



From rags to riches: Converting cellulose containing waste to 5-(chloromethyl)furfural (CMF)

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ABSTRACT

This study proposes a chemical recycling pathway for valorizing the cellulosic component of municipal waste streams such as textile, cleaning wipes, corrugated cardboard, contaminated cardboard (*i.e.* a pizza box), paper-plastic laminate (PPL) coffee cups and cigarette butts (CBs). The goal of this study is to establish an experimental procedure that allows to test a broad range of cellulose-containing waste materials, laying the groundwork for commercial deployment of their chemical recycling. The cellulose contained in these materials is transformed into 5-chloromethylfurfural (CMF), a precursor for bio-based plastics, without affecting the plastic counterpart (if present). We employ a biphasic system concept using aqueous HCl solutions for CMF formation and *in situ* extraction from the reaction medium using immiscible organic solvents, enabling straightforward product separation. This method allows to hydrolyze cellulosic materials from waste without affecting PET or polyolefin plastic also present, facilitating the subsequent recycling of this plastic as well. This study serves as a foundation to assess the feasibility of using cellulose-containing waste streams for chemical recycling and to offer recommendations on selecting optimal reaction procedures.

Introduction

Cellulose is often present in materials that we use in our daily lives. Whether it is in cotton-containing textiles, in cleaning wipes, corrugated cardboard, paper-plastic laminate (PPL) coffee cups or cigarette butts (CBs). All these products play a role in human-generated waste and pollution. Regarding recycling efficiency, cardboard materials stand out, often with well-established technologies supported by well-organized logistics and an infrastructure for effective waste management (Venkatesan et al., 2023; Eckhart, 2021). However, even these materials can present recycling challenges. These include concerns related to contamination, moisture levels, the impact of inks and dyes, and the quality and structural integrity (Ozola et al., 2019; Villanueva and Wenzel, 2007; Esmieo et al., 2018). Additionally, when cardboard is contaminated with food residues, such as in used pizza boxes, the recycling efficiency starts to decline rapidly. Grease is hydrophobic, and in high concentrations it interferes with inter-fiber bonding, resulting in a considerable loss of paper strength (Rock, 2020; machinedesign, 2018). Pizza boxes currently found in recycling streams have an average grease content of approximately 1–2 % by weight (Rock, 2020). Their recyclability is often an issue depending on the waste management of

different municipalities (such as post-consumer collection) and the recycling techniques available in the area (Reynolds, 2020).

Another cellulosic material that commonly constrains cardboard recycling facilities is the paper-plastic laminate coffee cup. It contains a plastic lining, typically polyethylene, which makes the cups waterproof. This plastic component is challenging to remove and once the cups are used, the paper part is contaminated by the cup's contents, complicating further its recycling (House of Commons, 2019). Annually, more than 60 billion PPL coffee cups are consumed globally and the majority ends up in landfills and incinerators due to this hydrophobic plastic inner-lining (Bilek et al., 2021). While recent advancements suggest the possibility of replacing these cups by fully recyclable polypropylene-lined (PPL) coffee cups, this is not yet standardized (Stora Enso, 2022).

While these sources of contamination are very present in our daily lives, the biggest source of (cellulosic) waste contributing to human pollution is still the textile industry. Within the European Union, the environmental and climate impact of textile consumption ranks on average as the fourth highest, following food, housing and mobility. Textile ranks as the third most impactful in terms of water- and land use, and the fifth highest in the utilization of primary raw materials and in the cradle-to-gate generation of greenhouse gas emissions (European

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Commission, 2023; Ernantez Efstathopoulou et al., 2017). In 2023, 5 million tons of clothing were discarded in the European Union (450 million people), which corresponds approximately to 11 kg per person, with only 1 % of this waste textile being recycled into new clothing (Commission, 2023). Therefore, in 2023 the EU started the Extended Producer Responsibility (EPR) initiative that forces manufacturers to bear the expenses related to the waste management of their textile. The financial contribution to the EPR scheme by producers will be adjusted based on the environmental performance of textiles, a concept known as 'eco-modulation'. For example, brands such as H&M and Zara have started to adopt the 'eco-modulation' concept in their textile production processes. This adjustment aims to incentivize producers to design more environmentally friendly products, thereby reducing the environmental impact of textiles throughout their lifecycle (Commission, 2023; Fashion Revolution, 2023).

Also included in our preliminary proof-of-principle investigation are cigarette butts (CBs), one of the most littered cellulosic-based waste. Despite a global decline in smoking rates, middle-income nations have experienced a rise in consumption, possibly attributed to increased affordability and a lack of public awareness (Vanapalli et al., 2023). The significant environmental concerns associated with CBs stem from the low biodegradability of cellulose acetate filters and the release of toxic chemicals from these filters. The small size and limited economic value of CBs contribute to inefficiencies in existing waste collection and management systems. In the majority of instances (84 %) the waste management of cigarette butts (CBs) results into solid-state products (Marinello et al., 2020; Escobar Gómez et al., 2021). Cigarette butts, composed of cellulose acetate, are converted into porous carbon materials during recycling. These porous carbons exhibit diverse physico-chemical structures and characteristics, which depend on the specific treatment applied to the CB samples. The products of these recycling approaches are usually composite materials, involving the blending of CBs (or a fraction thereof) with other products such as fired clay bricks, absorber materials or bitumen mixtures (Marinello et al., 2020).

All waste streams considered in this study have in common the presence of cellulose (or a derivative thereof), and we wish to establish a method that allows to chemically recycle this saccharide-bearing component without affecting the pastic counterpart. Following previous studies from Mascal and our group (Mascal and Nikitin, 2009; Bueno Moron et al., 2023), the cellulose fraction undergoes hydrolysis and dehydration to furanic platform chemicals. Under acidic conditions and at slightly elevated temperatures, the glucose resulting from cellulose hydrolysis undergoes a rapid transformation into 5-(hydroxymethyl) furfural (HMF), most likely through a dehydration reaction in aqueous HCl (van Putten et al., February 2013). While HMF holds significant value as a platform chemical in the chemical biorefinery sector, it is marked by its limited thermal and chemical stability, as well as the difficulty in its isolation and purification. (van Putten et al., February 2013; Zhu et al., 2020). However, the chlorinated analogue of HMF, commonly denominated as CMF, is rapidly formed *in situ* and can be isolated via extraction. It is also easier to handle, isolate, and purify compared to the hydroxy-analogue HMF. According to recent studies, CMF has a lower polarity that enhances its partitioning in biphasic systems, making it more suitable for extraction from the aqueous solution using immiscible organic solvents (Soukup-Carne et al., 2024). The basis and principles of this CMF extraction and production from biomass and saccharide solutions was developed and extensively investigated by Mascal and Nikitin in the early 2000 s (Mascal and Nikitin, September 2008; Mascal and Nikitin, 2009; Mascal and Nikitin, May 2009; Mascal and Nikitin, February 2010) with further studies in recent years by our group (Bueno Moron et al., 2023; Bueno Morón et al., 2024; Bueno Morón et al., 2023). The objective of this study is to examine the feasibility to use (new) cellulose containing waste streams and establishing an experimental procedure that enables the evaluation of these cellulosic waste materials as potential candidates for CMF synthesis in the presence of plastic/man-made materials.

