



# **Preparing Fuel-Range Chemicals via the Direct and Selective Pyrolysis of Disposable Mask Waste for Sustainable Environment**

Xin Gao <sup>1</sup> and Chun-Ran Chang <sup>1,2,\*</sup>

- <sup>1</sup> Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China; xggao@xjtu.edu.cn
- <sup>2</sup> Shaanxi Key Laboratory of Low Metamorphic Coal Clean Utilization, School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, Shaanxi, China
- \* Correspondence: changcr@mail.xjtu.edu.cn

**Abstract:** After stepping into the pandemic, it has been entirely not bizarre to wear facial masks to diminish the spreading of viruses in human daily outings. Due to the low expense and stable protection capability, disposable masks are the most widely used types of medical masks. By functionalities and medical standards, disposable masks mainly consist of surgical masks and N95/KN95 respirators in the market. In the assembling scheme, there are typically three or more polymeric layers (i.e., mainly polypropylene) in disposable masks; in addition, the ear loops in masks are usually made from textile constituents, such as polyamides. Therefore, the vast utilization and rapid accumulation of disposal mask waste can directly bring an emerging crisis of foreseeable environmental pollution. To minimize and prevent such mask-led microplastic pollution, chemical pyrolysis of mask waste is one of the most feasible and promising strategies. Via the direct and selective pyrolysis of disposable masks, it can effectively convert the mask waste into high-value fuel-range chemicals, e.g., liquid hydrocarbon blends, aromatics,  $C_{1-5}$  gas alkanes/alkenes, hydrogen, etc. In this way, it can not only tackle environmental challenges from plastic waste but also afford sustainable fuels with low carbon emission and circular economy.

**Keywords:** disposable masks; fuel-range chemicals; selective pyrolysis; sustainable environment; plastic upcycling

# 1. Introduction

There is a universal consensus that exceedingly tremendous amounts of plastic wastes (e.g., polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET)) have already been accumulated in the natural environment (e.g., the ocean, the land), and it is also well known that waste plastics are very difficult to decompose in natural settings. In this respect, a host of recycling and upgrading approaches have been proposed in the past decades, for instance, chemical upgrading [1–5], mechanical upcycling [6–9], and biological upgrading [1,10–13]. Chemical upgrading is a feasible approach that consists of various routes, such as pyrolysis [14–17] and hydrogenolysis [15,18–20]; wherein, due to the inexpensive and efficient process, non-utilization of specialty chemicals, use of inert gas, and broad suitability of different materials, chemical pyrolysis has become one of the most promising processes. This process has been recurrently reported toward the upcycling of plastics into value-added chemicals and fuels through a range of pyrolytic methods, such as catalytic pyrolysis, which might be usually conducted at milder conditions (e.g., lower temperature) by decreasing reaction barriers with using solid catalysts (including zeolites, metals, metal oxides, and non-metals) [14,20–23]; non-catalytic or thermal pyrolysis [3,17,24–26]; and copyrolysis of various feedstocks, by virtue of the synergistic interactions of different reacting compounds [27–31]. In detail, chemical pyrolysis of polymeric molecules is supposed to



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). crack macromolecules to a mixture of molecular species along with temperature ramping up under inert or non-combustible carrier gases. Accordingly, many reaction parameters, e.g., heating rate (slow, medium, fast or flash) [32–34], maximum pyrolysis temperature, flow rate of carrier (or purge) gas, etc., can make imperative impacts to pyrolysis activity, selectivity, and stability. For catalytic schemes, there are extra pyrolytic factors, such as catalyst composition and loading. For co-pyrolysis of different feedstocks, the co-feeding ratio can be pivotal to the reaction activity and product distribution as well. To this end, it is meaningful to explore the optimized reaction conditions for highly efficient pyrolysis.

Owing to the pandemic, disposable medical masks, mainly made from polymers (e.g., PP), has turned out to be the most essential personal protection equipment in human daily use (Figure 1). It has been surprisingly but soundly estimated that the amounts of consumed facial masks can reach about 290 billion per year in the Asian area and over 60 billion per year in Europe [35]; plausibly, it was also reported that the global mask consumption might be close to 130 billion per month [36,37]. Furthermore, one inevitable trend may suggest that medical masks will be continuously employed in the future society and therefore massive disposal of mask waste is continuously expanding at high speed [35]. At this point, the environmental challenges have been again significantly elevated by the extremely outstanding utilization of polymer-made disposable masks, and it is becoming greatly vital and urgent to build up an effective chemical upgrading system for the conversion of disposal masks to value-added chemicals or fuels via chemical routes, especially at this relatively early stage of massive waste mask accumulation in the natural environment. Comparing to many other plastic consumable products, the disposable masks possess several advantages in the recovery and sorting process prior to chemical upcycling, such as distinguishable appearance (mainly dark blue and white colors, similar shapes and sizes) and frequent disposal places (e.g., hospital, station, mall, park, office) [38].



**Figure 1.** The direct and selective pyrolysis of polymer-made disposable masks (surgical masks and KN95 masks) to produce fuel-range chemicals with three different methods: thermal pyrolysis, catalytic pyrolysis, and co-pyrolysis. All the masks are assembled with multiple facial layers of polymeric materials, stretchable ear loops, and nose holders.

Recently, a few reports have addressed a series of pyrolysis methods to appropriately upgrade the mask waste to liquid, gas, and solid products to fulfill the circular economy [39–43]. Particularly, although carbon-based solids, such as carbon nanotubes (CNTs) [38,44,45], graphene [43,46,47], and carbon fibers [48], can be synthesized from the direct pyrolysis of disposable masks or other PP-concentrated polymers, the quality of such evolved carbon materials cannot be guaranteed with uniform structures and expected physicochemical properties due to complex chemicals in disposable mask feedstock [38]. Hence, simultaneously meeting both the crucial environmental challenges from waste masks and the large requirement of sustainable fuels offers quite meaningful and promising motivation to produce affordable fuel-range chemicals (e.g., hydrocarbon blends, aromatics, hydrogen, etc.) from the direct and selective pyrolysis of medical masks (Figure 1). On the other hand, the qualities of plastics (e.g., properties and concentration of one specific substance in polymer waste) could significantly influence the expected efficiencies of chemical pyrolysis regardless of pyrolysis methods. That said, due to the complexity and diversity of chemical compositions in disposable masks from a variety of manufactories, the direct pyrolysis of realistic masks is suggested to be vitally different from single PP, PE or PET compounds, and it is therefore highly required to investigate the direct pyrolysis of realistic masks to selectively synthesize a series of fuel-range liquid and gas products instead of the pyrolysis of pure PP, PE or PET models. Hence, we would like to leverage this presenting paper to specially emphasize the chemical pyrolysis of disposal mask to form value-added fuel-range molecules in a catalytic, non-catalytic or co-feeding manner. Specifically, we analyze in depth the following aspects: direct characterizations of disposable masks (including determination of disposable mask constituents and identification of mask degradation temperatures) and selective production of fuel-range molecules (including liquid hydrocarbon blends, aromatic liquids, oxygenates, C<sub>1-5</sub> gas molecules, hydrogen, and syngas) through the direct pyrolysis of disposable masks. Specifically, three different approaches, non-catalytic pyrolysis, catalytic pyrolysis, co-pyrolysis of disposable masks and other feedstocks (e.g., biomass, etc.), and CO<sub>2</sub>-mediated pyrolysis (CO<sub>2</sub> as both carrier gas and oxidizing agent), are discussed. We finally present the further outlooks of mask pyrolysis for better enhancement of environmental remediation and circular economy of disposable masks.

