Upcycling disposable face masks into fuel range iso-alkanes through hydropyrolysis coupled with vapor-phase hydrocracking

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Abstract

The COVID-19 pandemic has resulted in an alarming accumulation of plastic waste. Herein, an integrated hydropyrolysis and hydrocracking process was performed to upcycle disposable masks into fuel-range iso-alkanes over carbon supported ruthenium (Ru/C). Experimental results indicated that catalyst type significantly affected product distribution during the hydropyrolysis and vapor-phase hydrocracking of disposable masks. Compared with zeolites-induced catalytic cascade process where up to ~25.9 wt% yield of aromatic hydrocarbons such as toluene and xylenes were generated, a ~82.7 wt% yield of desirable iso-alkanes with a high C_5-C_{12} gasoline selectivity of 95.5% was obtained over Ru/C under 550 ^{o}C hydropyrolysis temperature and 300 ^{o}C hydrocracking temperature at 0.2 MPa H_2. The cascade hydropyrolysis and hydrocracking process also exhibited high adaptability and flexibility in upcycling single-use syringes, food packaging, and plastic bags, generating 79.1, 81.6, and 80.3 wt% yields of fuel range iso/n-alkanes, respectively. This catalytic cascade hydrotreating process provides an efficient and effective approach to convert pandemic-derived plastic waste into gasoline-range fuel products.

Keywords: COVID-19 pandemic; Plastic waste; Disposable masks; Catalytic cascade processing; Waste to fuels.

1. Introduction

Plastics are ideal materials for disposable medical tools and packaging, and the COVID-19 pandemic has demonstrated their essential roles in the healthcare sector and public health safety [1]. For instance, to prevent rapidly spreading COVID-19 virus, there is a dramatic increase in global demand for single-use personal protective equipment (PPE) such as polypropylene-based disposable masks [2]. Correspondingly, unusual massive use of PPE has resulted in an alarming increase in plastic waste [3]. It's estimated that the global pandemic-derived plastic waste was over 8 million tons in 2021 [4]. However, the treatment capability of plastic waste is not parallel with the generation rate, leading to a huge accumulation of plastic residues [5]. Specifically, China and USA have the largest share of plastic residues in the world (Fig. 1) [6]. Unfortunately, the mismanaged plastic waste has been discharged into soil and aquatic ecosystems. Over 1.56 billion disposable masks ended up in the oceans in 2020, resulting in the formation of micro-plastics (100 nm to 5 mm) and nano-plastics (< 100 nm) which are potential vectors for pathogens and toxic contaminants [7].

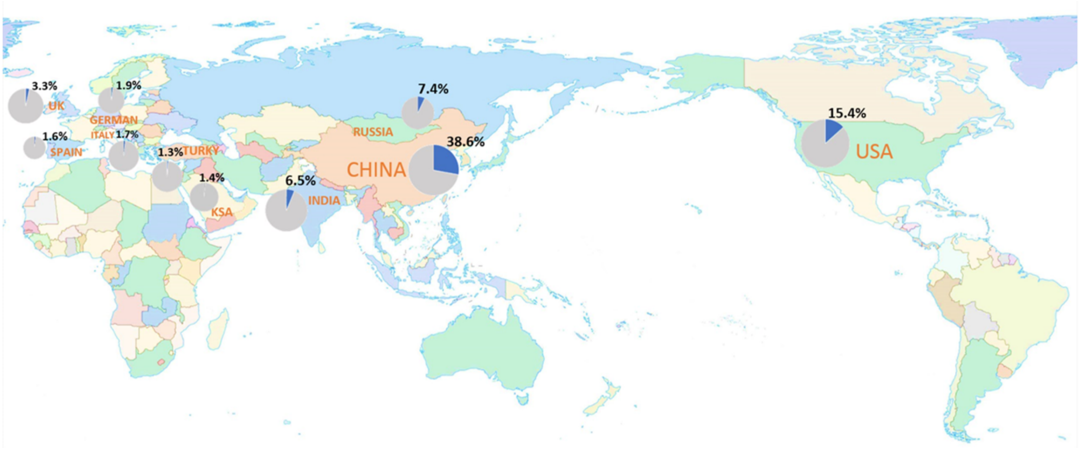


Fig. 1. World map distribution of COVID-19 associated plastic residues.

Given the waste management of pandemic-associated PPE plastic waste, in general, such potentially contaminated plastic waste is restricted at conventional recycling centers to prevent cross-contamination, indicating that incineration and landfilling are prioritized approaches [7]. However, these waste treatment programs are a clear deviation from environmental sustainability [8]. Serious air pollution can be caused by incineration via long-term emission of volatile toxins such as dioxins and furans. Moreover, harmful substances may be leached from landfilled plastic waste, especially for these PPE medical waste, inducing other environmental issues (e.g., groundwater contaminations). On the other hand, the goal of achieving a closed-loop plastic circular economy also necessitates a shift to more effective waste recycling routes [9]. It's noteworthy that chemical upcycling which aims to produce value-added monomeric compounds or high-quality liquid fuels from contaminated plastic waste has gained increasing attention as an alternative strategy [10].

Among the chemical upcycling routes used for plastic depolymerization, the hydrogenolysis of polyolefins over metal-based catalysts (such as Ru- and Pt-based) has been widely studied [11]. Typically, hydrogenolysis takes place at the active metal sites of catalysts, and the C-H bonds in polymer chains are firstly activated and then dehydrogenated, followed by C-C cleavage to produce short-chain intermediates that are subsequently hydrogenated and desorbed [12]. Over a commercial Ru/C catalyst polyethylene (PE) plastics can be deconstructed via hydrogenolysis, yielding 45 wt% n-alkanes with carbon numbers ranging from C_7 to C_{45} under 2 MPa H_2 in 16 h [13].

Moreover, recently, hydrocracking of plastic waste over bifunctional catalysts, i.e., active metals (Pt, Pd, and Ni, etc.) for hydrogenation and acid sites for cracking, have been highlighted. For instance, PE hydrocracking over a bifunctional catalyst (i.e., $Pt/WO_3/ZrO_2$ + HY zeolites) gave ~85% yield of liquid fuels under 3 MPa H_2 in 2 h [14]. Despite value-added fuel-range n-alkanes or iso-alkanes can be obtained via hydrogenolysis or hydrocracking under low reaction temperatures, the wide carbon number distribution (e.g., from C_7 to C_{45}) in produced alkanes limits its commercial application as “drop-in” fuels. At the same time, high reaction pressure and long reaction times in hydrogenolysis or hydrocracking also result in an increased cost of reactor and low efficiency in waste management, in particular for combating such suddenly generated COVID-19-associated plastic waste. Therefore, the development of a catalytic approach that is tunable in narrowing the carbon number distribution in alkanes with high efficiency can enhance the economical chemical upcycling of plastic waste.