Materials and methods

Materials

Reagents and Solvents. Hydrochloric acid (HCl) solution in water (37 wt%), chlorobenzene (99.6 %), and fluorobenzene (99 %), were purchased from Fisher Scientific Solvents (technical grade).

The saccharide composition of the waste streams used in this study are detailed in the supporting information (Table S1). Cotton-containing textile (jeans) were provided by HEMA, a local supplier of clothing in The Netherlands. Cleaning wipes containing cotton mixed with polyolefins (polypropylene or polyethylene) were provided by Montvale and Reckitt laboratories, respectively. The samples of corrugated cardboard included in this study are standard shipping boxes employed by Amazon. The samples corresponding to mixed waste cardboard belong to pizza boxes collected from local pizzerias (NY Pizza). Cigarette butts were collected from local metro stations and paper-plastic laminate (PPL) coffee cups were collected from local cafeterias. The sugar composition of all these cellulosic-containing waste streams was determined by Celnis Analytical and can be found in the Supporting Information.

HCl solution in water (42 wt%) was produced by absorbing 100 % HCl gas in a 36 wt% HCl solution. This was achieved at room temperature and 7 bar of pressure where the 36 wt% HCl solution entered from the top and 100 % HCl gas entered via an adsorption column (graphite column lined with PTFE) at the bottom of an absorber chamber. Unabsorbed HCl gas re-entered the HCl solution at the bottom of the adsorption column. At the end of the cycle, the 42 wt% HCl solution was cooled to 6 °C and reduced to atmospheric pressure. A 1 mL aliquot of the resulting supersaturated HCl solution was diluted with 100 mL with demineralized water, the HCl molarity was determined in triplicate by titrimetric analysis at 25 °C using a 809 Titrando unit (Metrohm AG) with a 1.0 M aqueous NaOH solution.

Equipment

CMF Synthesis. The reactions were performed in 9 mL Ace glass pressure-rated reaction tubes purchased from Sigma Aldrich (product code: 8648-17). The tubes were used in an aluminum heating block custom made by Observator Precisiestechniek B.V.

Characterization methods

Ion Exchange Chromatography. Ion exchange chromatography (IC) was used for the quantification of soluble saccharides using a Dionex ICS-5000 system with a CarboPac PA1 Analytical Anion Exchange Column (250 × 2 mm) and a pulsed amperometry detector (PAD). The mobile phase consisted of 0.1 M sodium hydroxide (NaOH) in MilliQ water.

High Performance Liquid Chromatography. High Performance Liquid Chromatography (HPLC) was used to determine the concentration of sugar degradation products. HPLC was performed on an Agilent 1260 Infinity II system with a 1260 series refractive index (RID) and diode-array (DAD WR) detectors. The column was an Aminex HPX-87H (300 × 7.8 mm; dp 9 µm) using 5 mM sulfuric acid (H₂SO₄) in MilliQ water as the mobile phase.

Gas Chromatography. The target product CMF was determined using an Agilent 5975C gas chromatograph (GC) with a triple axis mass selective detector (MSD). The system was equipped with an Agilent J&W DB624 column (20 m × 0.18 mm × 1 µm) using helium as the carrier gas. CMF and co-products were quantified with a Thermo Scientific Trace 1310 GC equipped with a flame ionization detection (FID) using an Agilent J&W 624 UI (30 m × 0.25 mm × 1.4 µm) column and helium as carrier gas.

¹H NMR Spectroscopy. ¹H nuclear magnetic resonance spectroscopy (¹H NMR) analysis was performed on a Bruker Avance III HD (600 MHz).

Samples were dissolved in deuterated chloroform (CDCl_3).

Synthesis of CMF from cellulose-containing waste streams

In a typical procedure, 10 to 20 mg of the cellulose-containing waste material, 1 to 2 mL of HCl 37 wt% and 3 to 5 mL of the organic solvent of choice (chloro- or fluorobenzene) were introduced in an Ace glass high-pressure rated tube (batch reaction). The volume ratio of the aqueous phase used in our experiments was approximately 1:3. The reaction was carried out at 80 °C for 3 h under magnetic stirring using process conditions optimized before for wood-derived saccharide solutions (Bueno Moron et al., 2023). After completion, the reactor was crash cooled to room temperature by placing in an ice bath. The organic phase was collected and the remaining aqueous phase was washed using 3 to 5 mL of the organic solvent of choice for 1 h under stirring at room temperature. The organic layer was collected and the washing step repeated again. The organic layers from the reaction and the two washing steps were combined and the solvent was evaporated by rotary evaporation under reduced pressure. NMR and GC–MS analyses were performed and compared to NIST 11 libraries to confirm compound identities. GC-FID with reference materials and internal standards were used to quantify their concentration.

Results and discussion

Biphasic reactions

The utilization of biphasic systems has emerged as an established approach for the transformation of saccharides, leading to the high-yield production of 5-chloromethylfurfural (CMF) (Mascal and Nikitin, 2009; Mascal, 2009; Mascal, September 2015; Mascal, March 2019; Mascal and Nikitin, May 2009). This method involves the continuous extraction of the furanic compound with an immiscible organic solvent. This strategy significantly reduces undesired acid-catalyzed side-reactions of furanic compounds by isolating the CMF from the concentrated acid aqueous phase.

The initial use of biphasic systems for CMF synthesis and isolation trace back to 1944, with Haworth first reporting the use of a biphasic reactor system and obtaining 21.3 % CMF molar yield from sucrose (Haworth and Jones, 1944). In a patent publication granted to Hamada in 1978, a CMF yield of 77.5 % was achieved by processing hexose monosaccharides (glucose only) and disaccharides (sucrose) dissolved in an aqueous HCl solution in the presence of either toluene or carbon tetrachloride (Hamada et al., 1978). Subsequently, Szmant adopted analogous reaction conditions in 1981, accomplishing an impressive CMF molar yield ranging between 92–95 % from fructose (Szmant and Chundury, May 1981).

In the early 2000 s, Mascal and Nikitin played a pivotal role in elucidating the underlying reaction mechanisms and influential parameters in the conversion of saccharides to CMF in biphasic systems (Mascal and Nikitin, September 2008; Mascal and Nikitin, 2009; Mascal and Nikitin, May 2009; Mascal and Nikitin, February 2010; Mascal, 2009). In the early stages of their research, the conversion of monomeric sugars and microcrystalline cellulose was investigated. Subsequently, their research endeavors extended to encompass a wider feedstock spectrum, including biomass sources such as corn stover, (ball-milled) wood, and high-oil content biomass, exemplified by soybean and sunflower seeds (Mascal and Nikitin, May 2009; Mascal and Nikitin, February 2010; Origin Materials, 2023; Origin Materials, 2023).

