DMSO	189	1.10		DMSO [78]	-	IFP
Sulfolane	-	287	1.26	2.00	Sulfolane [83]	ED sulfolane [83]	UOP/Shell
Techtiv 100	-	280–290	1.24–1.27	2.44	-	GT-BTX [84]	GTC-Sulzer
Techtiv 500	-	-	-	2.83	-	GT-BTX Select [84]	GTC-Sulzer
No solvent	-	-	-	0.57	-	-	-

Rv = relative volatility nC₇/benzene. Techtiv 100 and 500 are proprietary (GTC-Sulzer) blended systems containing sulfolane, co-solvent, and additives.

This technology can be applied to full gasolines or to thin fractions such as different heart cuts produced by simple distillation, as reported above. LLE usually is most convenient for feeds with reduced aromatics content [76].

Attempts to improve the processes using more environmentally friendly solvents have been recently undertaken. Ionic liquids have been found to be very selective for aromatics extraction but present troubles for the regeneration step due to their very low volatility [85].

Renewable and biodegradable solvents such as furfural and related compounds such as furfuryl alcohol and tetrahydrofurfuryl alcohol (THFA) have also been considered [86].

4.3. Extractive Distillation (ED)

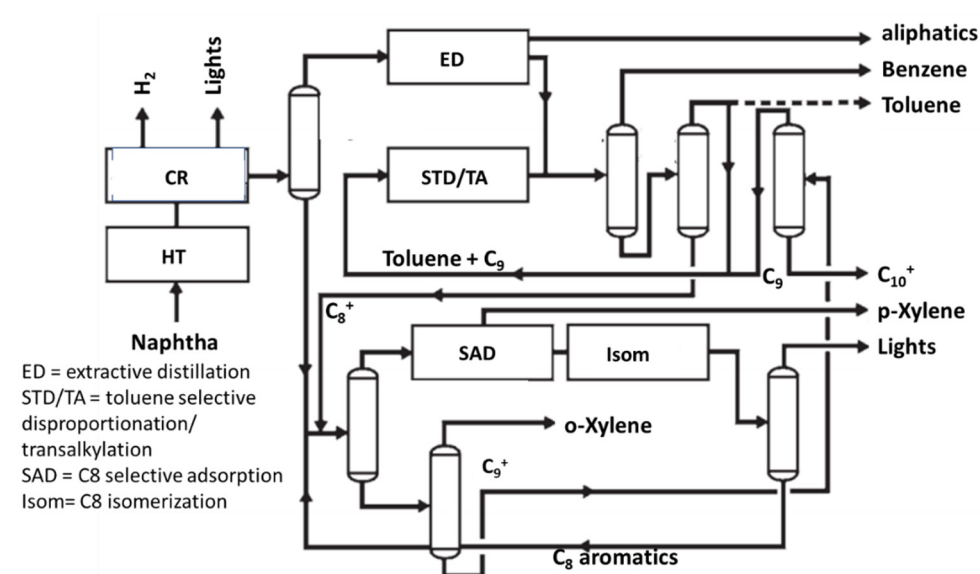
The same solvents reported in Table 4 may also act as entrainers to separate aromatics from aliphatics by extractive distillation (ED). In fact, being these solvents far less volatile than C_6 – C_8 hydrocarbons, they lower the vapor pressure of the aromatic molecules they dissolve, without modifying volatility of the aliphatics that are not dissolved. Thus, aliphatic molecules can be easily distilled from the aromatic–entrainer solution. In a second step, the aromatics can be distilled from the solvent which is recirculated to the ED column. ED is commonly used in refineries' aromatic complexes and may be applied in different ways in refinery/petrochemistry complexes [87].

4.4. Azeotropic Distillation

Azeotropic distillation can occasionally also help in the separation of aromatics from aliphatic hydrocarbon. All hydrocarbons form homogeneous minimum azeotropes with methanol. However, aliphatic hydrocarbon–methanol azeotropes boil at a lower temperature than aromatics–methanol azeotropes. Thus, azeotropic distillation of a C_7 cut allows the separation of toluene, as a bottom product, from aliphatic–methanol azeotropes. Such azeotropes can be broken by washing with water, while the resulting water–methanol solution is distilled easily to recycle both water and methanol [5].

5. The Aromatics Loops

The loop of the aromatics (Scheme 3 [81,88]) is a set of processes that allows the separation of the most useful components (benzene, p-xylene [89], and o-xylene) and the recirculation and reuse of the less profitable aromatics. A reformate splitter allows to distill a light reformate (the C_7^- fraction and maybe most of C_8 aliphatics, with $T_{eb} < 135$ °C) from C_8 aromatics and C_9^+ hydrocarbons. Extractive distillation is carried out on the light reformate fraction to recover benzene and toluene that are later separated by fractional distillation. The heavy reformate is distilled to separate the m-xylene/p-xylene/ethylbenzene mixture (T_{eb} 138–139 °C) from o-xylene (T_{eb} 144 °C) and C_9^+ , and again later to produce pure o-xylene from C_9^+ hydrocarbons.



Scheme 3. The petrochemical aromatics loop.