Compared with hydrogenolysis or hydrocracking, pyrolysis is a more efficient and effective approach to upcycle plastic waste into liquid products and/or syngas [15]. Pyrolysis has been commercially used for plastic upcycling by some petrochemical companies worldwide. For instance, BlueAlp will assist the Shell company by providing its innovative pyrolysis technique for achieving 1 million tons of plastic waste upcycling per year by 2025 [12]. Moreover, a ChemCycling project aiming at transforming plastic waste into liquid oil as secondary raw material was launched by the BASF company (supported by the Quantafuel) in 2018, yielding a 65% pyrolysis oil from HDPE (high-density polyethylene, HDPE) [12]. Furthermore, to upgrade the primary products obtained from pyrolysis, catalytic pyrolysis has also been widely investigated [16, 17]. In this sense, Lee et al. [18] studied the catalytic pyrolysis of wasted COVID-19 masks to produce value-added aromatics over several types of zeolite catalysts, where they observed that HBeta zeolites illustrated high activity in converting disposable masks into aromatic hydrocarbons with a high BTEX (i.e., benzene, toluene, ethylbenzene, and xylene, BTEX) content of 49.4%. Simultaneously, unsaturated olefins are always accompanied by aromatic hydrocarbons in zeolites induced catalytic pyrolysis, because of the absence of hydrogenation capability compared with that of hydrocracking. From the viewpoint of “drop-in” fuels, alkenes are needed to be hydrogenated to avoid gum formation during the storage [19]. On the other hand, besides valuable BTEX aromatics, iso-alkanes are key components in fuels because they can improve low-temperature performances [20]. Therefore, we proposed a novel catalytic cascade process where pyrolysis is coupled with hydrocracking, providing a promising approach to upcycle disposable masks into iso-alkanes instead of BTEX when taking the “drop-in” fuels production and environmental protection into consideration.

Here, a two-stage pressurized fixed-bed reactor was designed to achieve an integrated hydropyrolysis and hydrocracking process for the chemical upcycling of single-use masks. Specifically, the hydropyrolysis of disposable masks was conducted in the first reactor, subsequently, the vapor-phase hydrocracking of produced primary alkene intermediates over Ru/C was performed in the down-stream second reactor. The underlying reason for using Ru/C as a catalyst is that it shows high catalytic activity in breaking C-C bonds in polyolefins. First, a series of catalysts including USY, HBeta, HZSM-5, and Ru/C were employed to study the effect of catalyst type on product distribution via the cascade hydropyrolysis and hydrocracking process, with an emphasis on exploring suitable catalysts for producing high-quality fuel-range iso-alkanes. Secondly, an optimization study, i.e., the hydropyrolysis temperature in the first reactor and the hydrocracking temperature in the second reactor, was conducted to maximize desirable iso-alkanes production. Finally, the adaptability of this cascade hydropyrolysis and hydrocracking process in terms of upcycling other PPE-derived plastic waste, including single-use syringes, food packaging (polypropylene, PP), and plastic bags (polyethylene, PE), was evaluated. This cascade hydrotreating process shows high advantages in upcycling various PPE-associated plastics into fuel range alkanes with high efficiency at near atmosphere pressure (i.e., 0.2 MPa H_2), illustrating significant potential for waste to energy compared with single pyrolysis or hydrocracking.

2. Experimental

2.1 Materials

The PPE-associated plastic waste including disposable masks (body part, mainly including PP and PE), single-use syringes, food packaging (PP), and PE plastic bags, were collected from the Medical Center in Southeast University, Nanjing, China. The plastics were ground with an average particle size of ~0.3 mm, and the elemental analysis was conducted by Vario EL II elemental analyzer (results shown in Table S1). Commercial 5 wt% Ru/C catalysts were provided by Sigma-Aldrich (characterization results shown in Table S2). Zeolites including USY, HBeta, and HZSM-5 were purchased from the Catalyst Plant of Nankai University, Tianjin, China. A series of external standards (>99.9%) for GC calibration, including iso-alkanes, *n*-alkanes, and aromatic hydrocarbons (such as toluene, *p*-xylene, *o*-xylene, and naphthalene) were purchased from National Center for Standard Substances, Henan, China.

2.2 Reaction procedure

A tandem two-stage fixed bed reactor (RX3050TR, Frontier Lab. Japan, Fig. 2) connected with an online GC/MS-TCD (8890 GC-5977B MS, Agilent) was used to conduct the hydropyrolysis and subsequent vapor-phase catalytic hydrocracking of disposable masks. In detail, two identical deactivated stainless-steel reactors (i.d. = 4.6 mm, length = 120 mm) were connected vertically. The temperature of each reactor could be controlled separately, with reaction temperatures ranging from 100 to 900 ^{o}C for the first reactor and 100 to 600 ^{o}C for the second, respectively. A high-pressure solid sampler was used to feed disposable masks (2 ± 0.05 mg) for hydropyrolysis in the first reactor, and a quartz tube (i.d. = 3 mm, o.d. = 4 mm, L = 78 mm) was used to load catalysts (diluted 30 times with SiO_2) for hydrocracking in the second reactor. The hydrogen flow rate was controlled at 100 mL/min, and the mass of catalysts was 2 ±

0.05 mg. The Ru/C catalysts were in-situ reduced at 450 °C for 2 h under H_2 in the second reactor before each experiment. The reaction pressure (Max. = 3 MPa) and flow rate of both carrier and reactant gas in the fixed-bed reactor were controlled by a high-pressure flow controller (HP-3050FC).

A HP-PONA chromatographic column (50 m x 0.20 mm x 0.50 um, Agilent) was used to identify hydrocarbons obtained from the depolymerization of disposable masks. The initial temperature of GC oven was 45 °C for 3 min, then was heated to 200 °C at 5 °C/min (hold for 1min at 200 °C), and the temperature was further increased to 320 °C at 15 °C/min and hold for 3 min. The MS detection *m/z* was controlled from 2-550. The NIST MS library was used to identify produced hydrocarbons, and external standards were employed to calibrate products. Each experiment was carried out at least thrice, and the average with a standard deviation < 7% was reported.