The synthesis of CMF from C_6 sugars in biphasic systems is illustrated in Fig. 1. The dehydration of C_6 sugars in the acidic aqueous medium yields 5-hydroxymethylfurfural (HMF), followed by the subsequent chlorination of HMF to generate CMF. Additional research findings have revealed that the yield of CMF benefits from the utilization of organic solvents with affinity for the extraction of HMF from the aqueous phase (Lane et al., 2016). It is noteworthy that HMF and CMF exist in

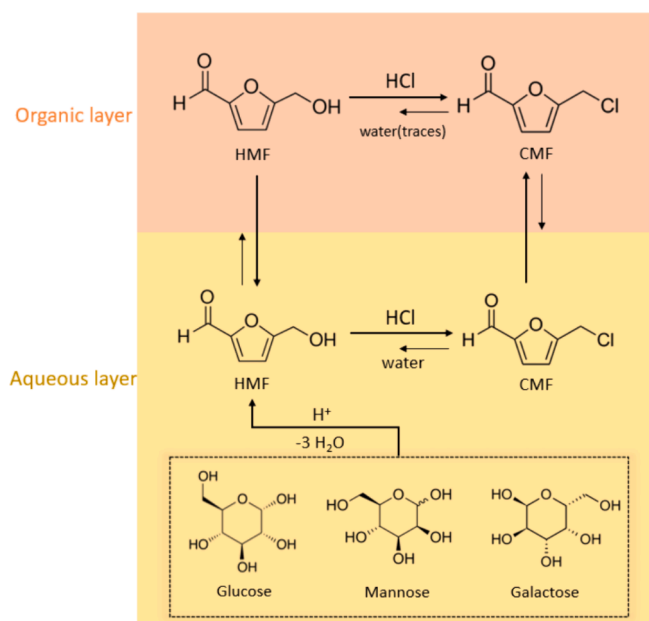


Fig. 1. Conversion of C_6 lignocellulosic sugars to CMF employing biphasic systems. The yellow section represents the aqueous phase, containing the C_6 sugars within a concentrated aqueous HCl solution. The orange portion represents the organic phase, assumed to possess a lower density, where 5-hydroxymethylfurfural (HMF) and CMF are perpetually extracted and safeguarded against the acidic solution, thereby facilitating the desired conversion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equilibrium and have the capacity to inter-exchange in the presence of water and HCl. Therefore, it is advisable to swiftly extract HMF from the aqueous HCl solution. This action may help protect HMF from the excess HCl, which could otherwise lead to undesired side reactions, such as levulinic acid, formic acid, and polycondensation compounds like humins (Lane et al., 2016; van Zandvoort et al., 2013).

Cotton-containing textile

A first set of experiments to convert the cellulose-containing textile (fabric mixed with either PET, PE or nylon) into CMF was conducted using reaction conditions replicated from previous studies by Mascal (Mascal, 2009; Bueno Morón et al., 2023) and our group (Bueno Moron et al., 2023). A reactor tube was loaded with 15 mg of cotton-containing jeans fabric. The cotton content of the fabric used was (according to the label) 98 %, but was by independent analysis identified to be 95 %. 1 mL of 37 wt% aq. HCl solution was added and the organic phase, comprising 3 mL of chlorobenzene, was layered atop the reaction mixture. The reactor tube was placed in a pre-heated aluminium block at 80 °C and kept under stirring for 16 h. The organic phase was analyzed for CMF at different time-intervals and the results are shown in Fig. 2.

This experiment showed a steady increase of CMF yield at longer reaction times. However, after 16 h the formation of solid humins by-products impeded the stirrer to work and the experiment was then terminated. Solid humins by-products are carbonaceous materials formed during the reaction. While they are often considered waste, humins can be used as precursors for activated carbon or as soil amendments due to their high carbon content (Liu and Humins, 2023; Titirici et al., 2006; Schmidt and Wilson, 2014).

To reduce a possible decomposition of CMF in the organic phase, the reaction was repeated in semi-continuous mode, during which the organic phase was replaced with fresh solvent at fixed times during the total reaction time of 5 h. In this way, the CMF in the organic phase is separated from the acid phase of the reaction mixture and, thereby,

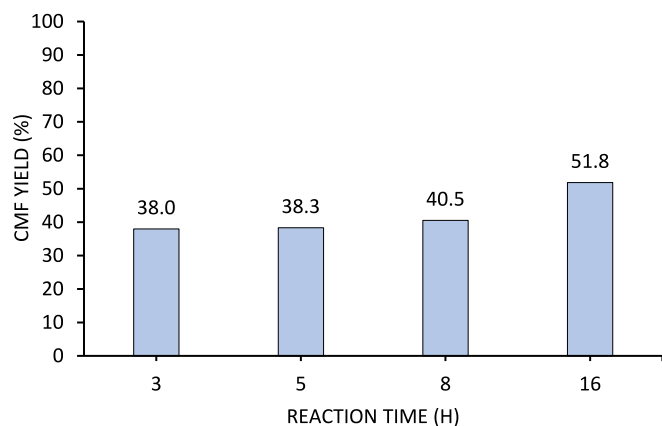


Fig. 2. Conversion of cotton-containing textile to CMF. Batch reactors containing waste textile, 1 mL of HCl 37 wt% and 3 mL of chlorobenzene were kept under stirring at 80 °C for 16 h.

reducing CMF decomposition. Four different reactor tubes were loaded with 15 mg of cotton-containing jeans fabric together with 1 mL of aq. 37 wt% HCl and 3 mL of chlorobenzene. The reactors were placed in the same pre-heated aluminum block at 80 °C and kept under stirring. During reaction, the organic phase was replaced and analyzed for CMF. Fig. 3 shows the visual observations of the reaction mixture during reaction. The CMF yield obtained at each solvent removal time is shown in Fig. 4.

An average cumulative CMF yield of 56.9 % was observed for the four reactors after 5 h, surpassing the yield observed in the initial batch experiments (Fig. 2, 38.3 after 5 and 51.8 % after 16 h, respectively). Furthermore, Fig. 4 illustrates that most of the CMF is formed in the first 2 h, with the last 3 h serving more as a washing phase, wherein residual CMF in the aqueous phase is transferred to the organic layer. In our experiments, the amount of solid humins formed was approximately 5 % of the initial mass in the batch system and 3 % in the semi-continuous system. However, in both systems (batch and semi-continuous), less than 1 wt% of the initial cellulosic material was detected in the aqueous

solution upon completion of reaction. Given that cotton's saccharide composition is exclusively glucose, the observed decrease in humin formation and residual sugars suggests that glucose obtained from cotton hydrolysis still undergoes transformation into unidentified byproducts.

Similar results were obtained after applying pre-treatments to facilitate cotton hydrolysis (Bergius, March 1937; Bergius, June 1937). Cotton-containing textile was stirred overnight (16 h) in 37 or 42 wt% HCl at 20 and 30 °C. During this time, some of the cellulose could start to hydrolyze and a small fraction of CMF could be formed even at these low temperatures. Therefore, 3 mL of chlorobenzene was added to the reactor tubes to extract any formed CMF. After each pre-treatment, the biphasic mixture was heated to 80 °C for 5 h with a semi-continuous extraction of the aqueous layer after every hour. The pre-treatments tested and the CMF molar yield achieved are summarized in Table 1.