To increase the yield in benzene and o- and m-xylenes, chemical transformations of the less useful compounds, i.e., toluene, meta-xylene, and C_9 aromatics, together with

ethylbenzene, which is mainly produced *ex novo*, are realized (Figure 5). They are (i) the transalkylation process [90] converting C_9 hydrocarbons and toluene into mixed xylene isomers, (ii) the toluene selective disproportionation process [91] producing selectively *p*-xylene and benzene, and (iii) the xylene isomerization process, usually producing an equilibrium mixture of the three xylene isomers (thus regenerating *p*-xylene and *o*-xylene from the meta isomer), which can be realized either in gaseous phase [92] in liquid phase [93]. Ethylbenzene, although a very useful compound (see above), creates troubles in the aromatic loop. Thus, it can be separated by an onerous superfractionation step (it boils only 2 °C below meta and para xylene) or is dealkylated to benzene and ethylene in the same gas-phase xylene isomerization reactor [92]. With other catalysts, it can be hydrodealkylated, by reacting with hydrogen, to benzene and ethane [94].

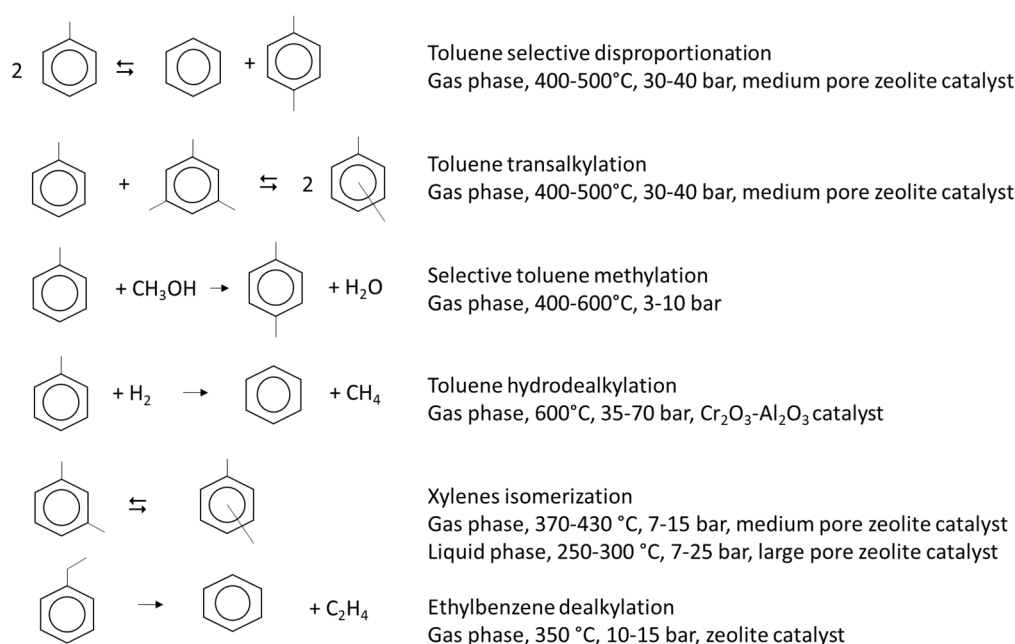


Figure 5. Chemical reaction processes in the aromatics hydrocarbon conversions.

Other possibilities to convert toluene (and also C_{9+} aromatics) to more useful products include the hydrodealkylation process [95], producing benzene and methane in the presence of hydrogen, or methylation with methanol over shape-selective zeolites to produce *para*-xylene [96]. From the *m*-xylene/*p*-xylene/ethylbenzene mixture, the most useful compound *p*-xylene is separated by selective adsorption on faujasite zeolites (Parex process [40]) or by fractional crystallization [97].

For the production of *m*-xylene, the superfractionation step to separate ethylbenzene from *m*/*p*-xylene mixture is needed followed by fractional crystallization or selective adsorption to separate meta- from *para*-xylene [98].

Similar or simplified process schemes are used for treatments of pyrolysis gasoline and coke oven gas-oils [81], which, however, need previous hydrotreatings to saturate dienes and acetylenics. From these mixtures, benzene and maybe toluene are mostly separated.

6. Potential Green Processes for the Production of Monocyclic Aromatic Hydrocarbons

6.1. Biomass vs. Fossil Raw Materials

In Table 5, typical proximate analyses of biomasses are reported. Typical biomasses (wood, grass, straws, barks) are essentially constituted of polysaccharides (cellulose and hemicellulose) and lignin, in different relative amounts. Indicative structures of these biomass components are reported in Figure 6. In such materials, other relevant biomass components such as proteins and lipids are almost absent. The latter compounds are instead abundant usually in fruits and can be extracted from them. In un-treated algal biomasses,

proteins and lipids may also be present. Additionally, biomasses also contain a number of other compounds, such as several extractable organic compounds and inorganics-based ashes, which represent 0.1–5% of the overall biomass and contain a number of other elements such as Si, Al, Fe, Ca, Mg, Na, K, P, Ti, and Mn [99,100].

Table 5. Proximate analysis of bio-organic raw materials.

Biomass Type	Cellulose	Hemicellulose	Lignin	Proteins	Lipids	Ash
Woody	42–64	7–33	10–36	0–0.5	-	0.8–10
Barks	19–25	30–60	20–45	-	-	2–7
Grasses	31–50	25–53	6–34	-	-	0.8–10
Straws	29–55	23–35	15–35	-	-	4–20
Algae	0–28	21–66	0–15	7–50	1–9	8–49
Vegetable oils *	-	-	-	-	>95	<2

* crude or waste.