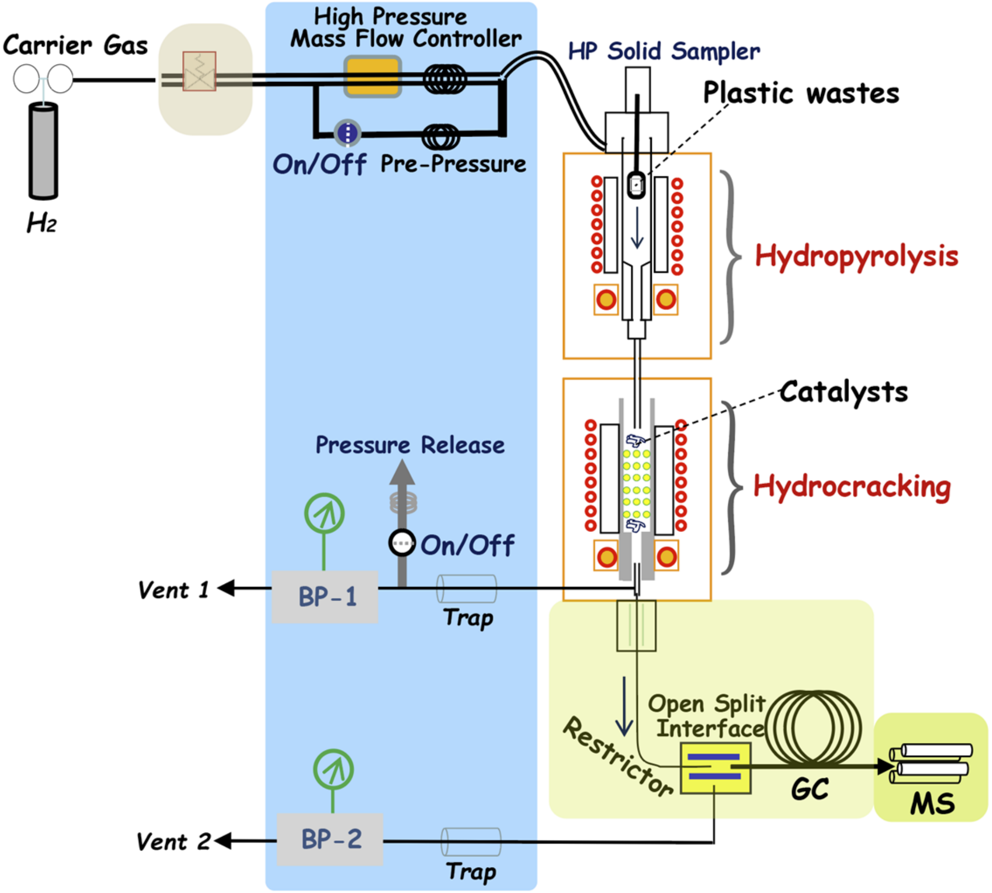


Fig. 2. Scheme of the pressurized two-stage fixed-bed reactor connected with an online GC/MS.

2.3 Data analysis

The yield of condensable hydrocarbons was calculated as:

$$y_i = \frac{m_i}{m_0} \times 100\%$$

where m_i is the mass of produced hydrocarbons, m_0 is the weight of the feedstock.

The selectivity of hydrocarbons was calculated as below:

$$S_i = \frac{m_i}{\sum m_j} \times 100\%$$

where $\sum m_j$ is the total mass of condensable hydrocarbons.

3. Results and discussion

3.1 Upcycling disposable masks over different catalysts

Catalysts play a determining role in tailoring product distribution during the thermochemical conversion of plastic waste [21]. To explore how catalysts affected hydrocarbons formation in the catalytic cascade processing of pandemic-associated plastic waste, polypropylene-based disposable masks were used as feedstock, and Ru/C, USY, HBeta, and HZSM-5 were employed as catalysts. The reaction pressure, hydropyrolysis/hydrocracking temperature, catalyst to feedstock (C/F) mass ratio, and gas hourly space velocity (GHSV) was controlled at 0.2 MPa, 550/300 ^{o}C, 1, and 15 s^{-1}, respectively. Fig. 3 shows the experimental results as a function of catalyst type. The non-catalytic degradation of disposable masks was conducted to make a comparison and the results are embedded in Fig. 3. Generally, the decomposition of plastic polymers follows a random C-C scission process producing a series of free radicals, and these radicals further undergo intramolecular hydrogen transfer reactions to generate alkenes and alkanes with varying carbon lengths [12]. As expected, both alkenes and alkanes were produced in the non-catalytic conversion of disposable masks, which agreed well with previous studies [22, 23]. Among the produced hydrocarbons, unsaturated alkenes were the main compounds with a high yield of 58.7 wt%, in contrast, only a small number of desirable iso-alkanes (~10.1 wt% yield) were generated (TIC chromatograms shown in Fig. 4). Moreover, the selectivity of produced hydrocarbons was calculated, and the results are summarized in Fig. 5. As shown, a ~85.3% selectivity of alkenes was obtained from the non-catalytic deconstruction, which was 70.6% higher than that of alkanes. As previously mentioned, to inhibit gum formation in fuels during storage, the content of alkenes is limited to below 1%, indicating that these unsaturated alkene intermediates must undergo further catalytic upgrading to generate stable fuel range components [19].

In terms of catalytic upgrading of primary unsaturated alkenes derived from the non-catalytic deconstruction of plastic waste, zeolites are most widely used with an emphasis on generating aromatics such as benzene, toluene, xylenes (i.e., BTX) in previous studies [24]. In the present work, a comparative study by employing zeolites (including USY, HBeta, and HZSM-5) as catalysts during the catalytic cascade hydrotreating process of disposable masks was conducted, and the experimental results are shown in Fig. 3. As expected, the zeolites-induced vapor-phase catalytic upgrading of primary olefin intermediates yielded iso-alkanes and aromatics at the expense of alkenes. The total yield of condensable hydrocarbons was 63.0, 44.7, and 45.5 wt% for USY, HBeta, and HZSM-5, respectively. A series of aromatics such as toluene, xylenes (*p*- and *o*- xylene), and naphthalene and its derivatives (PAHs) were generated regardless of zeolite type (Fig. 4). Specifically, the yield of aromatics reached 24.1 wt% for USY, 23.8 wt% for HBeta, and 25.9 wt% for HZSM-5, respectively. The selectivity of aromatics was calculated, and it was observed that the total aromatic selectivity reached 38.2% for USY, 53.2% for HBeta, and 56.8% for HZSM-5, respectively (Fig. S1). Toluene and xylenes are the predominated aromatic components, followed by 1,2,4-trimethyl-benzene and PAHs. Taking the HBeta catalyzed disposable masks for an example, the selectivity to toluene, xylenes, and PAHs was 27.2%, 20.8%, and 2.2%, respectively (Fig. 5).