Experiments with 42 wt% aqueous HCl showed slightly higher CMF yield compared to the experiments using HCl 37 wt%, but overall these pre-treatments did not significantly increase the CMF yields. The combination of pre-treatments and semi-continuous extraction of the organic phase was further investigated in combination with increasing volumes of the HCl solution and chlorobenzene and extending the reaction time. The 15 mg of cotton-containing textile were stirred at room temperature overnight with 2 mL (instead of 1 mL) of 42 wt% hydrochloric acid solution and 5 mL (instead of 3 mL) of chlorobenzene. After 16 h, the reactor tube was placed in the pre-heated aluminium blocks at 80 °C. The amount of chlorobenzene added for extracting the samples was also increased from 3 to 5 mL. The replacement of the organic phase was done after 1, 2, 4, 6, and 8 h and the CMF yield obtain from these reaction times are summarized in Table 2.

The cumulative CMF yield found after 4 h (51 %) is similar to the cumulative yield observed in previous experiments using smaller volumes of HCl and chlorobenzene (Table 1, Entry 2, cumulative CMF yield after 4 h, 55.4 %). However, longer reaction times (from 5 to 8 h), led to a slight increased cumulative CMF yield of 63.5 % (from 58.5 %, table 1). The absence of humins after 4 h may indicate that most of the cellulose material had been converted to CMF by this time, reducing the formation of solid by-products. While this observation suggests the potential for further optimization of the reaction conditions, it also shows

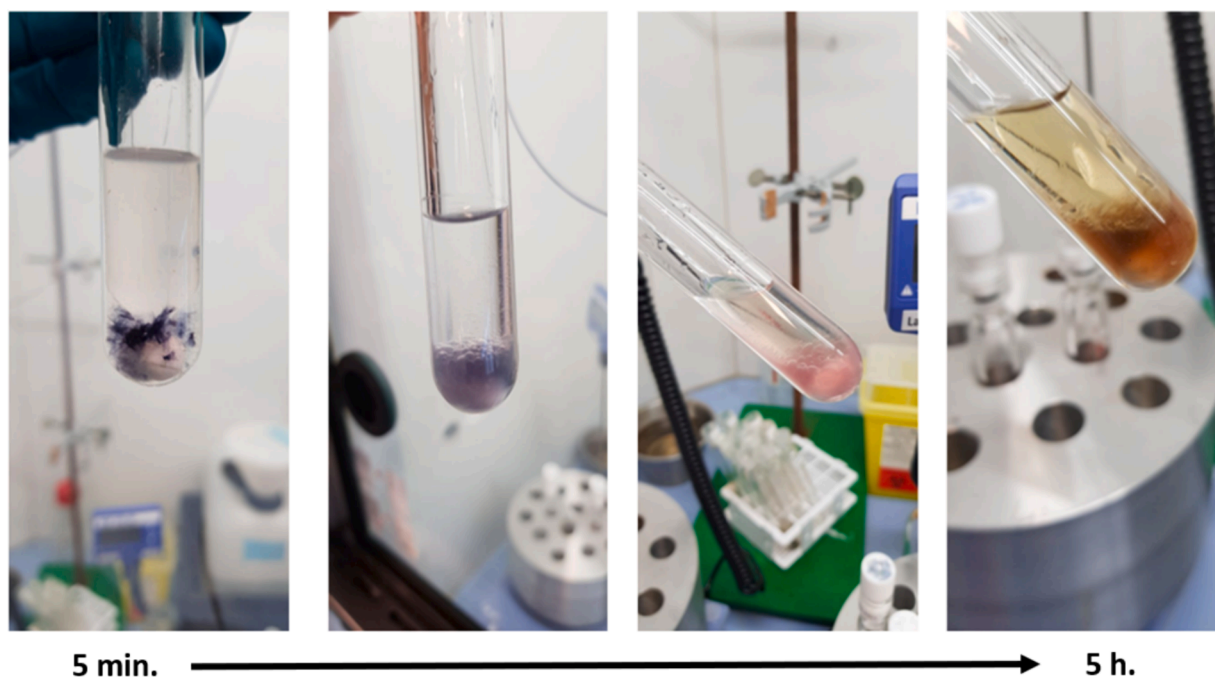


Fig. 3. Visual observation of the reaction mixture during the conversion of cotton-containing textile to CMF. The batch reactor contained 15 mg textile, 1 mL of 37 wt % HCl and 3 mL of chlorobenzene. The mixture was stirred at 80 °C and the organic phase was replaced at different reaction times.

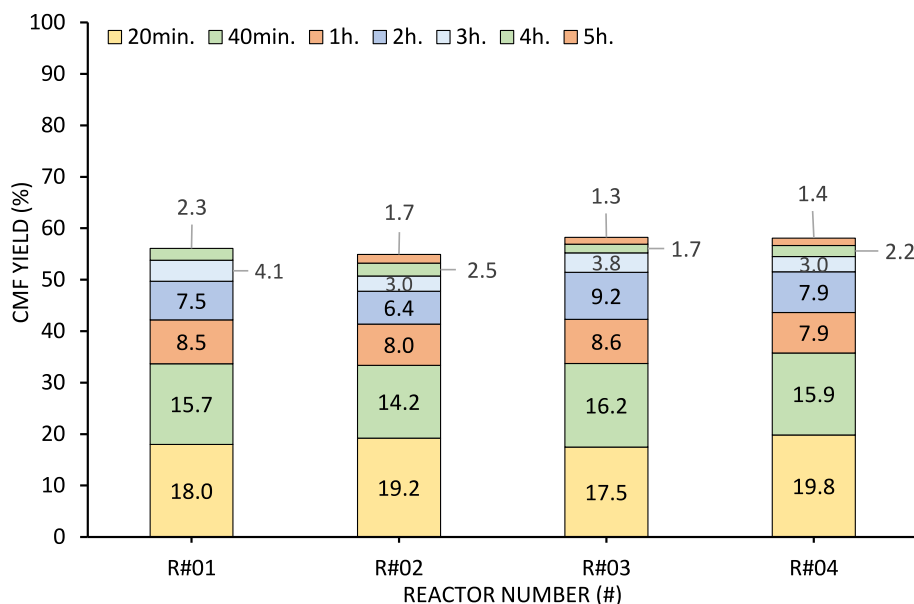


Fig. 4. Semi-continuous extraction of CMF from cotton-containing textile at 80 °C in quadruplicate. The reaction mixture contained 15 mg textile in 1 mL of 37 wt% and 3 mL of chlorobenzene. The mixture was stirred at 80 °C and the organic phase was 5x replaced during reaction after every 20 min time until reaching 1 h reaction time, and then after every 1 h until reaching 5 h of total reaction time. The cumulative CMF yield for each reactor is 56.1 % (R#01), 55.0 % (R#02), 58.3 % (R#03) and 58.1 % (R#04).

Table 1

Pre-treatments applied to textile before full conversion to CMF. After pre-treatment, each solution containing cotton in HCl 37 or 42 % and chlorobenzene was heated at 80 °C for 5 h. During reaction, aliquots were taken after 1, 2, 3, 4 and 5 h to analyze the CMF content.