# 2. Direct Characterizations of Disposable Masks

#### 2.1. Determination of Disposable Mask Constituents

Typically, the largely used disposable masks are surgical masks and N95/KN95 respirators to prevent viruses accessing both nose and mouth from sprays and droplets. At this point, the medical masks are able to essentially hinder the spreading rate of bacteria. In addition, to avoid losing the efficacy of the original function of such medical masks when they are moisturized, smudged, or damaged, the masks must be replaced as needed or periodically. To concurrently qualify for these requirements, the function of mask materials should not only be virus-blocking but also single-use with low expense. Herein, plasticmade disposable masks can be an excellent option. As suggested by the World Health Organization (WHO), the most widely used or commonly seen disposable masks are dominantly surgical masks and N95/KN95 respirators [49–52]. By disassembling items, either surgical masks or N95/KN95 respirators mainly consist of the mask layers for blocking viruses, the nose holder for tightening the mask to adhere to the face, and the stretchable ear loops for fixing the mask without any dropping (Figure 1). Furthermore, the N95/KN95 respirators may also be attached with breathing valves. Specifically, for the mask layers, the N95/KN95 respirators are thicker than the surgical masks, where generally three layers of polymers are in the surgical masks, but four to six layers of various polymeric materials are in the N95/KN95 respirators. What is noteworthy is that there is at least one filter layer of melt-blown PP and a variety of extra layers of non-woven polymers for breathable and comfortable functions in surgical masks and N95/KN95 respirators. On the other hand, the nose holders are usually made from base metals in both the surgical masks and the N95/KN95 respirators, e.g., aluminum [53] or iron [40]. However, depending on the mask manufacturer, nose holders can also be produced from polymeric chemicals in N95/KN95 respirators [39].

With respect to the chemical properties of disposable mask layers and stretchable ear loops, Szefer et al. conducted a Fourier Transform Infrared Spectrometer (FT-IR) study to identify the molecular species in the mask products from three different manufacturers [54]. For the two types of disposable masks, one is a multi-layer respirator with a breathing valve,

and another is a three-layer melt-blown (or surgical) mask. From the FT-IR profiles of mask layers in Figure 2a,b, there are primarily two types of vibrational bands (the broad range with 2835–2952 cm<sup>-1</sup> and 1164–1452 cm<sup>-1</sup>) that are associated with -CH<sub>3</sub> and C-C species, together representing for PP chemical structure [54,55]. Furthermore, the profiles recognize that the PP-involved breathing valve in the multi-layer respirator shares the similar band ranges and types with mask layers (Figure 2a). Relating to the stretchable ear loops in the multi-layer respirator that contains a breathing valve, the vibrational profile demonstrates that PET and rubber materials are clearly detected from the corresponding vibrational bands of significant functional groups, such as -OH, methylene groups, C-O-C, and -CH<sub>2</sub>- [56,57]. In contrast, based on the observed vibrational bands regarding CO-NH amide group (mainly the band 1535 cm<sup>-1</sup> and 1631 cm<sup>-1</sup>) and N-H group (3100–3500 cm<sup>-1</sup>) in ear loop profiles of the three-layer melt-blown mask (Figure 2b), it is revealed that polyamide (PA) 6 or 66 is the main chemical composition contained in the stretchable ear loops of the melt-blown mask [58–60]. In this respect, it is consistently reported that the ear loops are made from nylon 6 and the mask layers are made from PP in both surgical masks and N95/KN95 respirators [32,61–64]. Noteworthily, owing to the variation of mask brands and manufacturers in the market, other polymeric materials are employed in the disposable mask products; for instance, polyethylene (PE) is identified as the major compound not only in one layer of the four-layer mask [40] but also in nose holders of disposable masks [39]; polyurethane (PU) is applied in the ear foam for comfort and a small portion of PU is also doped with nylon materials in the ear loops [62,63]. Overall, the major chemical ingredients of disposable masks are presented in Figure 1. One can conclude that carbon and hydrogen are the most abundant atoms in the common disposable masks without doubt. In contrast, the compositions of oxygen and nitrogen elements are much less [39,53,64,65]. Practically, the weight percents of atomic carbon, hydrogen, oxygen, and nitrogen were comparably quantified as 75.9%, 14.8%, 8.5%, and 0.8%, respectively, by Lee et al. [64], and 76.4%, 11.65%, 4.65%, and 1.12%, respectively, by Skrzyniarz et al. [66]. Such results could also prove that the quantity of elemental constituents in disposable masks are distinguishable from pure PP or PET [66]. Therefore, it totally cannot be ignored that the direct pyrolysis of disposable masks is a simultaneous pyrolytic process of multiple categories of polymers.



**Figure 2.** FT-IR spectra profiles of different parts in (**a**) N95/KN95-like multi-layer respirator with an FFP3 breathing valve and (**b**) three-layer melt-blown mask. Reproduced with permission from Ref. [54]. Copyright 2021 The Authors. Published by MDPI.

# 2.2. Identification of Disposable Mask Degradation Temperatures

In advance of the direct and selective pyrolysis of disposable masks, thermal fragmentation testing is informative in receiving a couple of important take-home messages. One can identify the possibility that such carbon-based polymeric materials could be thermally degraded and further upcycled to value-promoted chemical products, and another possibility is to acquire the suitable temperature range for the direct pyrolysis of disposable masks. However, it is worth noting that effective temperature intervals of selective pyrolysis also heavily depend on appropriate temperature of the product formations during or after the polymeric degradation. Thus, the optimization of pyrolysis temperature should be under consideration in both direct and selective pyrolysis. In this section, the general temperature range for the thermal decomposition of disposable masks is a central point to be discussed. In a typical experiment of mask decomposition, nitrogen, as an inert gas molecule, has been widely employed as the carrier gas in the thermogravimetric analysis (TGA) and the differential thermogravimetric analysis (DTG); meanwhile, the temperature ramping with a fixed rate could be set up from room temperature to 600 °C and the highest even could reach 900 °C [40,62,64,65,67,68]. For instance, Ali et al. comprehensively studied the mask layers with multiple layers, the stretchable ear loops, and the nose holders in the surgical mask and the N95 respirator with TGA and DTG [62]. For the evaluation of mask layers, the TG profiles of three layers and the PP reference were obtained from 100 °C to 600 °C with the rate of 10 °C min<sup>-1</sup> (Figure 3A for N95 respirator and Figure 3B for surgical mask). From both results, the TG curves smoothly transit approximately from 330 °C with substantial thermal degradation and finally end up around 480 °C. To distinguish the peaks of decomposition temperatures, the DTG analysis presents that the degradation peaks occur at about 452 °C consistently for all the examined layers in the N95 respirator and the PP reference as well (shown in Figure 3A); on the other hand, although the materials of all three layers in the surgical mask are characterized as PP, the decomposition temperature peaks of layer 1 and layer 3 are observed at about 455  $^{\circ}$ C, consistent with the PP reference, and layer 2 exhibits a lower degradation peak (420 °C) (shown in Figure 3B) [62]. Similarly, the decomposition temperature peaks of disposable masks are also obtained as 455 °C under both N<sub>2</sub> and CO<sub>2</sub> gas flow, and the key degradation temperature range happened from 330 °C to 495 °C [40]. Meanwhile, it is worth mentioning that CO<sub>2</sub> was purposefully employed to be the testing gas molecule to identify the existence of other side reactions (i.e., the mask layer material reacts with  $CO_2$ ) in the whole thermal degradation course [40]. In addition, to study the effect of temperature ramping rate during the thermal decomposition process of disposable masks, the comparisons of such temperature ramping speeds were carefully reported [67,68]. For instance, Yousef et al. conducted a thorough comparison of various temperature ramping speeds from 5 °C min<sup>-1</sup> to 30 °C min<sup>-1</sup> in the TG testing of a three-layer disposable mask [68]. As exhibited in Figure 3C, the significant decomposition is in the labeled stage  $Y_2$  (405 °C–510 °C), where 95% of mass is lost. The stage  $Y_1$  may be ascribed to the minor loss of moisture [68], which is also consistently reported by others [62]. The further decomposition of char is regarded in the last stage  $(Y_3)$ . Furthermore, according to the comparison of heating speeds, the TG profiles manifest that lower heating speed results in earlier ending temperature of major decomposition, lower peak temperature of decomposition, and less intensity of the degradation temperature peak [68]. That is to say, from the aspect of degradation timespan, a high heating rate could improve the speed of degradation. Furthermore, according to Figure 3D, the temperature interval of decomposition peak (448  $^{\circ}$ C with the rate of 5  $^{\circ}$ C min<sup>-1</sup> to 476  $^{\circ}$ C with the rate of 30  $^{\circ}$ C min<sup>-1</sup>) fits reasonably with the earlier discussed result above (455  $^{\circ}$ C with the rate of 10 °C min<sup>-1</sup>) and other reports (488 °C with the rate of 30 °C min<sup>-1</sup>) [62,65]. Lastly, due to various additional polymeric molecules (e.g., PA, PE) in ear loops and nose holders of disposable masks, the corresponding decomposition temperatures of these two items can be different from mask layers [62].