It's reported that acid sites in zeolites play a determining role in aromatic formation during the catalytic depolymerization of plastics [25]. Specifically, the Brønsted acid sites in zeolites are of particular importance to promote aromatization reactions. For instance, Inayat et al. [26] probed the role of acid site density of HZSM-5 on aromatics and olefins formation in the catalytic pyrolysis of polyethylene, where they observed that the generation of aromatics enhanced with the increasing content of acid site density. Similar trends were observed in the present work as aromatics were facilitated over zeolites compared with that of the non-catalytic. Moreover, besides aromatics and alkanes, gas products such as propylene and butene were also enhanced in comparison to that of the catalyst-free run, suggesting that besides aromatization reactions, the C-C cleavage in olefin intermediates was also dramatically boosted over acid sites in zeolites during the hydrotreating process in the second reactor. Specifically, the gas yield reached 32.4, 50.8, and 49.9 wt% for USY, HBeta, and HZSM-5, respectively (Fig. S2).

On the other hand, despite aromatics are key building blocks in generating necessities in daily life, they are also known as the main volatile organic compounds (VOCs) which are one of the major environmental hazards in the air [27]. Specifically, VOCs not only damage the environment by forming photochemical smog but also harm human health and result in irreversible damage because of their toxic and carcinogenic properties. Moreover, PAHs such as naphthalene and its derivatives are crucial pollutants due to their carcinogenic, mutagenic, and toxic natures, leading to adverse impacts on both environment and human health [28]. Therefore, it’s essential to explore suitable catalysts in the chemical upcycling of plastic waste without inducing secondary environmental pollution.

Based on these considerations, experiments over Ru/C in the hydropyrolysis of disposable masks and subsequent vapor-phase hydrocracking of olefin intermediates were carried out, and the results are also shown in Fig. 3. Interestingly, employing Ru/C as a catalyst effectively hydrocracked the alkenes and long-chain alkanes with iso-alkanes being the predominated fractions. The yield of iso-alkanes reached 82.7 wt%, corresponding to an 7.6-fold, 2.2-fold, 4.0-fold, and 4.2-fold increases compared with that attained from the non-catalytic, USY, HBeta, and HZSM-5 catalyzed trials, respectively. It's noteworthy that no aromatic VOCs were generated in the catalytic cascade processing of disposable masks over Ru/C, indicating that aromatization reactions did not take place (Scheme 1), showing high environmental feasibility by inhibiting VOCs production.

Moreover, a relatively narrow carbon number distribution in iso-alkanes with carbon length ranging from C_5 to C_{15} was obtained as shown in Fig. 4, which well fits the gasoline range components. More specifically, a high 95.5% gasoline (C_5-C_{12}) selectivity in produced iso-alkanes was attained (Fig. 5), higher than previous studies [13, 14]. Furthermore, only a ~12.7 wt% yield of gas products (selectivity: 56.4% propane, 23.8% isobutane, and 19.8% ethane, Fig. S3) was produced with Ru/C, much lower than that obtained from zeolites catalyzed trials (Fig. S2), suggesting that higher carbon efficiency in terms of upcycling plastics into liquid fuels over Ru/C can be obtained.

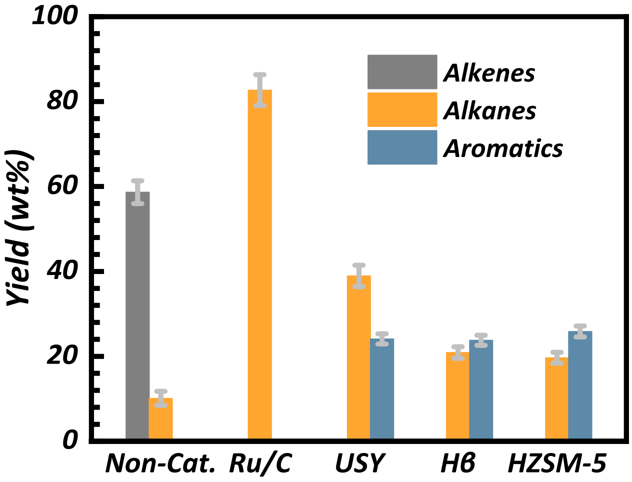


Fig. 3. Hydrocarbons obtained from non-catalytic and hydropyrolysis and catalytic hydrocracking of disposable masks over different catalysts: The reaction pressure: 0.2 MPa, hydropyrolysis/hydrocracking temperature: 550/300 °C, C/F mass ratio: 1, GHSV: 15 s^{-1}.