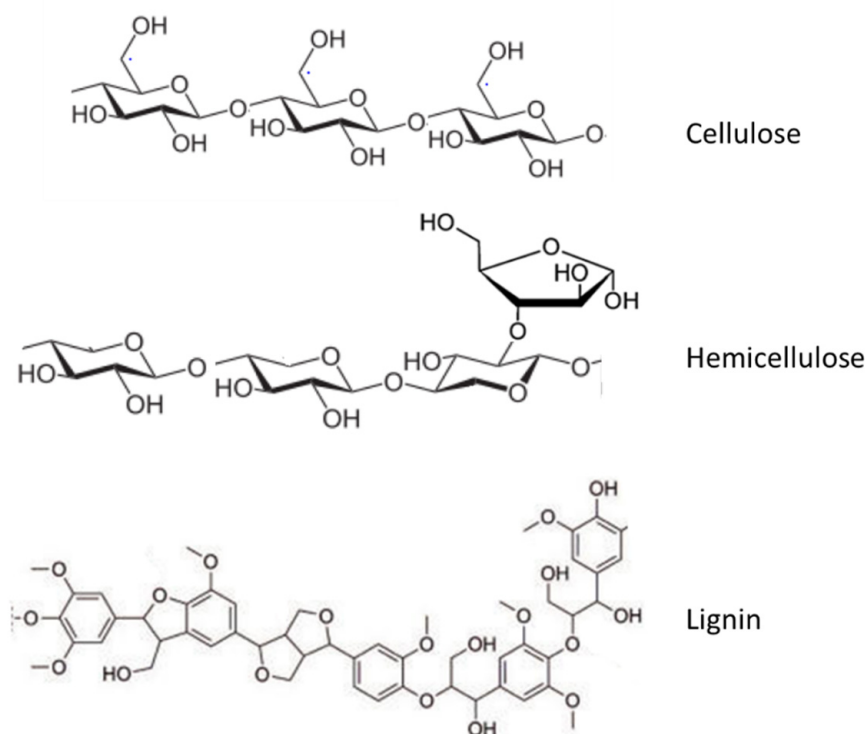


Figure 6. Indicative structures of cellulose, hemicellulose, and lignin.

In Table 6, ultimate analyses of starting raw materials for chemicals and fuels production are compared. As it is well known, biomasses typically contain a large amount of oxygen, and this is the main reasons for the lower calorific value they have with respect to fossil raw materials, which are almost oxygen-free. Obviously, to produce renewable hydrocarbon, deoxygenation procedures are needed. Most biomasses may contain small amounts of nitrogen, sulfur, and chlorine. However, “treated biomasses”, such as industrial lignins, may contain larger amounts of sulfur. Algal biomass contains protein components, thus resulting in higher nitrogen content.

Among biomasses, those containing more carbon and less oxygen, and thus appearing in principle to be more convenient for hydrocarbon production, are vegetable oils and lignins. The latter contain already aromatic rings while the former only contain linear hydrocarbon chains.

Table 6. Ultimate analysis of organic raw materials (wt% on dry and ash-free basis [100–103]).

Biomass Type	C	O	H	N	S	Cl
Woody biomass	42–58	34–49	3–9	0.1–3.4	0.01–0.6	0.01–0.8
Grasses	46–52	42–44	5–6.5	0.3–2.6	0.04–0.27	0.04–0.83
Straws	48–51	40–45	5.5–6.5	0.5–2.8	0.08–0.28	0.03–0.64
Industrial lignins	55–70	23–40	4.5–6.0	0–0.2	0.01–6	-
Cellulose	40–46	45–55	6–6.5	0.1–1.5	-	-
Triglyceride oils *	70–78	10–15	10–13	0.05–0.1	0.01–0.1	0.003
Algae	38–54	26–53	4.5–13	1.1–12.5	0.5–3.3	0.2–2
Coal (mean)	63–87	4–30	3.5–6.3	0.5–2–9	0.2–9.8	0.05–0.11
Crude oil	83–87	0.05–1.5	10–14	0.1–2.0	0.05–6.0	0–0.3

* crude or waste.

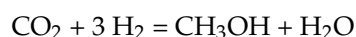
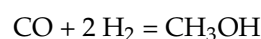
6.2. Biomethanol to Gasoline and Aromatics

6.2.1. Processes for Producing Biomethanol

Different process pathways can be used to produce renewable gasolines and aromatics through methanol [104]. In fact, biomethanol can be produced by renewable sources in different ways [105,106]. In early times, and up to the 1970s, significant amounts of methanol (which in early times was called “wood alcohol”) was produced by destructive hardwood distillation [107,108]. Methanol evolution from wood mainly occurs at about 380 °C, and it is likely caused by the cracking of lignins methoxyl groups.

Methanol can also be produced by fermentation processes, although this does not seem to have been developed at the industrial level [108]. Attempts to convert methane (which can also be biomethane) to methanol by fermentation on *Clostridium* Bacteria have been undertaken recently [109].

For a century, methanol has been synthesized starting from “syngases”, i.e., by hydrogenation of carbon oxides, CO, CO₂, or their mixtures.