**Figure 3.** TGA and DTG profiles of various layers: **(A)** N95 respirator and **(B)** surgical mask. Reproduced with permission from Ref. [62]. Copyright 2021 Elsevier Ltd. **(C)** TGA and **(D)** DTG profiles of three-layer surgical mask with various heating rates. Reproduced with permission from Ref. [68]. Copyright 2021 Elsevier B.V.

# 3. Fuel-Range Liquids via Selective Mask Pyrolysis

# 3.1. Liquid Hydrocarbon Blends

In the pressing era of resolving environmental crises and developing sustainable fuels and chemicals to afford both transportation tools (e.g., vehicles, motors, airplanes, ships, etc.) and consumer products (e.g., coatings, medicines, food, etc.), the chemical processing of carbon-enriched renewable energy resources, such as biomass, have been immensely developed to catch up with the sustainability goals [69–71]. Likewise, as they are polymer-derived chemical products, it is completely reasonable to selectively convert the disposable mask materials into fuel-range organic liquids with a variety of carbon lengths and molecular structures. In this regard, high-temperature pyrolysis could be a sensible strategy with molecular cracking and additional chemical transformations in either a catalytic or non-catalytic manner. Muhyuddin et al. analyzed the pyrolytic liquid products from disposable masks based on various carbon ranges with  $C_{6-30}$  and even larger hydrocarbons [41]. As exhibited in Figure 4A, a total of six groups of hydrocarbon molecules are summarized with respect to their percentages at different temperatures at 500 °C, 700 °C, and 900 °C, respectively. In general, the  $C_{10-15}$  range molecules are the most recovered liquids among all carbon ranges above  $C_6$  at all the three temperatures; especially, the fraction of  $C_{10-15}$  could be achieved as the highest at 700 °C [41]. There is no prominent tendency of produced percentages regarding all carbon ranges except for  $C_{6-10}$  substances, where their fraction declines from low to high temperature. Thereupon, these findings could suggest that  $C_{10-15}$  and  $C_{6-10}$  are the key products at low temperature (500 °C), then shifting to the condition that  $C_{10-15}$  and  $C_{30+}$  are the dominating chemicals from pyrolysis of disposable masks [41]. In this regard, an analogous study of pyrolysis temperature demonstrated that diesel ( $C_{8-21}$  range hydrocarbons) held the highest yield among all the carbon ranges from the mask pyrolysis at all temperatures from 500 °C to 900 °C. Moreover, the molecules in all carbon ranges were achieved as their optimal yields at 700 °C, which includes the similarly high amounts for both jet fuel and motor fuel. However, the gasoline yield presented at a lower level [53].



**Figure 4.** (**A**) Percentages of different ranges of carbon chain lengths from disposable mask pyrolysis. Reproduced with permission from Ref. [41]. Copyright 2021 The Authors. Published by Wiley-VCH GmbH. (**B**) Product distributions of catalytic (HZSM5, HBeta, HY and Al-MCM-41) and non-catalytic (represented by NC in the figure) pyrolysis of disposable masks. Reproduced with permission from Ref. [64]. Copyright 2021 Elsevier Ltd.

As discussed in the earlier section about mask characterizations, despite PP primarily being the most common polymers in disposable mask layers, other polymers may also be detected in manufactured mask products including mask layers, nose holders, and stretchable ear loops, such as polyolefins (i.e., PE) [39,40,62], polyesters (e.g., PET) and polycarbonates [62], polyamides (e.g., nylon 6) [40,53,62], polyurethanes and polyacrylonitrile [53,62,72], etc. Based on this, the pyrolytic substances across a long carbon range can consist of an enormous group of chemicals with multiple functional groups. Dominantly, carbon- and hydrogen-enriched alkanes/alkenes with linear/branched chains or cyclic or aromatic structures are generally formed via molecular cracking and additional chemical formations during or after pyrolysis. For instance, the branched alkene 2,4-dimethyl-1heptene was substantially formed with high selectivity in the non-catalytic pyrolysis of disposable mask layers [73]; high compositional olefins and naphthenes were prepared by catalytic pyrolysis over HZSM-5 and HBeta zeolites [64]; aromatic molecules and oxygenates could be evolved from pyrolysis [43,64,74]. Other hydrocarbons were also widely and frequently reported based on the recent advances [32,40,53,64,73]; for example, a concise product library of  $C_{1-6}$  mixture via pyrolysis of mask layers is shown in Table 1 [32]. However, more possible products can be generated with applying various mask feedstocks and reaction conditions. Moreover, other types of liquid products with different functional groups may also be evolved, such as oxygenated organic chemicals (e.g., alcohols, aldehydes, ethers, esters, ketone, and acid) [32,42,63,74], nitrogenated chemicals (e.g., amines and amides) [42,62,63,74], halogenated chemicals (e.g., fluorides and chlorides) [42,74]. Wherein, owing to the considerable pyrolytic compositions and the extensive applications of aromatic hydrocarbons and oxygenated substances in high-quality transportation fuels and specialty chemicals [70,75,76], we will further evaluate in detail the selectivity control of those two produced materials from disposable masks in the following separate sections.

**Table 1.** Product distributions of  $C_{1-6}$  molecules from pyrolysis of disposable mask layers. Reproduced with permission from Ref. [32]. Copyright 2021 Elsevier Ltd.

No.	Possible Products	Formula	Molecular Weight	Family
1	methane	CH <sub>4</sub>	16	Alkanes
2	water	$H_2O$	18	inorganic substances
3	ethylene	$C_2H_4$	28	alkenes
4	carbon monoxide	CO	28	inorganic substances
5	propylene	$C_3H_6$	42	alkenes
6	carbon dioxide	CO <sub>2</sub>	44	inorganic substances
7	acetaldehyde	$C_2H_4O$	44	aldehydes
8	butene	$C_4H_8$	56	alkenes

No.	Possible Products	Formula	Molecular Weight	Family
9	acetone	C <sub>3</sub> H <sub>6</sub> O	58	ketones
10	1,3-pentadiene	$C_5H_8$	68	alkenes
11	2-amylene	$C_{5}H_{10}$	70	alkenes
12	1,2-dimethyl cyclopropane	$C_{5}H_{10}$	70	naphthenic hydrocarbons
13	methacrylaldehyde	$C_4H_6O$	70	aldehydes
14	pentane	$C_{5}H_{12}$	72	alkanes
15	2,4-hexadiene	$C_{6}H_{10}$	82	alkenes
16	2-methyl-1,3-pentadiene	$C_{6}H_{10}$	82	alkenes
17	2-hexene	$C_{6}H_{12}$	84	alkenes

Table 1. Cont.