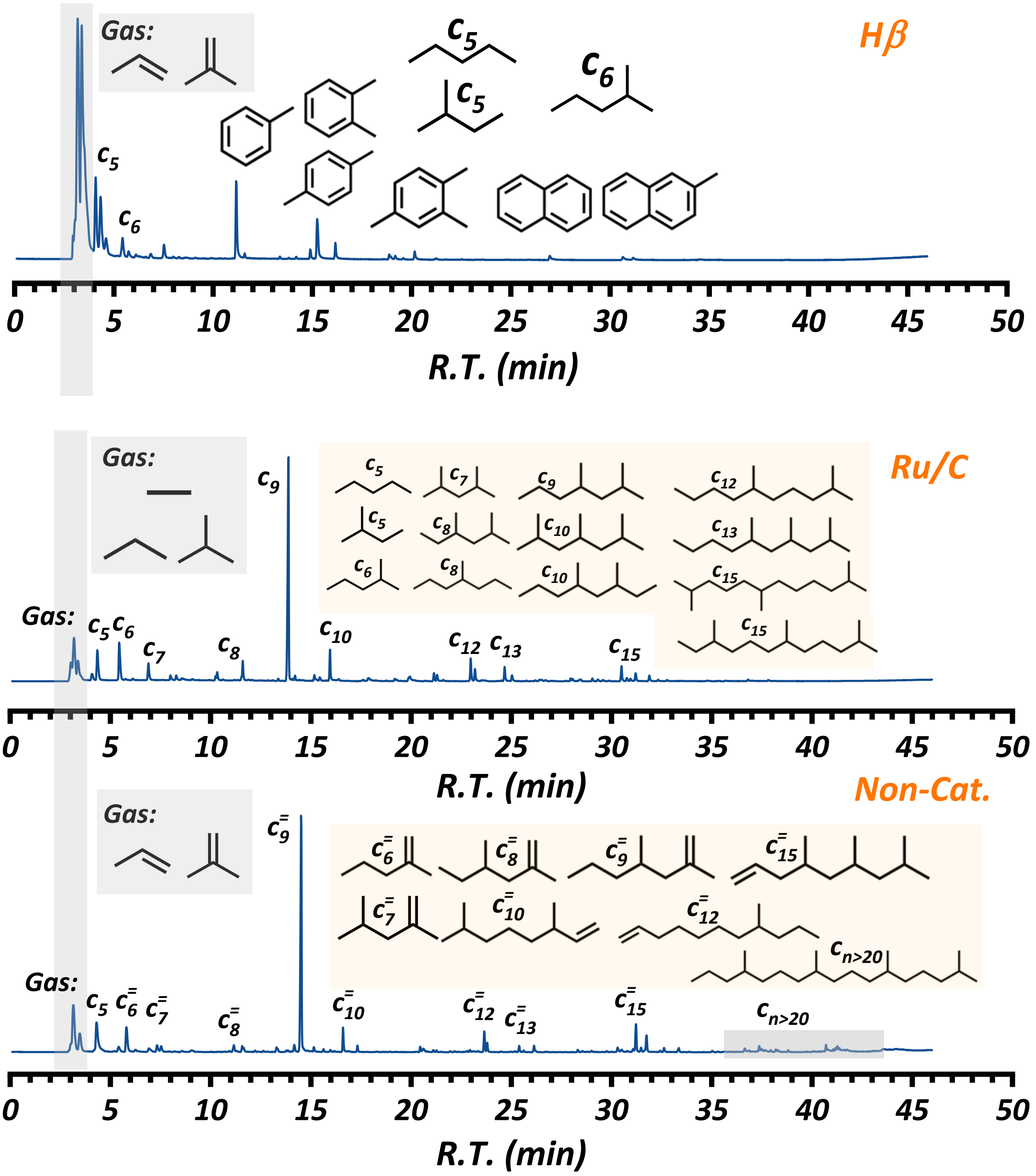


Fig. 4. Chromatograms of hydrocarbons obtained from non-catalytic and catalytic cascade processing of disposable masks.

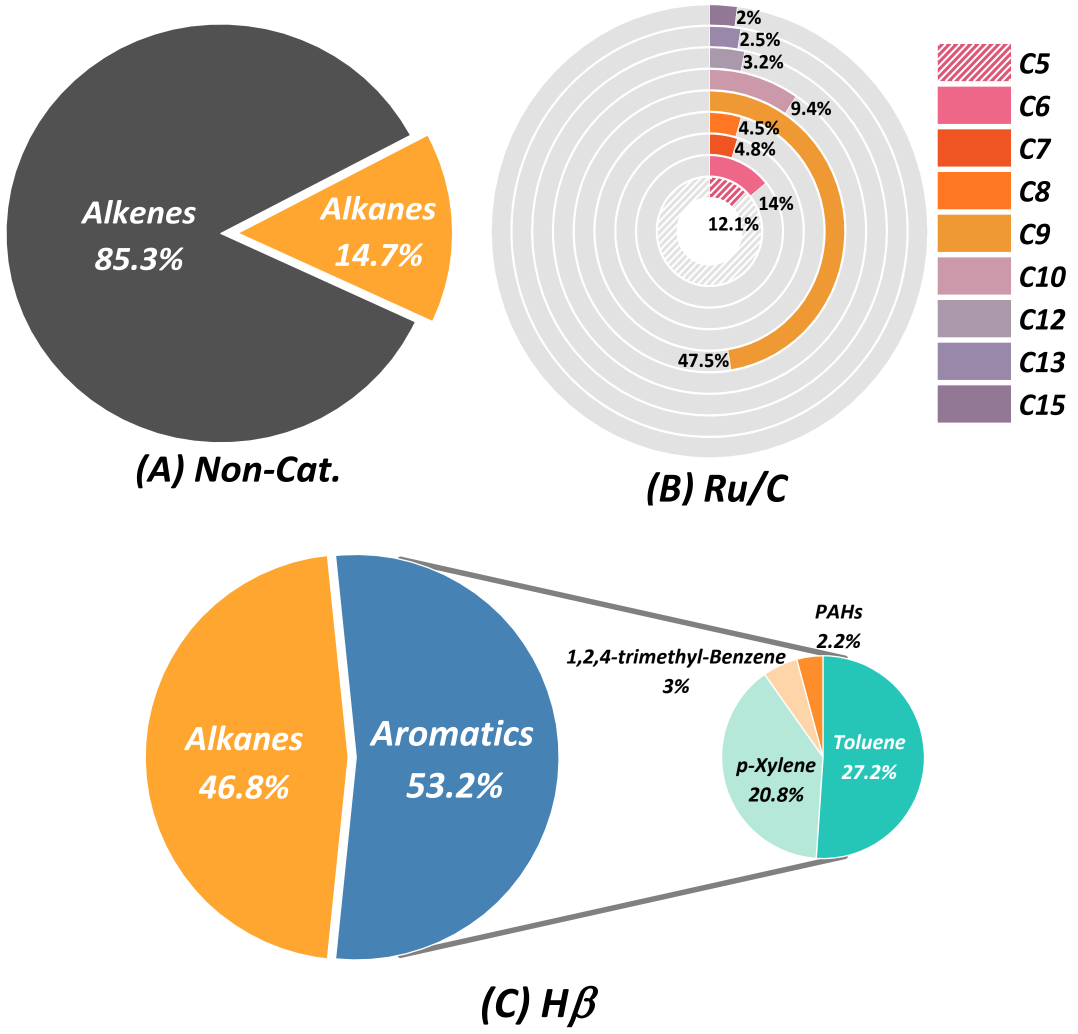
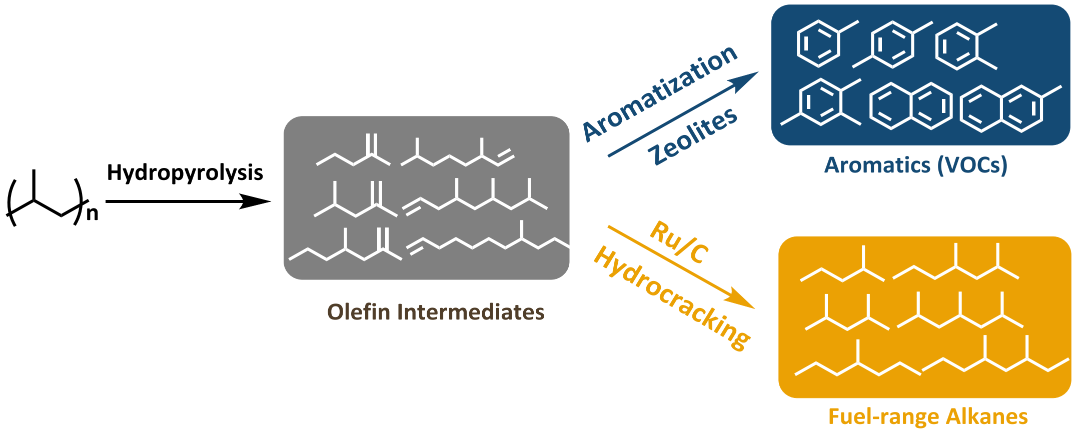