These reactions were first reported by Paul Sabatier and Jean-Baptiste Senderens in 1905 to occur over a copper catalyst. The industrial “high temperature and pressure process” (P > 200 bar and T > 400 bar) was developed at BASF around 1920 under the leadership of Carl Bosch [110] using ZnO/ZnCr₂O₄ catalysts which work also in the presence of sulfur impurities. In the past 50 years, sulfur-free syngases have become available, allowing the use of copper-based catalysts. The “low temperature” process is realized today at 50–150 bar and 250–300 °C over Cu/ZnO/Al₂O₃ catalysts using syngases containing 4–8% CO₂, and H₂/CO+CO₂ compositions not too far from 2:1 [111]. However, methanol synthesis can also be realized by hydrogenation of pure CO₂ feed in quite similar conditions, although there is a need for more water-tolerant catalysts that can give a longer lifetime in the plant [112]. Indeed, catalysts allowing efficient and stable conversion of CO₂ to renewable methanol were recently developed. The Topsoe MK-317 SUSTAIN™ specific for this application is also based on the Cu/ZnO/Al₂O₃ system [113]. In any case, methanol synthesis processes using copper-based catalysts need gas feed highly pure from sulfur, chlorine, alkali, tars, and particulate matter [114]. For less pure feeds, catalysts based on Co-Mo sulfides or Zn chromites could be applied.

Hydrogenation of captured CO₂ with renewable electrolytic hydrogen can also produce biomethanol. Renewable methanol can be synthesized by reacting renewable hydrogen with CO₂ captured from combustion waste gases or directly from air. Carbon Recycling International, Iceland, produces renewable methanol, named Vulcanol™, by a

process of hydrogenation of captured CO₂ using hydrogen produced by water electrolysis powered by renewable electrical energy [115]. Thyssen-Krupp, in cooperation with Swiss Liquid Future (SLF), have developed the SLF/Uhde Methanol production technology, also based on electrolytic hydrogen and captured CO₂, and it is reported to be ideally suited to plants in the 10–100 tpd range [116].

CO₂ can be also be separated by biogases, as a byproduct of biogas upgrading to biomethane by adsorption zeolites [117]. The rejected CO₂ can be used to produce biomethanol with renewable hydrogen. This was recently executed by the BioMCN company in the Netherlands [118].

Among the advantages of this processes is the high purity of H₂ and, usually, also of captured CO₂. However, the high cost of renewable electrolytic hydrogen, depending on the cost of renewable electrical energy, may be a drawback.

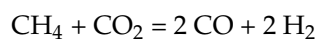
Conversion of syngas produced by biomass/waste gasification is also a means of producing biomethanol. Syngases for methanol synthesis can be derived by gasification or reforming of biomasses, biomass-derived compounds, or wastes [119,120]. However, biomass gasification technologies are still under development [121–123]. A main problem concerns the amounts and types of impurities contained in biomass gasification gases (particulate matter, condensable organics, alkaline metals, nitrogen-, sulfur- and halogen-containing compounds), particularly in the case of fluidized bed gasifiers, and the resulting complexity of the technologies needed for syngas conditioning [124] to obtain sufficient purity for methanol synthesis. Some years ago, Topsoe and Carbona jointly developed a biomass gasification/syngas cleanup/methanol synthesis/methanol to gasoline process [125]. It is not clear, however, if real commercialization was raised. For several years, VärmlandsMethanol AB has produced biomethanol in Hagfors, Sweden, based on gasification of unrefined low-cost forest residue [126].

Municipal wastes can also be valorized by gasification technologies to produce syngases, allowing the production of energy and/or chemicals. In this case, gas cleaning is still a difficult task [127]. Enerkem produces methanol from syngas produced by waste gasification in several plants [128].

Conversion of syngas produced by glycerol reforming is another way of producing biomethanol. Glycerol is a natural compound that became available after the development of the industrial manufacture of biodiesel (Fatty Acid Methyl Esters, FAME) by transesterification of triglyceride-rich materials (e.g., palm or soybean oils). Crude glycerol is a impure byproduct of this technology, generally needing a previous onerous refining process to be used [129]. Pure glycerol can be converted to syngas by steam reforming or aqueous reforming processes. Steam reforming is realized in the gas phase over metal catalysts at 400–700 °C and 1–3 bar [130,131], a temperature where glycerol is already in part decomposed. Aqueous reforming is realized also with metal catalysts in water at 220–250 °C under autogenous pressure (up to 50 bar) [131].

The syngas produced by steam reforming of glycerol can be used for methanol synthesis [132]. The Dutch company BioMCN patented, developed, and realized a process for producing renewable methanol from glycerol at Delfzijl in the Netherlands [133]. More recently, however, this company turned to produce biomethanol using biogas-derived CO₂ with renewable electrolytic hydrogen.

Conversion of syngas produced by dry reforming of biogas can also produce biomethanol. As it is well known, biogases are essentially the products of anaerobic digestion of organic wastes [134]. It typically constitutes a mixture of CH₄ (~60%) and CO₂ (~40%) with a number of impurities including H₂S, ammonia, siloxanes, etc. After cleaning, most commonly realized using activated carbon adsorption [135], syngas may be produced by the dry reforming reaction:



realized over metal catalysts at 700–900 °C [136] coupled together with steam reforming of the excess methane [137]. The resulting syngas has a H₂/CO_x ratio not far from 2:1 and is

suitable for the production of methanol [138]. Oberon Fuels, a California, USA, company, is manufacturing DimethylEther from biogas-derived methanol through dry reforming [139].

Conversion of syngas produced by black liquor gasification is another way to produce biomethanol. Another source of syngas may be the black liquor coming from the Kraft paper manufacturing process. In the most common processing flowsheet, black liquor, a liquid containing caustic soda and sulfur compounds together with lignin residues, coming from the digester producing pulp from wood, is concentrated and later treated in a “recovery boiler”. In this step, the organic lignin residues are burned, while a mixture of sodium carbonate and sulfate is formed (green liquor). An alternative is to treat concentrated black liquor in a gasifier, where lignin residues convert into a syngas [140]. Chemrec, Sweden, is using waste from paper production called black liquor to produce biomethanol and bio-DME from a syngas produced by treating black liquor with an entrained flow gasifier working at 1050 °C and 30 bars with pure oxygen [141].