Entry	Pre-treatment	CMF yield (%) during reaction					Cumulative
		1 h	2 h	3 h	4 h	5 h	
1	16 h at 20 °C with 37 wt% HCl	22.4	12.1	11.0	4.2	3.2	52.8
2	16 h at 20 °C with 42 wt% HCl	19.1	15.5	14.2	6.6	3.0	58.5
3	16 h at 30 °C with 37 wt% HCl	16.8	14.4	13.9	3.8	1.4	50.3
4	16 h at 30 °C with 42 wt% HCl	21.4	13.4	10.9	3.9	3.2	52.8

Table 2

Cotton-containing textile to CMF conversion. First, using pre-treatment at room temperature with HCl 42 wt% (16 h) followed by heating at 80 °C for 8 h. The volume of the aq. conc. HCl and chlorobenzene were both also increased compared to previous experiments.

Reaction time	1 h	2 h	4 h	6 h	8 h	Total
CMF molar yield (%)	23.1	15.5	12.4	8.1	4.3	63.4

promising steps compared to previous studies on waste textile to furanics, which reported low average yields from cotton of 7.9 and 19.9 % for HMF and glucose, respectively (Kawamura et al., 2020).

Mixed cotton in cleaning wipes

Another source of cotton-containing textile material tested for the chemical recycling of the cellulosic fraction to CMF were cleaning wipes. The goal was to study if blends containing mixtures of cellulosic textile with polypropylene or polyesters, commonly found in cleaning wipes, could effectively be transformed into CMF, and if the plastic counterpart had a detrimental impact on the course of reaction. Two different types of cleaning wipes supplied by Montvale and Reckitt laboratories were

evaluated. Montvale wipes presented a mixture of wood pulp with polypropylene, while Reckitt wipes contained viscose mixed with polyethylene terephthalate (PET).

First, a screening for the conversion of the wood pulp present in the Montvale cleaning wipes (67 wt%) was undertaken. For this, 15 mg of the Montvale cleaning wipes was added into batch reactor tubes together with 1 mL of 37 wt% aq. HCl solution and 3 mL of an immiscible organic phase (either chloro- or fluorobenzene). The reaction mixtures were kept at 80 °C for 16 h, and the organic phase was sampled at different intervals. The CMF yield for each of the organic solvents tested are shown in Fig. 5.

Reactors containing chlorobenzene showed higher CMF yields, obtaining a maximum of 54.4 % CMF after 5 h. This yield was higher compared to previous tests on cotton textile under similar reaction conditions (Fig. 2, 38.3 % CMF yield after 5 h). The amount of humins found after 16 h of reaction was, however, significant, and resulted in CMF yields decreasing to 10–14 % (down from 30–54 % after 5 h). This trend is similar as in previous observations, where at longer reaction times cotton-containing textile showed CMF decomposition.

The CMF semi-continuous production was also applied to the Montvale wipes. Additionally, similar pre-treatments previously tested for cotton-containing textile (Table 1) were also applied here (Table 3). The wipes were stirred prior reaction at room temperature for 16 h in 42 wt% aq. HCl and chlorobenzene. Subsequently, the reactor tubes were heated at 80 °C for 3, 4 and 5 h. During reaction the organic phase was replaced after every hour, the combined organic layers were analyzed and the cumulative CMF yields are shown in Table 3.

A CMF yield of 60.7 % was obtained after pre-treatment and 5 h of heating at 80 °C. This result was slightly higher than the previously observed in Montvale wipes without pre-treatment (Fig. 5, 54.4 % after 5 h). After 3 and 4 h of semi-continuous reaction, the CMF yield was also slightly higher compared to previous experiments (Fig. 5, 25 % after 3 h and 29 % after 4 h). The amounts of humins formed during this reaction was similar to previous observations on cotton-containing textile to CMF. But in this case, a transparent residue was recovered from the biphasic product mixture after reaction, suggesting that the polypropylene residue was still intact (Fig. 6).

Similar experiments were executed using the wipes provided by

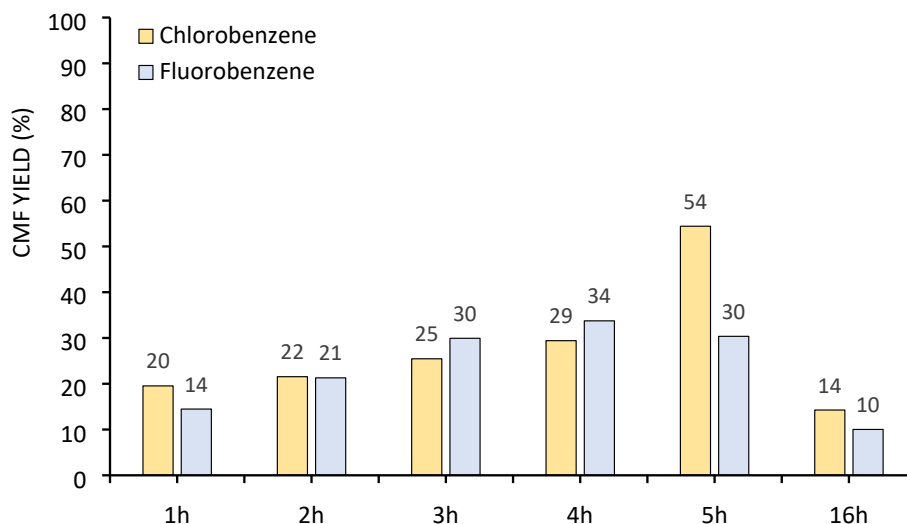


Fig. 5. CMF yield from the cellulose present in the wood pulp of Montvale wipes. Reaction condition: 15 mg wipe, 1 mL 37 wt% aq. HCl solution and 3 mL chlorobenzene (yellow) or fluorobenzene (blue), 80 °C. The organic layer was sampled and analyzed for CMF after 1, 2, 3, 4, 5 and 16 h of reaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

CMF yield from the cellulose contained in the wood pulp present in the Montvale wipes after 16 h of pre-treatment with 42 wt% HCl at room temperature. During reaction (80 °C), the organic solvent was refreshed after every hour. The CMF molar yield represents the yield of the combined organic layers.

Reaction conditions	CMF molar yield (%)
16 h at RT + 3h 80 °C	30.8
16 h at RT + 4h 80 °C	48.5
16 h at RT + 5h 80 °C	60.7

Reckitt laboratories. The cellulosic component in these wipes is viscose instead of wood pulp, and it is mixed with polyethylene terephthalate (PET). A quick first batch screening was done placing these wipes in 1 mL of conc. Aq. 42 wt% HCl and 3 mL of chlorobenzene. The mixture was stirred at 80 °C for 5 h and the organic layer analyzed, obtaining 48.2 % CMF yield. The semi-continuous reactor setup and pre-treatments tested before (Table 3) were also applied for these wipes

from Reckitt laboratories. The results and comparison with the Montvale wipes are shown in Fig. 7.