Fig. 5. Selectivity of hydrocarbons obtained from cascade hydropyrolysis and hydrocracking of disposable masks as a function of catalyst type: (A) Non-catalytic; (B) Ru/C; (C) HBeta: The reaction pressure: 0.2 MPa, hydropyrolysis/hydrocracking temperature: 550/300 °C, C/F mass ratio: 1, GHSV: 15 s^{-1}.



Scheme 1. Proposed reaction pathways of disposable masks over different catalysts

during the cascade hydropyrolysis and hydrocracking process.

3.2 Effect of hydropyrolysis temperature in the first reactor on iso-alkanes formation

To maximize the yield of desirable iso-alkanes in terms of improving carbon efficiency via chemical upcycling of disposable masks, several hydropyrolysis temperatures varying from 450 to 650 ^{o}C with an interval of 50 ^{o}C were employed to investigate the effect of degradation temperature in the first reactor on desirable iso-alkanes production over Ru/C. The reaction pressure, hydrocracking temperature, catalyst to feedstock (C/F) mass ratio, and GHSV were controlled at 0.2 MPa, 300 ^{o}C, 1, and 15 s^{-1}, respectively. As shown in Fig. 6, the hydropyrolysis temperature played a crucial role in the depolymerization degree of disposable masks. Under a low hydropyrolysis temperature of 450 ^{o}C, the disposable masks could not be fully deconstructed as a low iso-alkane yield of 24.7 wt% was attained; however, elevating the hydropyrolysis temperature to 500 and 550 ^{o}C significantly favored its degradation, yielding 74.9 and 82.7 wt% C_5-C_{15} iso-alkanes, respectively. In general, the cracking of disposable masks is an endothermic process, hence the higher the reaction temperature (i.e., available energy for breaking C-C bonds in polymer chains) the deeper the conversion degree. Nevertheless, a further increase in hydropyrolysis temperature from 550 to 600 and 650 ^{o}C prominently reduced the yield of desirable iso-alkanes to 79.4 and 59.3 wt%, respectively. This might be attributed to the secondary cracking reactions under high hydropyrolysis temperatures.

Regarding the target gasoline range hydrocarbons, a similar trend was observed for the total yield of iso-alkanes as shown in Fig. 6. The gasoline yield increased at first then decreased with the maximum of 78.8 wt% obtained at 550 ^{o}C. Moreover, C_5-C_{12} gasoline range products were the main fractions regardless of hyropyrolysis temperature. Specifically, the selectivity of gasoline was 95.5, 94.1, 95.5, 88.3, 93.9% for 450, 500, 550, 600, and 650 ^{o}C hydropyrolysis temperatures, respectively. The distribution in produced iso-alkanes obtained from catalytic cascade processing of disposable masks over Ru/C as a function of hydropyrolysis temperature is illustrated in Fig. 7. As shown, the carbon length in iso-alkanes ranged from C_5 to C_{15} centering at C_9 iso-alkane (2,4-dimethyl-heptane, MS data shown in Fig. S4) within the studied temperature range. For instance, the C_9 iso-alkane yield was 9.3 wt% for 450 °C, 29.8 wt% for 500 °C, 41.2 wt% for 550 °C, 35.9 wt% for 600 °C, and 22.3 wt% for 650 °C, respectively. Therefore, the hydropyrolysis temperature could be optimized at 550 °C to obtain a maximum iso-alkane yield with considerable gasoline selectivity.

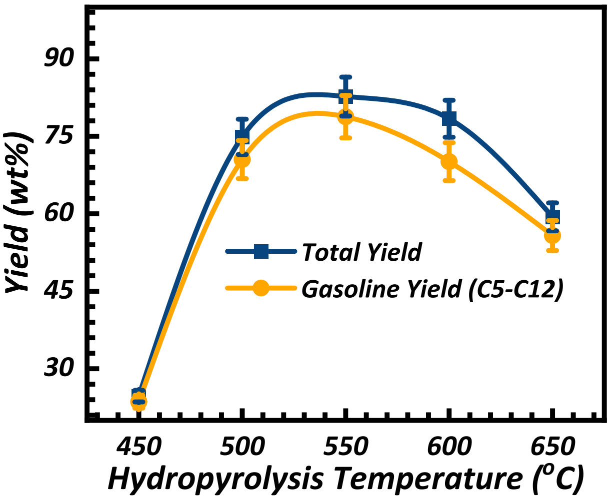


Fig. 6. The yield of iso-alkanes obtained from cascade hydropyrolysis and hydrocracking of disposable masks over Ru/C: Effect of hydropyrolysis temperature in the first reactor: the reaction pressure: 0.2 MPa, hydrocracking temperature: 300 °C, C/F mass ratio: 1, GHSV: 15 s^{-1}.