Conversion of syngases produced by other renewable sources can also produce biomethanol. In principle, biomethanol can be synthesized by converting syngases produced by other renewable syngases, such as those produced by converting bioethanol. Ethanol steam reforming (ESR) [142,143] is an endothermic reaction and thus favored at relatively high temperatures and low pressures. It is realized at 600–700 °C over metal catalysts such as supported Ni, Co, Pt, or Rh, frequently improved by alloying [144], with excess water. It seems that still this technology is not realized at the industrial level, but is seriously considered for commercial application [145]. It has been considered that ESR can be realized using existing hydrocarbon steam reforming plants, provided that effective catalysts have been developed [146]. On the other hand, it has been shown that Ni/Ca aluminate commercial catalysts for natural gas steam reforming are excellent catalysts for ESR, too [147]. Raw bioethanol must be distilled to avoid additional catalyst deactivation by organic impurities [148]. Due to the concurrence of the water gas shift equilibrium, the process produces a syngas composed of CO, CO₂, and H₂. Indeed, hydrogen production is usually limited by the presence of variable amounts of methane, which is at least in part formed by ethanol decomposition [149]. The alternative ethanol partial oxidation [150] and autothermal reforming [151] may help in reducing the amount of methane coproduced and in the reduction in catalyst deactivation by coking, with the drawbacks of the cost of oxygen and a reduction in the H₂/CO_x product ratio.

Vegetable oils, and in particular waste coking oil [152] and biodiesel [153], have also been considered for the production of syngas and hydrogen by steam reforming or partial oxidation [154].

Renewable hydrogen and CO₂ can also be produced by biomass dark fermentation processes [155], and can later be converted to methanol [156].

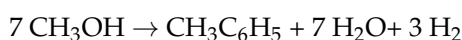
Another way to produce biomethanol is by direct conversion of glycerol and other polyalcohols to methanol. Recently, a new method for producing methanol from glycerol and other polyalcohols was proposed by reacting them in water in the presence of oxide catalysts. However, the selectivity to methanol does not exceed 60% [157].

6.2.2. Conversion of Biomethanol to Gasoline and Aromatics

MTG and/or MTA processes using methanol produced by renewable sources can be applied to the production of renewable gasoline and aromatics. As said, some years ago Topsoe and Carbona jointly developed a biomass-to-gasoline technology based on methanol synthesis from biomass gasification-derived syngas and the TIGAS™ (Topsoe Integrated Gasoline Synthesis) process, Topsoe’s version of Mobil’s MTG which can also be denoted as STG, Syngas to Gasoline [158]. It is not clear whether this process starting from biomass reached the commercial level.

It seems interesting to remark that the conversion of methanol to olefins, which are considered to be the first hydrocarbon products [60], is stoichiometrically a pure dehydration

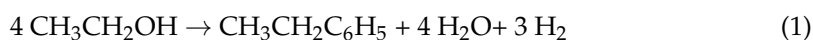
reaction, while the further conversion of olefins to aromatics implies a dehydrogenation step. The stoichiometry of the reaction giving rise to the main product toluene is:



Thus, part of renewable hydrogen used for biomethanol synthesis may be recovered and reused after the MTG/MTA process.

6.3. Bioethanol to Gasolines and Aromatics

In the near future, bioethanol produced by fermentation of cellulosic biomass or from microalgae feedstock [159,160] is expected to become a primary intermediate in the industrial organic chemistry based on renewables [161,162]. Somehow, this can be envisaged as a return to the past because bioethanol was largely used in the first half of the 20th century for the production of chemicals. As an example, ethylene has been produced from bioethanol in several countries since 1913 [163], while the production of butadiene from bioethanol was developed and applied industrially after 1920 [164]. The possibility to convert ethanol to gasoline was reported many years ago [165] and is considered today as a potential way for the production of renewable fuels [166]. Metal containing ZSM-5 zeolite catalysts are typically applied to this reaction [167], where ethylene produced by dehydration of ethanol is very likely the primary intermediate, followed by oligomerization and dehydrogenation [168]. The liquid product produced converting ethanol at 350 °C and atmospheric pressure over both Zn-ZSM-5 and Co-ZSM-5 was reported to be constituted by 97% vol of aromatics, with a predominance of ethylbenzene (>60%) [169]. In this case, the addition of gallium, whose compounds are usually active dehydrogenation catalysts, seems to increase the formation of aromatic hydrocarbons [170].



showing that renewable hydrogen is a coproduct of this process.

6.4. Hydrocarbons from Vegetable Oils

As previously said, vegetable oils are, of possible renewable raw materials, the richest in carbon and the poorest in oxygen (10–15 wt%). The hydrodeoxygenation of vegetable oils (usually palm oil) has been developed at the commercial level [171] by UOP-ENI (Ecofining Process [172]), Neste Oil (NEXBTL™ process [173]), Total (HVO100 [174]), and Renewable Energy Group Inc. (REG Renewable Diesel [175]), finally producing oxygen-free diesel fuels called “Green Diesel” or HVO (Hydrotreated Vegetable Oil). These biofuels are essentially constituted by linear paraffins, although some branching is realized by a mild cracking to reduce the pour point. Hydrodeoxygenation is realized over alumina supported sulfided NiMo catalysts at 280–380 °C under 40–90 H₂ bar. Obviously, to really obtain a renewable fuel, hydrogen would also be produced by renewable sources.