Viscose-containing wipes showed higher CMF yield after 3, 4 and 5 h (Fig. 7). In the context of upscaling this methodology, it's essential to note the significant improvements observed when transitioning from batch to semi-continuous experiments. However, the industry should ultimately aim to move from batch to fully continuous mode of operation, as this approach maximizes product output while minimizing costs and often results in higher yields (Cherkasov et al., 2023). To achieve this, there needs to be a transition from batch experimentation to semi-continuous operation. This transition is relatively easy to implement in the lab. Further scale-up efforts on this chemistry should focus on achieving a truly continuous mode of operation, for example, using a Continuously Stirred Tank Reactor (CSTR).

Specifically, in the case of experiments conducted on Reckitt wipes, the semi-continuous approach coupled with pre-treatments, resulted in a notable 40 % increase in CMF molar yield (Batch: 48.2 %, Semi-continuous: 85.9 %). This enhancement aligns with previous findings that highlight the advantages of semi-continuous reactor systems over



Fig. 6. Visual inspection of the reactor during the conversion of cellulose-containing wipes to CMF. The reactor contained Montvale wipes in 1 mL of 42 wt% HCl and 3 mL of chlorobenzene. The mixture was first stirred at room temperature for 16 h (middle picture) and then for 5 h at 80 °C, replacing the organic phase every hour during heating. The transparent polypropylene residue is visible after collecting the organic phase (right picture, in circle).

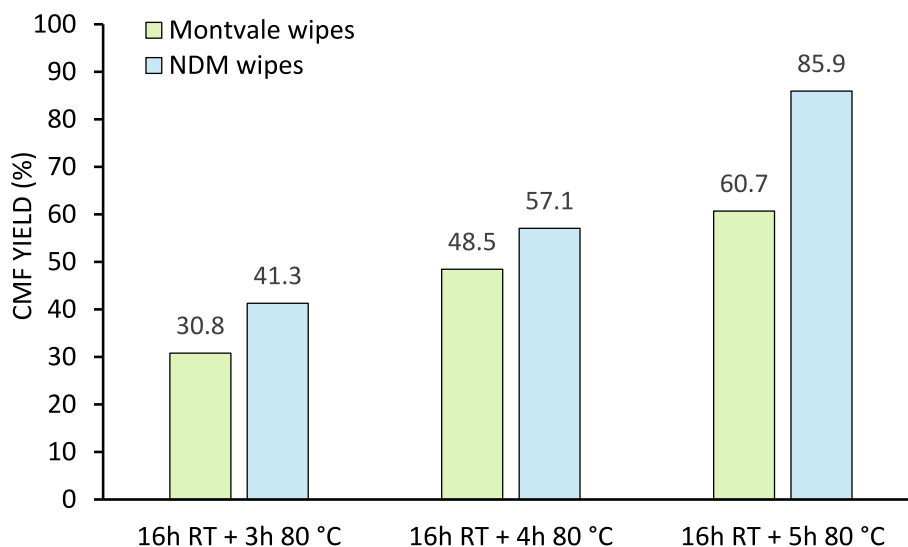


Fig. 7. Conversion of wood pulp Montvale (green) and viscose Reckitt wipes (blue) to CMF. 15 mg wipe sample was mixed with 1 mL of aq. HCl 42 wt% and 3 mL of chlorobenzene. The reaction mixture was first stirred at room temperature for 16 h and then heated to 80 °C for 3, 4 and 5 h. During heating the organic solvent was replaced after every hour and the analysis of the combined organic layers is shown as CMF yield. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

traditional batch setups. By periodically removing CMF from the system and replenishing the organic layer, the efficiency of extraction is enhanced, mitigating the risk of CMF decomposition.

Despite the complete conversion of the cellulose content into CMF and humins, there was no discernible impact on the residual plastic, suggesting its preservation throughout the process. This observation highlights the effectiveness of the method in selectively targeting cellulose while leaving the plastic component visually unaffected, ensuring its potential for subsequent mechanical, chemical, or pyrolytic reutilization.

Corrugated and mixed waste cardboard

The samples of corrugated cardboard included in this study were represented by standard shipping boxes commonly employed by e-commerce entities. The samples corresponding to mixed waste cardboard belong to pizza boxes collected from a local pizzeria (NY Pizza).

A first screening was accomplished using 20 mg of either corrugated or mixed cardboard in 2 mL of aq. conc. 37 wt% HCl and 5 mL of chloro- or fluorobenzene. The temperature studied ranged from 70 to 100 °C, and the reaction time was set to 3 h using closed reactors. After reaction, the organic layer was collected and the aqueous phase was washed with 3 mL of chloro- or fluorobenzene and stirring this mixture at room temperature for 1 h. The analysis of the combined organic layers is shown in Figs. 8, 9.

In our experiments, chlorobenzene consistently yielded better results compared to fluorobenzene, likely due to its higher boiling point and better solvation properties, which facilitates more efficient extraction of CMF from the aqueous phase. Even when the cardboard was co-mingled with food-waste contaminants, as typically found in pizza boxes, both materials still exhibited consistent trends under these reaction conditions. An initial rise in CMF yield was evident with increasing temperature, reaching a peak of 40–46 % CMF yield at 80 °C. However, subsequent elevations in temperature to 90 and 100 °C led to a reduction in CMF concentration, suggesting a temperature-induced decomposition of CMF.

Precipitated Calcium Carbonate (CaCO_3) is used as a filler and surface coating agent in the paper industry for premium quality paper products to enhance brightness, smoothness and opacity improvement. Calcium carbonate is also a common fire-retardant additive, which commonly impede or prevent fire outbreaks (Grover et al., 2014;

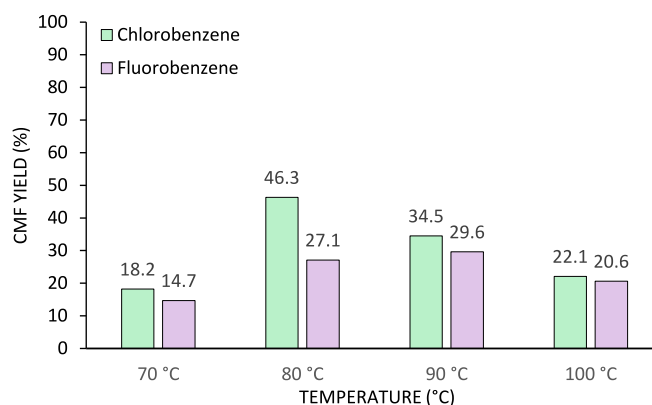


Fig. 8. CMF yield from the cellulose fraction in corrugated cardboard (Amazon box). 20 mg of cardboard was stirred for 3 h at different temperatures in the presence of aq. 37 wt% HCl and an immiscible organic solvent. After completion, the combined organic layers from the reaction and the washing step were analyzed for CMF.