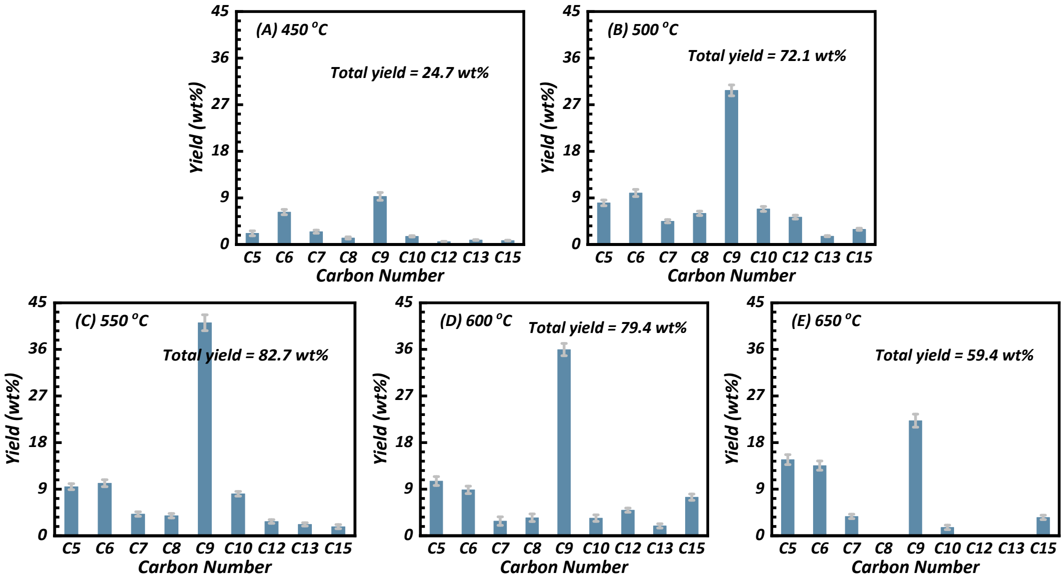


Fig. 7. The distribution of iso-alkanes obtained from hydropyrolysis and hydrocracking of disposable masks over Ru/C as a function of hydropyrolysis temperature.

3.3 Effect of hydrocracking temperature in the second reactor on iso-alkanes formation

The hydrocracking temperature in the second reactor is of vital importance in product distribution as it affects the hydrogenation and cracking of olefin intermediates generated from the first reactor. To explore the effect of hydrocracking temperature in the second reactor on product distribution, experiments with hydrocracking temperatures varying from 300 to 450 ^{o}C were conducted. The reaction pressure, hydropyrolysis temperature, catalyst to feedstock (C/F) mass ratio, and GHSV were controlled at 0.2 MPa, 550 ^{o}C, 1, and 15 s^{-1}, respectively. The results are summarized in Fig. 8. As expected, the hydrocracking temperature in the second reactor has a more significant effect on product distribution than hydropyrolysis temperature in the first reactor. Specifically, increasing the hydrocracking temperature from 300 ^{o}C to 450 ^{o}C dramatically decreased the total yield of iso-alkanes from 82.7 to 5.7 wt%. Similarly, the C_5-C_{12} gasoline yield also largely decreased from 78.8 wt% at 300 ^{o}C to 5.7 wt% at 450 ^{o}C, respectively. Furthermore, the hydrocracking temperature in the second reactor not only affects the yield but also impacts the distribution of produced iso-alkanes as illustrated in Fig. 9. The carbon number distribution in iso-alkanes was gradually narrowed with the increase of hydrocracking temperature. For instance, the yield of C_{10}-C_{15} iso-alkanes was 14.7 wt% at 350 ^{o}C, while it was decreased to 3.0 wt% at 400 ^{o}C, and a further increase in hydrocracking temperature to 450 ^{o}C eliminated the C_{10}-C_{15} fractions.

In general, Ru-based catalysts are very active in breaking C-C bonds in polymer chains, and this capability could be enhanced under high reaction temperatures, resulting in excess cracking to produce gas products [13, 22]. For instance, Rorrer et al. [13] explored the catalytic degradation of polypropylene over Ru/C aiming to produce alkanes, where they observed that increasing reaction temperature from 200 to 250 ^{o}C facilitated gas production, in particular, pure CH_4 was obtained at 250 ^{o}C with 3 MPa H_2 in 16 h. In the present study, a similar trend was also observed as a significant decrease in condensable iso-alkanes was associated with a dramatic increase in gas yield (shown in Fig. S5). Specifically, the yield of gas products was increased from 8.7 wt% (at 300 ^{o}C) to 34.5, 72.5, and 89.7 wt% for 350, 400, and 450 ^{o}C, respectively. Moreover, the hydrocracking temperature also played a key role in gas product distribution. For instance, below 350 ^{o}C hydrocracking temperature, no methane was identified in gaseous products; however, methane selectivity was dramatically increased to 52.1% and 73.0% when the hydrocracking temperature was elevated to 400 and 450 ^{o}C (Fig. S6), respectively, indicating that complete C-C cleavage induced by the metallic Ru was obtained. Hence, besides condensable iso-alkanes, this catalytic cascade hydrotreating process could also be employed to generate natural gas with high methane content from disposable masks by regulating operating parameters, showing high practicability and flexibility.

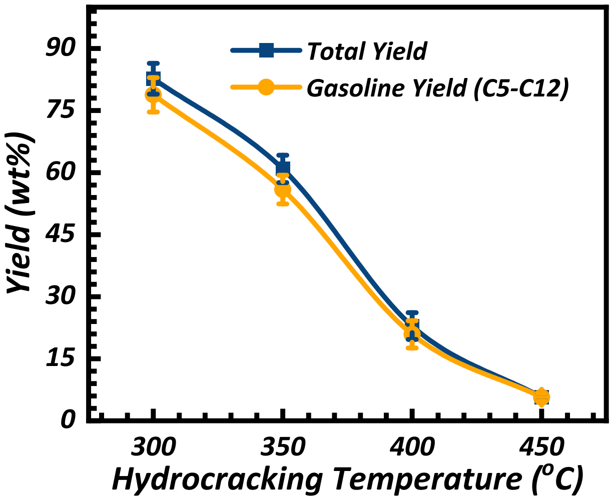


Fig. 8. The yield of iso-alkanes obtained from cascade hydropyrolysis and hydrocracking of disposable masks over Ru/C: Effect of hydrocracking temperature in the second reactor; The reaction pressure: 0.2 MPa, hydropyrolysis temperature: 550 oC, C/F mass ratio: 1, GHSV: 15 s^{-1}.