This family of processes could also be of interest to produce renewable gasolines, supposed further cracking and reforming processes, optimized for the conversion of such a feed, are developed. These aromatization processes would also coproduce renewable hydrogen.

Moreover, the thermal conversion of vegetable oils at 350–500 °C gives rise to hydrocarbon-rich liquid products with yields in the 60–80 wt% range [176]. During the Second World War, batch cracking processes were developed in China to produce motor fuels from tung oil [177]. In the late 1970s, this reaction was investigated at Mobil using acid zeolite catalysts, producing high-octane, aromatic-rich gasoline from corn and peanut oil [178]. The reaction has also been investigated using non-edible oils, such as jatrofa oil [179] and waste cooking oil [180]. Using mildly acidic or acido-basic catalysts at 400 °C, diesel-like oil is obtained. The reaction involves the cracking of the glycerol chain and the decarboxylation of the fatty acids. However, ketonization produces long- and small-chain ketones, which are the main oxygenated residual products [181]. To produce high-aromatic gasoline, higher temperature (e.g., 500–550 °C) and strongly acid catalysts, such as fluid

catalytic cracking catalysts based on Y zeolites and ZSM-5 catalysts or containing metals, are needed [182], giving rise to a combination of triglyceride ester cracking with reforming of hydrocarbons.

6.5. Lignin Conversion Processes

Among organic renewable natural resources, lignin is the most abundant class of compounds with an aromatic character [183]. Lignin represents around 18–40% of wood biomass, where it is present together with polysaccharides cellulose and hemicellulose as the largely predominant material, to which it forms molecular complexes [184]. It is present even in larger concentrations in waste biomasses such as olive husk and walnut shell [185]. Industrial lignin is produced as a byproduct of cellulose and paper manufacture, as well as byproduct of bioethanol synthesis by lignocellulosics. Today, approximately 98% of the lignin produced is used as fuel for heat and electricity [186]. Industrial lignins, which contain 30–50 wt% oxygen, are not pure materials typically containing 0.5–8 wt% ashes, variable amounts of sulfur up to 8 wt%, and 1–3% of sugars [187,188].

6.5.1. Lignin Thermal Pyrolysis

In an inert atmosphere, lignin begins to lose weight above 200 °C [189]. Depending on actual pyrolysis conditions, different amounts of gases, liquid bio-oils, and char are produced in the range 200–700 °C [190,191]. The gases are mainly composed of water, CO, CO₂, methane, higher hydrocarbons, and hydrogen, together with condensable alcohols and phenols [189,192,193]. In non-oxidative conditions, char residues may be of the order of 20–60 wt% depending on reaction conditions [190,194]. Such biochars are macroporous low-surface area materials, whose oxygen content decreases with increasing pyrolysis temperature while the aromatic carbon amount progressively increases [195].

Depending on pyrolysis conditions, bio-oil yield is in the range 20–60%. The main components of bio-oil are polyhydroxy- and/or polymethoxy-benzenes, sometimes containing C₁–C₃ alkyl chains and aldehyde functions [196]. The total oxygen content in the pyrolysis oils from wood, straw, grasses, and bran is still high, typically ranging 35–50% with the presence of 15–30% of water [197], with a strongly acidic character. A typical property of these liquids is their instability, with a progressive increase in viscosity during storage due to their susceptibility to repolymerization processes. Thus, rapid reprocessing is needed to remove oxygen.

6.5.2. Lignin Microwave Pyrolysis

In recent years, the application of microwaves to pyrolysis of biomass became of much interest [198]. As a result, more uniform heating microwave heating may allow for greater yields of bio-oil than thermal heating. The quality of the oil produced may also be different and, maybe, better.

6.5.3. Lignin Catalytic Pyrolysis

Catalysis may significantly influence the conversion of lignin and the product distribution. Different catalysts have been tested. For example, metal-doped TiO₂ was found to produce phenols with high selectivity, although with low yields [199]. Low-cost catalysts, such as red mud, bentonite, and activated carbons, give rise to liquid yields around 30 wt% maximum with limited amounts of hydrocarbons [200]. Acid zeolites, usually H-ZSM-5 [201,202], tested at 500–700 °C, were found to increase the amount of BTEX aromatic hydrocarbons together with oxygenated compounds in the produced bio-oil, but does not seem to increase significantly liquid yield, or even decreases it in favor of gases [203].

While solid catalysts may improve product yield, their quite rapid deactivation [204] makes necessary a frequent regeneration step. Coking is a likely main cause of deactivation, and can be reversed by coke combustion. Taking into account the presence of significant amounts of coproduced solid char, reactor design to allow continuous operation must be

developed. However, deactivation could also arise from contamination with inorganics (e.g., alkali ions) present in biomass, and this may result in difficult regeneration.

6.5.4. Upgrading of Lignin Pyrolysis Oils

As stated, typical components of lignin pyrolysis oils are guaiacols, siringols, alkylphenols, and catechols, with small amounts of hydrocarbons. Upgrading of lignin pyrolysis oils may be realized by catalytic cracking and catalytic hydrodeoxygenation [194]. Catalytic cracking is mostly realized with medium or large pore acid zeolite catalysts such as H-ZSM-5, H-Beta, and H-Faujasite. These microporous materials give rise to shape-selective catalysis, catalyzing the cracking of aliphatic chains but also of the methoxy-groups, finally producing mainly toluene, xylenes, and also naphthalene. Catalytic hydrodeoxygenation [205,206] is performed at 250–400 °C under hydrogen 1–20 Mpa in the presence of metal catalysts, usually Pt, Pd, Rh, Ru, or Ni supported on oxide carriers such as alumina, silica and zirconia, or on acid zeolites such as H-ZSM-5, H-beta, and HY. As an alternative, hydrotreating sulfide catalysts, such as Co-Mo sulfides, can also be used. Moreover, catalysts for bio-oil upgrading tend to deactivate by coking; thus, regeneration steps are needed [204].