Mccaskey and Edward Benson, October 1980). Calcium carbonate could react with HCl to form calcium chloride (CaCl_2) and carbonic acid (H_2CO_3), consequently reducing the HCl concentration in the aqueous phase. Therefore, the removal of CaCO_3 from the starting material was investigated. Both corrugated (Amazon box) and food co-mingled cardboard (pizza box) were found to contain 10–15 wt% CaCO_3 , which was removed by stirring 20 mg of these cardboards in aq. conc. 37 wt% HCl at room temperature for 1 h. The quantity of CaCO_3 in a 20 mg sample is insufficient to neutralize the excess of 37 wt% HCl deployed during CMF synthesis. Nevertheless, the removal of CaCO_3 was still examined and contrasted with samples that had not undergone this pretreatment. After the removal of CaCO_3 , the seemingly intact solid residue was introduced in another reactor tube along with 2 mL of aq. conc. 37 wt% HCl and 5 mL of chlorobenzene to replicate previous experiments. Both batch and semi-continuous reactions were tested for these conditions. For the semi-continuous reactor, the organic solvent was collected and replaced after every hour. The analysis of the combined organic layers is summarized in Fig. 10.

The cellulose present in pizza boxes showed slightly lower CMF

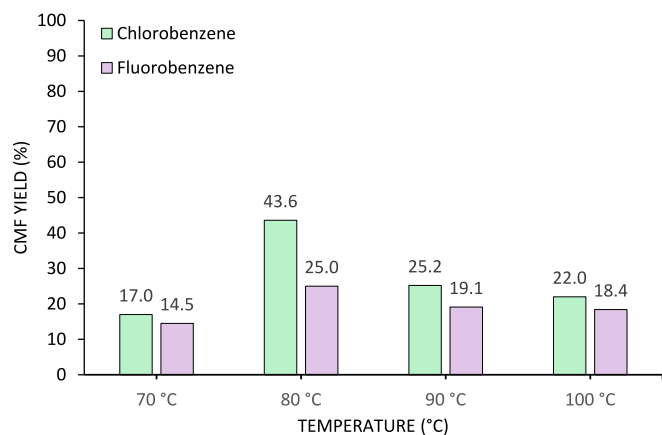


Fig. 9. CMF yield from the cellulose fraction in mixed cardboard (used/contaminated pizza box). 20 mg of cardboard was stirred for 3 h at different temperatures in the presence of aq. 37 wt% HCl and an immiscible organic solvent. After completion, the combined organic layers from the reaction and the washing step were analyzed for CMF.

yields compared to corrugated cardboard, as illustrated in Fig. 10. This aligns with *prior* indications that chemical reactions with cellulose from cardboard mixed with food can be hindered by these contaminants (Rock, 2020; machinedesign, 2018). However, the CMF yields observed with this cardboard were relatively close to the obtained with corrugated cardboard (approximately 10 % difference), and the choice of reactor system (batch vs. semi-continuous) did not significantly impact its overall performance. When CaCO_3 was present in the cardboard, bubble formation was observed after adding HCl, suggesting the formation of H_2CO_3 (and subsequently CO_2 and H_2O). However, the removal of CaCO_3 only showed marginal improvements in CMF yields during batch experiments. This can be explained by the fact that CaCO_3 present was masked by the 700–1200 fold excess of HCl in our reactions.

Cigarette butts (CB)

The conversion of cellulose acetate present in CBs to CMF was studied and a first screening was carried out in closed batch reactors. Samples were collected from ash trays located at local metro stations. 20 mg of this feedstock was added to 2 mL of 37 wt% HCl together with 5 mL of an immiscible organic solvent. The reactor tube was closed and maintained at a temperature of 80 °C for 2–4 h. The analysis of the

organic phase is shown after 2, 3 and 4 h reaction in Fig. 11.

Compared to previous experiments in this study, the cellulose acetate present in CBs exhibited higher yields to CMF. As shown in Fig. 11, a CMF yield of 93.2 % was obtained after 3 h using chlorobenzene. The high yield conversion of cigarette butts to CMF might be attributed to the presence of the acetyl group on the cellulose acetate chain, which could act as a protective group after hydrolysis, allowing the saccharides to convert gradually to CMF and be recovered before decomposition. Interestingly, despite the anticipated reduction in HCl concentration over time, the substantial excess present impeded this decline and consequently, signs of CMF degradation emerged after 3 h, likely catalyzed by the prevailing of this concentrated HCl in the aqueous phase.

Paper-plastic laminate (PPL) coffee cups

Samples were gathered from local cafeterias, and similar reaction conditions applied during this research were applied. In a batch reactor, 20 mg of PPL coffee cup was added to 2 mL of 37 wt% HCl and 5 mL of either chlorobenzene or fluorobenzene. The closed reactor was kept under stirring at 80 °C for 2–4 h, and the organic phase was analyzed after 2, 3 and 4 h (Fig. 12).

The results from Fig. 12 reveal a noteworthy observation; the reactor containing fluorobenzene exhibited a significant rise in CMF yield in the final hour of the reaction, from 10.2 to 39.9 % from 3 to 4 h reaction time, respectively. In contrast, chlorobenzene showed a higher CMF yield (49.3 %) after 3 h, followed by a slight decline (46.9 %) after 4 h. This decline in CMF yield was previously observed in other cellulosic waste material, albeit the time at which this occurs was different depending on the feedstock and the other components of the starting material.

Scale-up potential

This study shows the potential for scale-up and industrial application to develop a chemical process that feeds from a broad range of cellulosic waste materials for CMF production. In addition to our findings, it is important to note that a CMF process has recently been scaled up by Origin Materials, demonstrating its industrial viability (Masuno et al., 2012; Araiza et al., 2016). This industrial implementation highlights the practical potential of our research in contributing to the broader application of CMF production from diverse cellulosic waste materials. The versatility of this process, together with the use of biphasic reactor systems, facilitates the isolation of the final product CMF in the organic phase while the plastic residue and the byproducts, usually humins, are

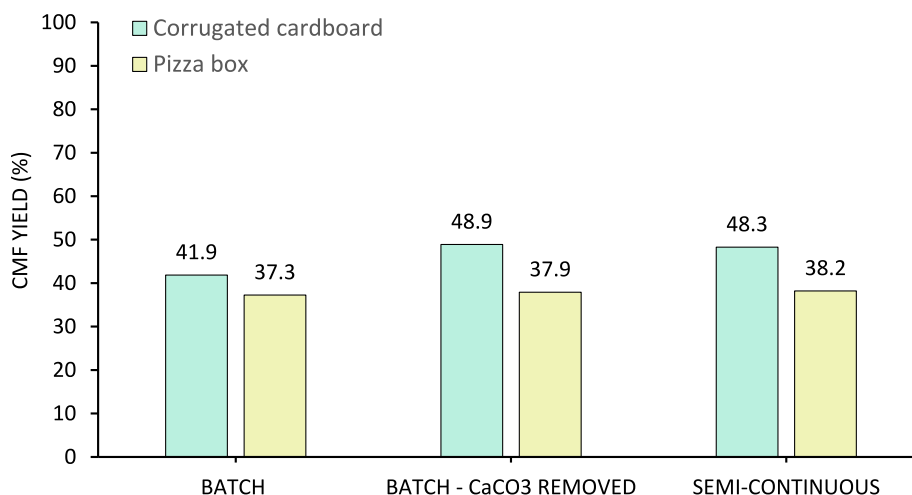


Fig. 10. Conversion of waste cardboard (corrugated and pizza box) to CMF. The removal of CaCO_3 *prior* reaction was done by stirring 1 h in HCl 37 wt% at room temperature. Reaction conditions: 20 mg of cardboard, 2 mL of 37 wt% aq. HCl, 5 mL of chlorobenzene, 80 °C for 3 h.