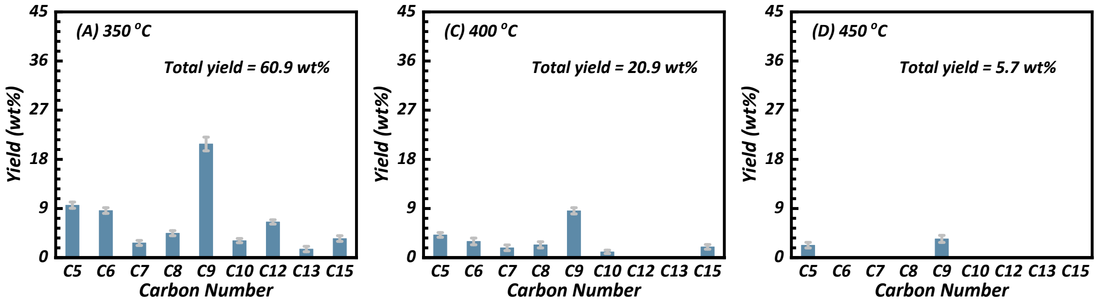


Fig. 9. The distribution of iso-alkanes obtained from hydropyrolysis and hydrocracking

of disposable masks over Ru/C as a function of hydrocracking temperature.

3.4 Adaptability evaluation of catalytic cascade process in upcycling other polyolefin waste

Besides disposable masks, other pandemic-associated plastics such as single-use syringes, food packaging, and PE plastic bags, are also largely consumed during the COVID-19 pandemic. For instance, massive consumption of take-away food packaging materials occurred because of lockdowns or social distancing requirements [7]. To further evaluate the applicability and flexibility of this cascade hydropyrolysis and hydrocracking process, real-world single-use syringes, PP food packaging, and PE plastic bags were employed. The reaction pressure, hydropyrolysis/hydrocracking temperature, catalyst to feedstock (C/F) mass ratio, and GHSV were controlled at 0.2 MPa, 550/300 ^{o}C, 1, and 15 s^{-1}, respectively. Fig. 10 shows product distribution in generated alkanes as a function of polyolefin type over Ru/C. As indicated, the catalytic cascade hydrotreating process illustrates high flexibility in upcycling single-use syringes, food packaging, and plastic bags into fuel-range alkanes. For the PP-based single-use syringes and food packaging, similar product distribution in iso-alkanes with C_9 iso-alkane being the predominated was observed compared with that obtained from disposable masks. More specifically, the total yield of iso-alkanes reached 79.1 wt% for single-use syringes and 81.6 wt% for food packaging, respectively. Furthermore, among the produced iso-alkanes, gasoline range components were the main fractions with a high selectivity of ~90% (i.e., 88.6% for single-use syringes and 91.4% for food packaging).

Regarding the tandem hydrotreating of PE bags, as shown in Fig. 10c, the catalytic cascade hydrotreating process can also effectively convert PE bags into fuel range saturated hydrocarbons over Ru/C. A ~80.3 wt% yield of n-alkanes with a narrow carbon number distribution ranging from C_5 to C_{17} was attained. Moreover, the carbon number distribution in produced n-alkanes suggested that gasoline range hydrocarbons were the main fractions with 86.6% selectivity. Therefore, it could be concluded that this tandem hydrotreating process shows great promise and industrialization potential in converting various polyolefins into gasoline fuels.

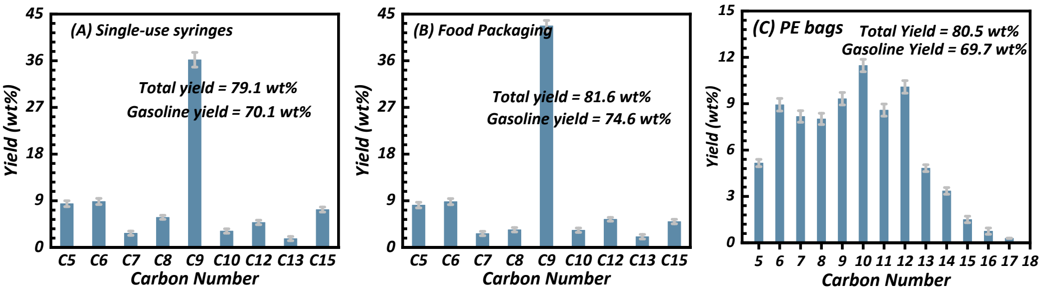


Fig. 10. Carbon number distribution in alkanes produced from cascade hydropyrolysis and hydrocracking of PPE-derived plastic waste: (A) single-use syringes; (B) food packaging; (C) PE bags: the reaction pressure: 0.2 MPa, hydropyrolysis/hydrocracking temperature: 550/300 °C, C/F mass ratio: 1, GHSV: 15 s^{-1}.

4 Conclusion

The cascade hydropyrolysis and hydrocracking process shows great promise in upcycling pandemic-associated plastic waste into iso-alkanes with considerable yield and high selectivity. The alkene intermediates generated from the hydropyrolysis of disposable masks in the first reactor could be effectively hydrocracked over Ru/C in the second reactor, producing a 7.6-fold yield increase in iso-alkanes compared with that of the non-catalytic. Catalytic cascade processing of disposable masks over zeolites favored aromatic hydrocarbons, as its selectivity reached 38.2% for USY, 53.2% for HBeta, and 56.8% for HZSM-5, respectively. The disposable masks could not be fully deconstructed under a low hydropyrolysis temperature of 450 °C, and elevating the hydropyrolysis temperature to 550 °C significantly favored its degradation. Increasing the hydrocracking temperature from 300 °C to 450 °C dramatically decreased the total yield of iso-alkanes from 82.7 to 5.7 wt%, and complete C-C cleavage induced by the metallic Ru was obtained under high hydrocracking temperatures. The applicability and flexibility of this cascade hydropyrolysis and hydrocracking process were evaluated by employing real-world single-use syringes, PP food packaging, and PE plastic bags as feedstock, giving considerable yields of gasoline-range products regardless of feedstock type. Given the micro-scale of the reactor used in this study, more attentions will be placed on the scale-up of this tandem process in terms of converting mixed plastic waste into fuels in our upcoming works.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found.

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