6.5.5. Lignin Hydroxylation

Hydroxylation, i.e., heat treatment in the presence of hydrogen, is also a potential approach to hydrocarbon production from biomass [207]. An industrial lignin hydroxylation process using an ebullated-bed reactor treating a slurry of pulverized lignin and a mixing oil coming from a recycle of a product of the same process was developed many years ago by hydrocarbon research to produce phenol. The product of this process was phenol with yields around 50% [5]. The direct conversion of lignin to hydrocarbon liquid fuels by one-pot hydrodeoxygenation has also been investigated. Ru/Al₂O₃, Ru/HY, and Ni/silica-alumina are among the catalysts that have been tested for this reaction [206]. Higher hydrogen pressure may allow higher hydrocarbon yield but lower aromatics yield. Moreover, in this case, catalyst deactivation must be considered due to the presence of sulfur and alkali in the biomass as well as catalyst coking.

6.5.6. Lignin Liquefaction

Lignin liquefaction consists of the treatment of lignin at 120–500 °C in the presence of a solvent, hydrogen, and a catalyst. The solvent may be water, in the presence of soluble bases (ammonia, sodium, or potassium hydroxides and carbonates), solid bases or acids, minerals, metals, etc. A large number of organic solvents have also been used, usually in the presence of acid and/or metal solid catalysts or of liquid catalysts, in sub or supercritical conditions, in normal conditions or under microwaves irradiation or in plasma electrolytic conditions [208]. Very high bio-oil yields are reported in several cases, although in most cases, high liquid yield (>90%) corresponds to still high oxygen content in the bio-oil (40%).

6.6. Conversion of Polysaccharides to Hydrocarbons

As already remarked, cellulose and hemicellulose have higher oxygen content than lignin and are, consequently, in principle less promising as feedstocks for hydrocarbon production than lignin. Hydrolysis of polysaccharides produces sugars (glucose, fructose, xylose) than can be later converted into furfural [209,210] and 5-hydroxymethylfurfural platform chemicals [211] and other furanics [212]. In fact, the most common way to exploit cellulose for the production of chemicals [213] consists of its hydrolysis producing glucose isomer, which can be later converted into some different platform chemicals. Similarly, hemicellulose can be converted to several oxygenate platform chemicals [214]. A number of routes have been developed for the catalytic conversion of sugar-derived furanics into aromatics via Diels Alder (DA) addition and subsequent dehydration reactions (i.e., a stoichiometric synthesis approach). Catalytic conversions of bio-based (isobutyl) alcohols and pinacol-acrolein to aromatics have also been reported [215]. HMF,

5-hydroxymethylfurfural, is considered to be a promising intermediate for the production of several chemicals. Catalytic pyrolysis of HMF at 600 °C using H-ZSM-5 zeolite catalyst was reported to produce up to 49% yield in aromatic hydrocarbons [216].

Pyrolysis of wood polysaccharides gives rise to volatile compounds at lower temperature than lignin, hemicellulose being more reactive than cellulose [193,217]. Pyrolysis of cellulose is reported to first give rise to an intermediate “active cellulose” without release of volatiles. This intermediate would in turn decompose through two competitive reactions: at a low temperature (below 280 °C) and low heating rate, char and gas formation are favored, while liquid mainly constituted by levoglucosan is the main product at a higher temperature (above 280 °C) [218]. The amounts of different phases strongly depend on the pyrolysis conditions. The gas produced is very rich in CO and CO₂ (>60% CO_x) with smaller amounts of H₂, CH₄, and light hydrocarbons, the latter increasing with increasing temperature [193]. Cellulose-derived bio-oil mainly consists of highly oxygenated organics, such as saccharides, furans, and ketones. With pyrolysis temperature rising (300–500 °C), the content of saccharides constantly reduces and the content of dehydrated carbohydrates (with big amounts of levoglucosan) significantly rises [193,219]. The oxygen content of the resulting char decreases with increasing pyrolysis temperature, with a parallel decrease also in the H/C ratio, leading to a graphite-like structure [220].

Pyrolysis of hemicellulose produces more gases than cellulose and lignin, giving rise to a liquid rich in acids and ketones [193].

The direct conversion of cellulose to hydrocarbons in the gasoline range has been reported to occur upon liquid phase heterogeneously catalyzed hydrogenation. C₅–C₆ paraffin yield above 60% was reported treating cellulose in acidic aqueous medium over Ru/C catalyst and cocatalysts at 230 °C under 60 bar of H₂, 24 h [221].

6.7. Pyrolysis of Wood and Other Whole Biomass

As is evident, the direct conversion of a whole biomass without previous pretreatments or separations would represent a convenient approach. Pyrolysis of wood has been realized for many centuries to produce charcoal, to be used as a better solid fuel than wood itself, as a pigment, and as a reducing agent to produce metals [222–224]. Still, today charcoal provides basic energy services for cooking and heating to millions of people living in underdeveloped areas [225].