#### 3.2. Aromatic Hydrocarbons

Aromatic hydrocarbons are well known to be commonly utilized in transportation fuels containing gasoline, kerosene, and diesel; for example, aviation fuel generally comprises certain fractions (~20%) of aromatic compounds [77]. Noteworthily, aromatic compounds are building blocks for fine chemical production [78,79]. Structurally, aromatic compounds can be distinguished as monoaromatics and polyaromatics, where the former mainly refers to benzene, toluene, ethylbenzene, and xylene (BTEX). Considering the plentiful resources of carbon and hydrogen, it is exceedingly rewarding and promising to upgrade the waste disposable masks into high-value aromatic compounds. Lee et al. investigated the direct-fast pyrolysis (heating rate as 200 °C min<sup>-1</sup>) of disposable masks (involving the mask layers, nose holders, and stretchable ear loops) with and without applying catalysts [64]. First, in the non-catalytic approach, an optimal yield of brunched-chain liquid oil (i.e.,  $C_{8-46}$ ) was obtained as 80.7% by weight at 550 °C. In comparison, the liquid oil production was diminished by the zeolite-catalytic (HZSM-5, HBeta, HY and Al-MCM-41) pyrolysis of disposable masks (Figure 4B). Instead, the gas molecules were generated in greater quantity in the catalytic process than in the non-catalytic manner [64]. According to the shift of liquid and gas production in the two different kinds of pyrolysis systems, it can be suggested that the active sites in the zeolite catalysts are responsible to boost the extent of molecular cracking from long to short carbon chains. Among the various tested zeolite catalysts, HBeta zeolite displays the best performance of catalytic cracking with less liquid fuel, and the HZSM-5 catalyst may drive the pyrolysis to evolve less liquids but more gas substances (Figure 4B). Significantly, although it is shown that the catalytic pyrolysis is not able to produce as high content of liquid oil as the non-catalytic method, it is much worth noting that a substantial quantity of monoaromatic liquids (i.e., BTEX) can be generated over the zeolite catalysts but the non-catalytic approach does not possess such capability. Furthermore, the full comparisons of oil product distributions from the catalytic pyrolysis are exhibited in Table 2, where the ranking of BTEX production ability increases as Al-MCM-41 < HZSM-5 < HY < HBeta. In particular, the HBeta catalyst with higher loading may synthesize more aromatics than that with low loading. Based on these transparent outcomes, such trends could be ascribed to the porosities and acid sites in the various zeolite-type catalytic materials [64]. In detail, the HBeta and HY zeolites possess larger pore sizes and higher amounts of acid sites to allow the branched-chain molecules to get through the catalyst pores and then effectively transform to aromatics by the active sites in zeolites. In this regard, this tendency could also explain the reason that the absence of acid sites in non-catalytic pyrolysis of disposable masks leads to the production of heavier molar weight chemicals with only branched chains [64,80]. Moreover, according to Table 2, BTEX are not the only types of monoaromatics synthesized from the catalytic pyrolysis. Relatively less amounts of other non-BTEX monoaromatics (OMAHs) and polycyclic aromatic hydrocarbons (PAHs) could be obtained along with BTEX in the pyrolytic oil mixture [64]; at this point, such activity of PAHs only exists with the HBeta and HY catalysts [64]. Noteworthily, via co-pyrolysis, a small amount of PAH liquids may

also be produced from the non-catalytic pyrolysis of disposable masks when food waste is co-fed with high loading [53].

**Table 2.** Compositions of liquid products from mask pyrolysis over various zeolite catalysts. Repro-duced with permission from Ref. [64]. Copyright 2021 Elsevier Ltd.

Catalyst	HZSM-5 <sup>a</sup>	HBeta <sup>a</sup>	HBeta <sup>b</sup>	HY <sup>a</sup>	Al-MCM-41 <sup>a</sup>
BTEX	21.07	49.41	1.12	35.21	11.53
Other mono-aromatic hydrocarbons other than BTEX (OMAHs)	5.53	21.48	0	28.12	1.26
Polycyclic aromatic hydrocarbons (PAHs)	0	7.04	0	2.51	0
n-Parafins	7.49	1.4	0	2.15	8.27
i-Parafins	0	5.25	0	23.4	0
n-Olefins	16.44	0.38	8.19	0	6.05
i-Olefins	31.68	7.56	78.51	5.63	41.18
Naphthenes	16.15	7.11	3.2	1.44	16.66
Ōthers <sup>c</sup>	1.65	0.37	8.98	1.54	15.05

<sup>a</sup>: Catalyst: feed = 1:1 (weight basis). <sup>b</sup>: Catalyst: feed = 1:5 (weight basis). <sup>c</sup>: Others include acids, aldehydes, ketones, furans, and alcohols.

Toward the production of aromatic substances, not only by zeolite-based catalysts, the polymeric layers of disposable masks could be pyrolyzed to yield monoaromatic chemicals over a series of biochar catalysts at various temperatures and with different ratios of catalyst to mask [65]. Upon the ratio study, the fraction of monoaromatic compounds goes up with increase of the ratio (from 1.6 to 4.4) between catalyst and mask at 600 °C, where the content of aromatics is quantified as 80% in the liquid products with the ratio of 4.4, compared to the lower composition of monoaromatics as 64.4% with the ratio of 1.6 (Figure 5A) [65]. In addition, regarding the temperature optimization, it indicated that the biochar-catalyzed pyrolysis is conducted most efficiently with 95% content in liquid products at 625 °C in the examined range from 529 °C to 671 °C (Figure 5B). At this point, such an increasing– decreasing trend of monoaromatic compositions from low to high temperature can be explained by the following two reasons: (a) the increase in monoaromatic compositions from 529 °C to 625 °C: the formation of monoaromatics from aliphatic molecules is favored by heat; (b) the decrease in monoaromatic compositions from 625 °C to 671 °C: the side production of di-aromatic chemicals at high temperature is promoted (i.e., 671 °C) [65,81]. In addition, it is meaningful to mention that a considerable amount of aliphatic  $C_{7-15}$ (acting as the vital components of transportation fuels) compounds could be prepared together with the aromatics from the disposable mask pyrolysis. Lastly, comparing to biochar-catalyzed pyrolysis, the researchers also addressed that monoaromatics were synthesized without catalyst although the evolved quantity is less than that via the catalytic approach [65]. Meanwhile, another non-catalytic pyrolysis of disposable masks produced aromatic substances that mainly comprised toluene, xylene, and mesitylene [62]. According to these findings on non-catalytic pyrolysis, such contradictions of aromatic production with the earlier discussion (aromatics were not observed in the products from non-catalytic pyrolysis) above may originate from multiple reasons, such as the differences of chemical compositions in the mask feedstocks, the differences of pyrolysis reaction parameters, etc.