When entire biomass pyrolysis is realized, a clear interaction occurs between its main components, lignin, cellulose, and hemicellulose [217]. For lignocellulosic biomass, less char and more tar were obtained than predicted from the components, which may be associated with the morphology of samples. Evolution of volatiles from wood occurs in the 300–400 °C temperature range, with a liquid yield above 60 wt% in the 500–600 °C range. The liquids obtained have an higher oxygen content (50–62%) than the starting biomass (40–45%) [226]. The porous structure of lignocellulosic biomass provided a release route for pyrolysis vapors.

UOP recently developed and commercialized the RTP (Rapid Thermal Processing) Technology, which is a thermal fast pyrolysis process, i.e., rapid heating of biomass in the absence of oxygen. The process utilizes a circulating transported bed reactor system, similar to a FCC reactor, in which sized and dried biomass is contacted with circulating hot sand in the reactor. The pyrolytic vapor is rapidly quenched to produce a high yield of liquid fuel, or RTP green fuel. RTP fuel is a dark liquid with an appearance similar to light petroleum oil. It is a water-soluble, oxygenated fuel consisting of depolymerized components of biomass [227]. This liquid can be used as a biofuel or treated together with heavy gas-oils in FCC plants to produce partially renewable gasolines [228].

6.8. Hydrocarbons from Algae

As it is well established, algae may represent a key raw materials in the future industrial chemistry, because they are essentially non-edible materials and their production cannot compete with food production. Petrochemical industries are considering algae as a

likely near-future raw materials for biofuels production [229]. The composition of algae in terms of organic matter is variable [230]. Most algae have very large protein content (up to 65 wt%), which also results in a large amount of nitrogen (>10 wt%), while few contain large amounts of carbohydrates (up to 65 wt%) with variable amounts of inorganics [102,103]. The amount of lipids in algae is usually small or moderate, but oleaginous algae contain up to 55 wt%. The lipid content may be increased by opportune treatments [231]. Growth enhancement techniques and genetic engineering may be used to further improve their potential as a future source of renewable bioproducts [232,233].

Pyrolysis of algae may produce up to 50 wt% bio-oils, together with fuel gas and char [234–236]. The resulting biochar has definitely higher calorific value than the starting biomass [237]. However, such bio-oils usually still contain significant amounts of both oxygen (carboxylic acids, phenols) and nitrogen (amides, amines, nitriles, pyrroles), together with aliphatic and aromatic hydrocarbons. On the other hand, the amount of nitrogen compounds in algae pyrolysis bio-oil can be significantly reduced if previous protein extraction is carried out [237].

Several studies were conducted on different species of microalgae using acid catalysts, in particular protonic zeolites [238,239] such as ZSM-5, zeolite Y, Mordenite, and Beta zeolite. In this case, ZSM-5 zeolite was mainly investigated for its ability to reduce oxygenates compounds and increase the aromatic fraction. Since the strong acidity of zeolite generally leads to deep deoxygenation and severe coke formation, mesoporous materials with milder acidity, such as silica-alumina [240] and its potassium-modified form [241], have been tested to solve this problem. Indeed, catalysts seem to have a moderate influence on the amounts and quality of the produced bio-oils and of the gases, as well.

7. Conclusions

The data summarized and discussed above show that a very large number of investigations have been undertaken in order to produce biofuels and chemicals from biomasses. Interestingly, a number of different approaches are under study; some of the investigated or potential pathways for aromatics-rich bio-gasolines production are summarized in Scheme 4. This refers not only to the academic research, but also to the approach of the different industrial entities, most of them belonging to the main international petrochemical groups. Such approaches differ concerning the type of biomass to be used as the starting raw material, type of processing, focus, etc. Indeed, it still does not seem that these efforts are converging in most promising technologies at the moment. A large number of pilot plants and projects have been reported and advertised in the past fifteen years, but several of them later disappeared and only a few of them are under development at the near-industrial level. Some industrial groups also evidently changed their approach in recent times, likely because drawbacks appeared in the technologies previously investigated and considered promising.

The main biofuels that are industrially available today at large scale (bioethanol, biodiesel, green diesel) are still mostly produced from edible raw materials (starch-rich vegetables and palm oil) and present a number of drawbacks and limits in their production and use.

One of the main points to be still defined is what are the best raw materials for biofuels production. While edible matter, such as starch and edible oils, are to be excluded for future biofuels production, the use of algae represents a very interesting approach. However, the complexity of the algal biomaterial appears to be a strong drawback for biofuels and chemicals production. On the other hand, the composition of algal matter is also variable, and the use of genetic engineering to produce algal organisms with the best properties for biofuels (and chemicals) manufacture could help in finding solutions. This would mean that the best biomass for industrial bio-organics product is still to be invented or discovered.

may pose problems, such as in separation processes using polar solvent where oxygenates are more soluble than aromatic hydrocarbons. On the other hand, most oxygenated compounds would boil at higher temperatures than the corresponding hydrocarbons, and this may allow the use of pure distillation processes, only if the presence of azeotropes can be managed.

On the other hand, at least in some cases, different paths for the production of chemical intermediates can be envisaged. For example, while today phenol is produced by oxidation of benzene (via the production of cumene), in the future phenol can be obtained directly from biomass (e.g., lignin) and benzene could be derived from phenol hydrogenation.

In any case, the main conclusion from the present work is that the best way(s) to produce monocyclic aromatic hydrocarbons and their secondary intermediate products, as well as gasoline from biomass, is still to be identified, and that deep investigation must be undertaken to find really promising technologies to be tested at the pilot plant level.

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