#### 3.3. Oxygenated Liquids

Oxygenates, which include a range of functional substances, such as alcohols, ethers and esters, are the key commodity chemicals to prepare fuels [82–86], fuel additives [87–89], and many other specialty chemicals [90–92]. Thus, it would be always highly worthwhile to synthesize oxygenates from renewable or recyclable oxygen sources. In this regard, a few studies have addressed that disposable-mask-pyrolytic liquid products may contain oxygenates except alkanes/alkenes [32,42,74]. Li et al. carried out the non-catalytic pyrolysis of the middle layers of disposable masks under both medium and slow modes [42]. As presented in Figure 6, the oil product distributions of medium and slow pyrolysis were

examined at three different temperatures from 350 °C to 650 °C. Especially, esters, ethers, and alcohols are the major products that are family members of oxygenates. According to the tendencies of produced oxygenate contents, it was effectively demonstrated that the selectivity of one expected oxygenate is tunable via adjusting pyrolysis temperature and mode. For instance, in the medium pyrolysis manner, both compositions of esters and ethers decline with increase in the pyrolysis temperature, where essentially ethers could be synthesized with the highest selectivity among other types of chemicals (Figure 6a) [42]. Meanwhile, alcohols are reported to only show up with a small amount at high temperature pyrolysis at medium mode; however, the amount of alcohols produced decreases as the temperature goes up in slow-mode pyrolysis (Figure 6b). On the other hand, the content of ethers could be promoted by turning up temperature at the low pyrolysis mode [42]. In contrast, in the catalytic pyrolysis approach, Yousef et al. used ZSM5 catalysts to synthesize vapor butanol along with a considerable quantity of CO2 [74], and by optimizing the heating speed and catalyst loading (determined by the mass ratio of catalyst to mask), the high butanol selectivity was achieved at about 31% under low heating speed (5 °C min<sup>-1</sup>) over 25 wt% loading zeolite [74]. Also notable is that the non-catalytic pyrolysis experimental results show that such relatively high selectivity of  $C_4$  alcohol could be ascribed to the catalytic decoupling of 2,4-dimethyl-1-heptene into C<sub>4</sub> substances (i.e., butanol) [74].



**Figure 5.** Liquid product distributions from mask pyrolysis with (**A**) different biochar-to-mask ratios at 600 °C and (**B**) multiple temperatures at the biochar-to-mask ratio of 3. Reproduced with permission from Ref. [65]. Copyright 2021 Elsevier Ltd.



**Figure 6.** Liquid product distributions from pyrolysis of the middle layer of disposable masks at 350 °C, 500 °C and 650 °C with (**a**) medium mode and (**b**) slow mode. Reproduced with permission from Ref. [42]. Copyright 2021 Elsevier Ltd.

In common, the comparably low feeding composition of oxygen atoms in disposable masks can lead to relatively low content of recovered liquid oxygenates in pyrolytic products [42,74], whereas it is still quite necessary to improve the selectivity of oxygenated compounds by virtue of facilitating the atom economy of carbon and hydrogen in disposable masks. In this regard, to effectively form a high concentration of oxygenated

compounds, the simultaneous pyrolysis of disposable masks and co-feeds containing sizable oxygen sources (e.g., biomass, biowaste, syngas) can be conducted [93]. For instance, Park et al. investigated the non-catalytic concurrent pyrolysis of disposable masks (including mask layers, nose holders, and stretchable ear loops) and food waste [53]. Specifically, the fractional loading of food waste was purposefully varied to probe the production distributions in a wide range with regard to oxygenates, N-containing species, hydrocarbons, PAHs, and phenolic compounds. The food waste loading-dependent pyrolytic liquid profiles are exhibited in Figure 7A. At 973 K (700 °C), five different food waste loadings are labeled in the x-axis from 0 to 100%. Macroscopically, the major pyrolytic products are oxygenates and hydrocarbons, which once again manifests the dominating feeding elements of carbon, hydrogen and oxygen from disposable masks and food waste. Due to the high oxygen storage in food waste, such as esters and fatty acids, the composition of pyrolytic oxygenated compounds is promoted when the food waste loading climbs up at 700  $^{\circ}$ C; whereas the production of hydrocarbons is diminished by co-feeding higher loading of food waste because more abundant oxygen dominates and participates in different reactions during pyrolysis testing [53]. Meanwhile, the nitrogen-involving substances in the food waste allows the evolved number of N-containing species to be elevated by turning up the food waste loading. On the other hand, the phenolic compounds become available in the pyrolytic liquid mixture at high loading of food waste [53]. In an analogous manner, pyrolysis-fractionation (or co-pyrolysis) of hydrogen-enriched disposable mask polymers and oxygen-/aromatic-abundant bio-oil (e.g., phenol, guaiacol, etc.) was reported as another practicable tactic to synthesize high-quality oxygenated liquids with non-catalytic fast pyrolysis [43]. Such co-pyrolysis was held at three temperatures from 700 °C to 900 °C. As shown in Figure 7B, the pyrolytic liquid products at 800 °C include a number of industrially relevant aromatic oxygenates, such as 2,4-dimethylphenol and p-cresol, as well as monoaromatics (e.g., styrene, 1,2-dimethylbenzene, etc.) and PAHs, such as biphenyl and 2-methylnaphthalene [43]. Although we aim to highlight the production feasibility of oxygenated molecules from mask pyrolysis here in this section, it is also evidently demonstrated that substantial types of monoaromatics and polyaromatics are also available in the pyrolytic liquids (Figure 7B) [43].



**Figure 7.** (**A**) Liquid product distributions from the co-pyrolysis of disposable masks and food waste at 973 K with various food waste loadings. Reproduced with permission from Ref. [53]. Copyright 2021 Elsevier Ltd. (**B**)  $C_{6+}$  liquid product abundances from the co-pyrolysis of disposable masks and bio-oil at 800 °C. Reproduced with permission from Ref. [43]. Copyright 2021 Elsevier Ltd.

Based on these findings above, despite tiny content of oxygen or nitrogen in the disposable masks, one can conclude that the large synthesis of oxygenates from selective pyrolysis can be potentially feasible by leveraging the other co-feeds that contain substantial oxygen or nitrogen atoms. To our best knowledge, although no additional studies have directly conducted the simultaneous pyrolysis of disposable masks and other oxygen-abundant feedstocks to produce oxygenate liquids, it is still worth emphasizing the prospective opportunities via co-feeding methods inspired by the co-pyrolysis of plastic waste and biomass or CO<sub>2</sub>-mediated plastic pyrolysis (CO<sub>2</sub> as both carrier gas and oxidizing agent) [93–98]. In turn, the selectivity improvement of hydrocarbons rather than oxygenates is also workable from such co-pyrolysis methods [97].

# 4. Fuel-Range Gases via Selective Mask Pyrolysis

# 4.1. C<sub>1-5</sub> Alkanes and Alkenes

In application, it is conventional and beneficial to classify organic molecules by their molar weights, structures, or boiling points. For instance, C<sub>1-4</sub> substances are typically in the gas phase under atmospheric pressure; in more detail, a portion of C<sub>5</sub> hydrocarbons are inclined to be in a gas state at temperatures between 30 °C and 40 °C. With respect to the pyrolysis reaction, the polymeric materials in disposable masks may be catalytically or non-catalytically cracked into short-carbon-chain chemicals, i.e., mainly  $C_{1-5}$  hydrocarbons [32,39,64,73]. In this regard, from mask pyrolysis, those short-carbon-chain compounds are hardly condensable at room temperature and could be directly extracted alongside carrier gas. Therefore, it becomes crucial to probe the selectivity tendencies of such low-carbon chemicals and further adjust the key factors in various ways to optimize the yields of  $C_{1-5}$ . Sun et al. carried out the disposable mask pyrolysis and promotional pyrolysis-cracking over solid zeolite and metal oxide catalysts to analyze the gas product distributions [39]. First, the pyrolysis experiment was held in a single down-flow fixed bed reactor that contained two stages, where the mask sample was packed in the upper stage and the catalyst was plugged in the lower stage. In this way, the experimental scheme is able to be comparative for the additional catalytic- or non-catalytic-cracking of pyrolytic volatiles from the upper stage. For the condition that no catalysts are packed in the lower stage, the evolved chemicals in the non-condensable gas stream are quantitively depicted in Figure 8A. As temperature increases, the total yield of gas products increases dramatically at temperatures lower than 420 °C, and subsequently climbs up gradually when the reactor receives more heat. However, especially when the pyrolysis temperature reaches 440 °C or above, the yield of each specific hydrocarbon is not vitally affected and therein is maintained with very slight amount of increase or fluctuation [39,99]. Individually, it is clearly revealed that the dominating productive hydrocarbons are  $C_5$ ,  $C_4H_8$ and  $C_3H_6$  regardless of the temperature values. In this respect, this is also comparable with the results from PP pyrolysis [66,100,101]. For instance, at 440  $^{\circ}$ C, the yields of C<sub>5</sub>, C<sub>4</sub>H<sub>8</sub> and  $C_3H_6$  are measured as about 13%, 3%, and 5%, respectively (Figure 8A). As for  $C_{1-2}$ hydrocarbons, the yields of  $C_{1-2}$  become slightly larger when temperature increases although the corresponding yields of  $CH_4$  and  $C_2$  are still lower than those for  $C_{3-5}$ . Such observations may be elucidated by the boosted cracking reactions of longer-chain chemicals at high temperatures [39]. At this point, similar trends of  $C_{1-2}$  yields were also reported in non-catalytic pyrolysis of disposable masks with different heating rates [42,53]. On the other hand, the selectivity of C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> were investigated by adjusting the residence time/reaction time and temperature of non-catalytic pyrolysis between 450 °C and 550 °C; therein, a high selectivity of  $C_3H_8$  or  $CH_4$  was able to be attained [73].



**Figure 8.**  $C_{1-5}$  gas product yields from (**A**) thermal pyrolysis of masks at different temperatures; (**B**) oxide-catalytic cracking of pyrolytic volatiles at 440 °C; (**C**) zeolite-catalytic cracking of pyrolytic volatiles at 440 °C. Reproduced with permission from Ref. [39]. Copyright 2022 Elsevier B.V.

In another way, the pyrolysis-catalytic-cracking (catalytic cracking of thermal pyrolytic products) mode demonstrated much better performance of volatile cracking, and accordingly promoted the total yield of non-condensable gases and individual yield of those  $C_{3-4}$ hydrocarbons [39]. In detail, the comparative product layout in the metal oxide-catalyzed cracking system at 440 °C is displayed in Figure 8B. All of the metal oxides (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, kaolin, and TiO<sub>2</sub>) could improve the total yield of non-condensable gases to various extents. For instance, the total gas yield is slightly higher with  $Fe_2O_3$  than the absence of catalyst in the reactor, whereas the most effective promotional gas yield is obtained over the catalyst,  $TiO_2$ . In the meantime, the major produced hydrocarbons are still  $C_5$ ,  $C_4H_8$  and  $C_3H_6$ , and the yields of  $C_{3-5}$  molecules share the similar increasing profile as "no catalyst" <  $Fe_2O_3$  <  $Al_2O_3$  <  $CeO_2$  < kaolin <  $TiO_2$  [39]. On the other hand, a small group of zeolites, including  $\beta(25H)$ , HZSM5, HY and  $\beta(60H)$ , are compared as well with respect to the non-condensable gas yield at 440 °C (Figure 8C). As a result, it is strongly proven that the most promising zeolites are HY and  $\beta$ (60H) catalysts because of their relatively better performances in both the total yield of gas production and the selectivity of  $C_{3-4}$  olefins compared to the other two zeolites [39]. Returning to such effects from the catalysts, it is reasonable to illustrate that the HY and  $\beta(60H)$  zeolites can enhance the cracking reactions of pyrolytic heavy compounds to smaller gas molecules, such as  $C_4H_8$ ,  $C_4H_{10}$  and  $C_3H_6$  [39]. In addition, other catalytic examinations of mask pyrolysis over different zeolites (e.g., HZSM5, HY, HBeta, MCM-41) also displayed analogous phenomena to selectively synthesize low-carbon substances [64].

# 4.2. Hydrogen and Syngas

Polymeric materials, especially polyolefins, contain not only massive carbon but also sizeable hydrogen sources. Herein, it is not unexpected that molecular hydrogen could be extracted from polymers or plastic wastes, such as disposable masks. Meanwhile, the production of hydrogen gas is a greatly attractive chemical process because hydrogen can be used as clean and sustainable fuels and chemicals for transportation and the fine chemical industry. To this end, several literatures have reported the chemical pyrolysis of waste plastics into hydrogen product [45,102–105]. For instance, Liu et al. prepared hydrogen by catalytic pyrolysis of PP [45]; hydrogen was synthesized via combined pyrolysis and catalytic reforming [102]. Thus, it would be valuable to generate hydrogen from mask pyrolysis to improve the atomic economy of hydrogen. Although it has been proven that molecular hydrogen is producible through mask pyrolysis in a few attempts, sufficient space is still available to boost the selectivity of hydrogen catalytically and non-catalytically by tuning the pyrolysis parameters e.g., maximum temperature, heating speed, carrier gas, etc. [42,73]. Jung et al. investigated the pyrolysis of disposable masks in various approaches with the carrier gases ( $N_2$  and  $CO_2$ ) under a one-stage and two-stage reactor setup, respectively [40]. For all the examined reaction conditions up to 600  $^{\circ}$ C with 10  $^{\circ}$ C min<sup>-1</sup>, the pyrolytic gases consistently consist of C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>; nonetheless, the concentrations can differ from each other. Essentially, the two-stage pyrolysis system equipped with two furnaces in series possesses advantages to form more hydrogen and  $C_1/C_2$  hydrocarbons from extra cracking of large molecules. Furthermore, for the  $Ni/SiO_2$  catalyst-assisted pyrolysis in the two-stage system, CO is detected along with hydrogen and  $C_1/C_2$  hydrocarbons in the mobile environment of  $N_2$  or  $CO_2$ . Especially, the  $CO_2$ -mediated ( $CO_2$  as both carrier gas and oxidizing agent) pyrolysis of disposable masks over catalyst Ni/SiO<sub>2</sub> produces a much larger amount of CO although the N<sub>2</sub>-participated pyrolysis makes more  $H_2$  and  $CH_4$  (Figure 9) [40]. After assessing the two possible reactions on catalyst surfaces, such as methane dry reforming and reverse water gas shift, the remarkable finding of enormous CO formation from CO<sub>2</sub>-mediated pyrolysis plausibly demonstrates that CO<sub>2</sub> acts as a co-fed oxidant in a homogeneous environment to convert the other higher-carbon molecules generated from mask pyrolysis. In addition, the Ni catalyst might be beneficial for the dehydrogenation of larger hydrocarbons. Consequently, it becomes feasible to effectively upgrade disposable masks and greenhouse gas (i.e., CO<sub>2</sub>) simultaneously to

hydrogen fuel via pyrolysis over supported metal catalysts [40]. Moreover, the catalytic pyrolysis of disposable masks could also be carried out with applying non-metal catalysts to prepare highly concentrated molecular hydrogen [65]. In this scheme, two key reaction parameters, the catalyst loading (referred to as the ratio of biochar to disposable masks) and the pyrolysis temperature, were adjusted to probe the tendency of gas product distributions over biochar catalysts. As a result, only the selectivity of hydrogen increased along with catalyst loading and pyrolysis temperature, respectively; whereas, the selectivity of  $C_{1-3}$  hydrocarbons declined in certain amounts with improving the catalyst loading. Moreover, the experimental finding of a temperature study from 529 °C to 671 °C conveyed that  $C_{2-3}$  (mainly  $C_3$ ) products may be responsible for the further cracking process to form methane and hydrogen. Quantitively, the selectivity of hydrogen was achieved above 60% during the testing of catalyst loading and pyrolysis temperature [65].



**Figure 9.** Producing concentrations of syngas and  $C_{1-2}$  hydrocarbons from the Ni/SiO<sub>2</sub>-catalyzed mask pyrolysis under the carrier gases N<sub>2</sub> and CO<sub>2</sub>. Reproduced with permission from Ref. [40]. Copyright 2020 Elsevier B.V.

Alternatively, the direct and selective pyrolysis of disposable masks to hydrogen and syngas could be carried out without catalysts. However, one needs to note that such non-catalytic processes require greater energy input to afford the high reaction temperature. Moreover, appropriate co-feed can be an essential promoter during mask pyrolysis. By doing so, Park et al. has reported the simultaneously pyrolysis of food waste and masks [53]. In detail, the major gas products from the co-pyrolysis were hydrogen, CO, CO<sub>2</sub>, C<sub>1-3</sub> hydrocarbons. Initially, in the non-co-feeding system from 500 °C to 900 °C, there was almost no detectable hydrogen molecules in the outlet gas stream from the mask pyrolysis, but a tiny amount of CO was formed. After introducing the food waste as second reactant, the chemical distributions of gas effluents received a significantly quantitative impact.

Owing to the abundant oxygen atoms in the food waste feedstock, the selectivity of syngas (hydrogen and CO) was improved gradually with increasing the pyrolysis temperature from 500 °C to 900 °C and food waste loading from 0 to 75%. As a complement, it is worth mentioning that the selectivity of hydrogen was lower from the pyrolysis of whole food waste feed (100% loading food waste) without disposable masks [53]. Numerically, the selectivity of syngas could be obtained around 50% out of the total pyrolytic gas fraction. Despite such sizable content of syngas formed from the pyrolysis at suitable temperatures (e.g., 700 °C), about 30–40% portion of CO<sub>2</sub> was evolved as well [53]. Therefore, there are definitely more desirable efforts for the mitigation of CO<sub>2</sub> production. To this end, a series of pyrolysis parameters may be tuned purposefully, such as the carrier gas type and flowrate, heating rate, or even suitable catalyst as needed. Furthermore, the results also presented that the selectivity of  $C_3H_6$ ,  $C_2H_4$  and  $C_2H_6$  significantly declined as food waste loading increased, which may refer to the fewer polyolefins in the reactant mixture when more food waste was fed instead of disposable masks [53].

In addition to the experimental approach for plastic pyrolysis, computer-aided simulation could be a powerful tool to provide detailed and efficient pyrolytic product analysis with relatively low cost in materials and energy. Skrzyniarz et al. applied computational modeling with a pilot continuous pyrolysis reactor to investigate the gas product distribution from the thermal pyrolysis of various feedstocks, such as face masks, PP, PET, and refuse-derived fuel [66]. As shown in Figure 10A,  $H_2$ ,  $CH_4$ , and  $C_6H_6$  are the three most abundant products from the thermal pyrolysis of face masks and PP; especially, it is transparent that the selectivity is distributed as  $H_2$ ,  $CH_4$ ,  $C_6H_6$ , in decreasing order, whereas it is demonstrated that CO has the highest selectivity from the thermal pyrolysis of PET and refuse-derived fuel [66]. Noticeably, the product distributes more diversely by refusederived fuel pyrolysis. Meanwhile, such computational outcomes could be fair evidence to prove that the polymeric material in face masks is much similar with PP compounds but not PET or refuse-derived fuel. According to the comparison of energy density, the pyrolytic products from face masks and PP have higher calorific quantities than PET and refuse-derived fuel, shown in Figure 10B [66]. At this point, it could be suggested that there is great potential of generating fuel-range chemicals from face mask waste or PP waste. Furthermore, simulation study of mask pyrolysis was conducted by Foff et al. to evaluate product distribution and energy consumption [106].



**Figure 10.** (**A**) Gas product distribution from thermal pyrolysis of various feedstocks. (**B**) Calorific quantities of gas products from thermal pyrolysis of various feedstocks. RDF represents refusederived fuel. Reproduced with permission from Ref. [66]. Copyright 2022 The Authors. Published by MDPI.

#### 5. Comparison of Various Pyrolytic Processes

Based on the analysis from previous sections, it has been demonstrated that the selectivity control of pyrolytic products is an overall result of different pyrolytic strategies, reaction conditions, reactor types, and other factors. Thus, it is quite meaningful to conduct

the comparison of various pyrolytic processes for the understanding of fuel-range chemical synthesis. First, thermal pyrolysis is an approach to carry out the degradation of disposable masks to form a series of monomers at high temperature by only using thermal energy, but without any additional assistance of chemical substances. Alternatively, catalytic pyrolysis of disposable masks is another type of pyrolytic process over solid catalysts. Generally speaking, solid catalysts could play vital roles to enhance the mask pyrolysis. First, it might stabilize the activation energy of the polymer decomposition to form various monomer products. Secondly, the special microstructures of solid catalysts could present considerable performance of molecular shape screening to tune the pyrolytic product selectivity via different reaction routes. In this regard, the rational design and development of solid catalysts is directly beneficial to the product selectivity control. Moreover, the direct pyrolysis of disposable masks could be generated by co-feeding of other feedstocks, such as biomass. Here, the biomass compounds can be broadly comprised of biooil, biowaste, cellulose and many others. Due to the distinct molecular structures and atom contents between masks and biomass, or masks and CO<sub>2</sub> (CO<sub>2</sub> as both carrier gas and oxidizing agent), the synergetic effect during pyrolytic processes could easily lead to a range of different chemical products. Therefore, such a manner is efficient to simultaneously upgrade disposable mask waste and biomass or CO<sub>2</sub> into value-added molecules for the circular carbon economy. To purposefully arrange the pyrolytic product distribution, the appropriate selection of pyrolytic process is shown to be an effective factor to consider and apply. In the meanwhile, to precisely adjust the selectivity of desirable products, the corresponding reactor configurations and reaction conditions highly demand to be varied as well.

In Table 3, the fundamental comparison of the three various pyrolytic processes is exhibited by evaluating a host of key pyrolytic factors in the disposable mask pyrolysis. Wherein, the key pyrolytic factors are comprised of reactor type, reactor stage, reaction temperature range, reaction heating rate, reaction carrier gas, and additional mediator as needed in the different pyrolytic manners. Although a fluidized bed reactor or semi-batch reactor could be utilized, a fixed bed reactor typically acts as the main reactor for the three pyrolytic processes. However, the reactor stage could be varied according to the pyrolysis performance and selectivity requirements. The one-reactor stage means that one reactor bed is employed during disposable mask pyrolysis, but the two-reactor stage represents that there are two reactor beds in series. For the one-reactor-stage scheme, solid catalysts, such as zeolites and metal oxides, are conventionally loaded in the reactor bed; moreover, other biomass feedstocks, such as biooil and biowaste, could be co-fed in the reactor along with disposable masks for synergetic co-pyrolysis. For the two-reactor-stage system, it can offer increased residence time of the polymers in the reactor bed to allow the cracking of polymers into various monomers to take place more sufficiently. Especially, when catalytic pyrolysis is conducted, it is feasible to load solid catalysts in both of the two reactor beds or only in the second reactor. In this regard, it becomes catalytic processing or cracking of pyrolytic volatiles if solid catalyst is used only in the second reactor bed. In addition, the main reaction temperature ranges and reactor heating rates are quite similar for the three types of pyrolytic approaches. It is worth mentioning that the mask pyrolysis can be either conducted at a fixed high temperature or with temperature-programmed mode. Owing to its inert characteristic,  $N_2$  is widely used as the carrier gas in the three pyrolytic processes. However, considering the reasonable treatment of CO<sub>2</sub> greenhouse gas, employing  $CO_2$  as a carrier gas for the mask pyrolysis has been shown as a workable strategy. Essentially,  $CO_2$  is not only a carrier gas but also an oxidizing agent because of its store of oxygen atoms. Last but not the least, there are variations of main product ranges in thermal pyrolysis, catalytic pyrolysis, and co-pyrolysis. A more diverse product distribution including alkanes/alkenes and ethers in the resulted liquid blends can be recovered from the thermal pyrolysis; in addition,  $C_{1-4}$  gases are also available in the thermal pyrolysis. Oppositely, catalytic pyrolysis generates more structure-selected products, such as BTEX, OMAHs, PAHs, and  $H_2$ /Syngas due to the mediation of solid catalysts. On the other

hand, upon the abundance of oxygen and nitrogen atoms in biomass (e.g., biowaste), when co-pyrolysis of disposable masks and biomass is applied, oxygenates and N-containing chemical compounds (e.g., amines) are easily prepared.  $C_{6+}$  hydrocarbons may be formed in the liquid blends toward biofuel applications. From all of the above, these differences clearly reveal that the appropriate selection of pyrolytic processes has a direct and large influence on product distribution.

Key Pyrolytic Factors	Thermal Pyrolysis	Catalytic Pyrolysis	<b>Co-Pyrolysis</b>
Main Reactor Type	Fixed bed reactor	Fixed bed reactor	Fixed bed reactor
Main Reactor Stage	1 or 2	1 or 2	1
Main Reaction Temperature Range (°C)	400–900 or fixed temperature	200–900 or fixed temperature	500–900 or fixed temperature
Main Reaction Heating Rate (°C/min)	5–30	5–30	5–30
Main Reaction Carrier Gas	N <sub>2</sub> or CO <sub>2</sub>	N <sub>2</sub> or CO <sub>2</sub>	N <sub>2</sub> or CO <sub>2</sub>
Main Mediator	N/A	Solid catalysts (e.g., zeolites, metal oxides, etc)	Biomass (e.g., biooil, biowaste, etc)
Main Products	Liquid blends Alkanes/Alkenes Ethers C <sub>1-4</sub> gases	BTEX OMAHs PAHs Alkenes Oxygenates C <sub>1-4</sub> gases H <sub>2</sub> /Syngas	C <sub>6+</sub> hydrocarbons Oxygenates Amines Alkanes/Alkenes

**Table 3.** Comparison of various pyrolytic processes.

# 6. Conclusions and Outlooks

Based on the discussions above, we have assessed and demonstrated the outstanding feasibility of disposable mask pyrolysis to selectively obtain a variety of high-value chemical compounds in fuel ranges involving liquid hydrocarbon blends, aromatics, oxygenates,  $C_{1-5}$  gas alkanes/alkenes, hydrogen, syngas, and amines. To attain the optimal conversion of disposable masks and high selectivity of such fuel-type chemicals, the direct mask pyrolysis may be performed with or without catalyst, or co-feeding with other feedstocks (e.g., biomass), and by operating suitable reaction conditions. Importantly, this review has presented that product selectivity control depends on a host of reacting parameters, e.g., heating speed during pyrolysis, maximum temperature of pyrolysis, etc. Therefore, an optimal pyrolysis condition to acquire the most desirable product may be achieved by tuning those key factors. Furthermore, based on pyrolysis scheme, the selective formation of fuel-range chemicals from disposable masks can be practically optimized either in single-bed (catalytic or non-catalytic) pyrolysis, or combinational mode involving polymer cracking and subsequent catalytic reactions in two or multiple reactors. Importantly, it is feasible to consider the mask pyrolysis not only in fixed bed reactors but also in fluidized reactors and semi-batch reactors [106,107]. Fundamentally, mask layers have been studied as the major starting materials in pyrolysis; however, they cannot represent the real-world pyrolysis of waste masks that additionally includes ear loops and nose holders. Thus, it would be much more valuable to focus on the simultaneous upcycling of mask layers, nose holders and ear loops for a realistic conversion of plastic and textile materials. Although carbon and hydrogen are the dominating elements in disposable mask layers, nitrogen could be involved in the ear loops and nose holders; so, a denitrogenation process is necessary to produce high-quality fuel-range chemicals to avoid further NO<sub>x</sub> emissions. On the other hand, what is noteworthy is that all pyrolytic products require

quality improvements via various purifying methods (e.g., distillated refining of heavy carbon molecules, hydrotreating) before their utilizations. For catalytic pyrolysis, owing to pyrolysis at mid-high temperature and product complexity, the stability, recovery, and reuse of solid catalysts become challenging issues during catalytic pyrolysis, where the catalyst structures may change and the spent catalysts are easily mixed with residuals generated from pyrolysis. To this end, the surface investigations of pyrolysis mechanism and catalyst deactivation are very meaningful with combinational instrumental analysis, such as TG-FTIR-GC-MS. In addition, computational modeling can be a great tool to forecast and prove the pyrolytic process with efficiency. Finally, via comparing the efficiencies of thermal pyrolysis, catalytic pyrolysis, and co-pyrolysis, it is often reasonable to conduct thermal pyrolysis with higher reaction temperature than catalytic pyrolysis. In this regard, it could require a harsh environment for energy consumption and cost of thermal pyrolysis. Moreover, it cannot be always well guaranteed that the pyrolytic product distribution can be controlled by reaction parameters and reactor setup in the thermal pyrolysis process. Conversely, it has been shown that solid catalysts are able to destabilize reaction barriers during catalytic pyrolysis to produce certain types of chemical molecules (e.g., aromatics, gas alkanes and alkenes); thus, it is still highly demanded to design and synthesize more selective and active catalysts for the practical improvement in the selectivity and yield of desirable products. At this point, zeolite-based catalysts could be applied to efficiently tune product molecular shapes and structures in catalytic pyrolysis. Alternatively, copyrolysis of disposable masks and biomass or  $CO_2$ -mediated ( $CO_2$  as both carrier gas and oxidizing agent) mask pyrolysis may have the synergetic capabilities to selectively synthesize specific products (e.g., oxygenates) because of the abundant oxygen atoms in biomass and  $CO_2$ . Consequently, it can be foreseen that the further work on combinational pyrolysis, such as catalytic co-pyrolysis of disposable masks and other feedstocks, will lead to remarkable results.

Overall, considering that plastic-made disposable masks will continuously be used as common and vital medical equipment in the on-going and post pandemic phase, it is strongly foreseeable that the mask waste will accordingly keep growing fast globally. Consequently, more research endeavor on the direct and selective pyrolysis of disposable masks is required for environmental improvement and the circular economy. Meanwhile, there are great opportunities to improve the upcycling of other medical plastic waste by leveraging the direct and selective pyrolysis of masks. Cautiously, considering the potential risk of virus infection from waste masks, it is worth pointing out that the disinfection of waste disposable masks prior to chemical upcycling is a compulsory pretreatment process to avoid any further contamination via labor or equipment during waste handling. Lastly, it has never been an individual effort of chemists or chemical engineers to tackle the mask pollution issue and further upgrade disposable masks to high-value chemical products. As a teamwork of the entire scientific community, experts in many other scientific fields, such as social science, economics, environmental science, etc., are expected to make their unique and cooperative contributions as well.

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