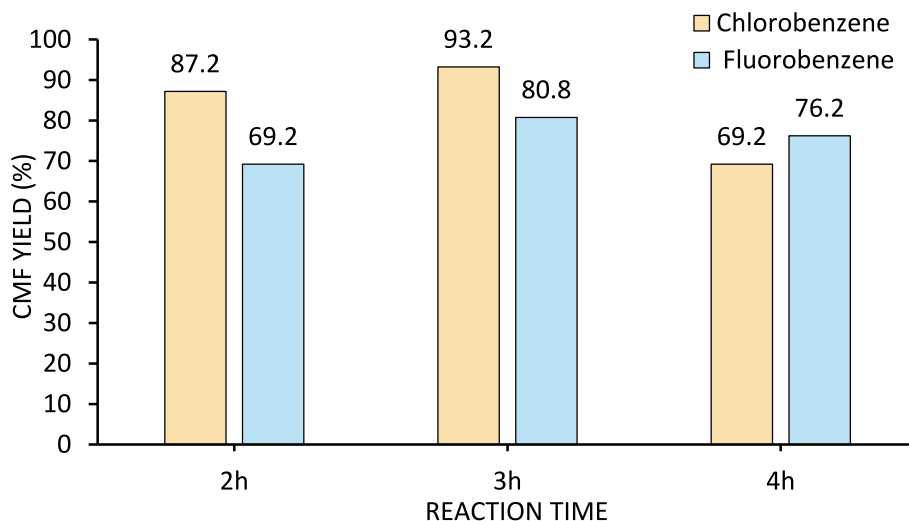


Fig. 11. Conversion of the cellulose acetate present in CBs to CMF. Reaction conditions: 20 mg of CB, 2 mL of conc. aq. 37 wt% HCl, 5 mL of organic solvent, 80 °C and 2–4 h reaction time.

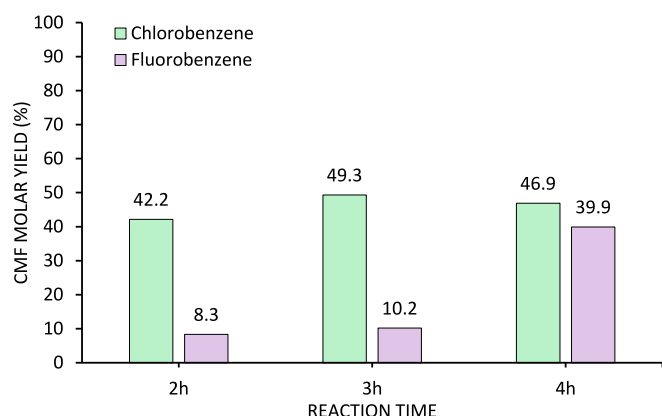


Fig. 12. Conversion of the cellulosic component in disposable PPL coffee cups to CMF. Reaction conditions: 20 mg of PPL coffee cup, 2 mL of conc. 37 wt% aq. HCl, 5 mL of organic solvent, 80 °C and 2–4 h.

found as solid materials or in solution in the aqueous phase.

In scaling up the CMF production process, mass transfer considerations become increasingly significant. Parameters such as particle size and sample preparation methods, which were controlled in our small-scale experiments, will need to be carefully managed in larger-scale operations. For instance, while grinding samples might enhance reaction efficiency in small-scale setups, implementing such methods on an industrial scale can be more challenging depending on the substrate.

Regarding the use of halogenated aromatic solvents for the extraction of CMF during the reaction, this study examined the use of chlorobenzene and fluorobenzene for CMF production. However, dichloromethane (DCM) and 1,2-dichloroethane (DCE) have also been reported to perform well in similar reactions (Mascal and Nikitin, 2009; Bueno Moron et al., 2023). Their use is restricted in the EU due to environmental and safety concerns. Nevertheless, with an effective recycling process, these solvents could potentially offer advantages in CMF production. Future research could explore the feasibility of using these solvents sustainably, balancing their chemical performance with environmental regulations.

The main advantages related to the scale-up of this process are the waste reduction, its versatility to accommodate different waste streams and the potential applications for the CMF and the residue behind (the plastic component). A chemical recycling process that group the

(otherwise) different recycling techniques for each of the materials fed into the system, increases the resource efficiency and contributes to the overall reduction of waste. The final product CMF can find after subsequent transformation, application in various materials, such as textiles, composites, and packaging, while the residual plastic, usually PET and polypropylene from textile clothing or disposable cleaning textile, can be of economic value via standard mechanical or chemical re- and/or upcycling processes.

However, while designing a process that covers a broad range of waste feedstock increases versatility, it also raises the possibility of encountering undesired contaminants and the potential risks associated with the formation of unwanted byproducts. For instance, contaminants from cigarette residues may introduce toxic components, warranting careful consideration during process design. The logistics may be complex, particularly considering that the sources of materials studied in this research are geographically distant. While cardboard and textiles are commonly found in waste containers, cigarette butts are typically located in ashtrays. Overall, while scaling up the chemical recycling process covered in this study offers numerous benefits, addressing challenges related to contaminants, logistics, optimization, regulatory compliance, and economic viability will be essential for successful implementation in the recycling industry.

Conclusion

This study successfully achieved a proof-of-principle valorization of various cellulose-containing waste streams using similar reaction conditions. Valuable guidance on selecting reaction conditions for testing very diverse sources of cellulosic waste was provided. Our conclusion emphasizes that, in the context of biphasic systems, a temperature of 80 °C and a reaction time of 3 h is advised for the conversion of the cellulose fraction present in waste materials into CMF. An excess of HCl was used, so investigating lower HCl-to-substrate ratio is recommended to bring this studies to the next stage of development. By switching the reactor system from batch to semi-continuous, CMF yields improved up to 50 % for cotton chemical recycling (Figs. 2, 5 h vs Figs. 4, 5 h). However, some materials such as corrugated or contaminated cardboard did not improve when switching to semi-continuous reactors, showing that further investigation in the reaction mechanism is required for these materials. From this study, the highest CMF yields were found when using cleaning wipes (85.9 %) and cellulose acetate in cigarette filters (93.2 %), making them excellent candidates for further studies and upscaling. In particular when using cleaning wipes, part of the solid

residue could be recovered after reaction. A first visual inspection of this residue showed that the plastic component remained intact after reaction, opening the possibility for its chemical (or maybe even mechanical) recycling. When cotton-containing textile (jeans) were used for CMF synthesis, the yields were lower (60 %), but optimizing reaction conditions allowed to increase this yield in this research. In the case of corrugated and grease-contaminated cardboard, and for disposable coffee cups, the CMF yields were slightly lower (around 45 %). This later materials might present less recalcitrant cellulose when compared to cotton and textile, but more research needs to be done to conclude it. We suggest that lower temperatures and overall milder reaction conditions could lead to new higher yields for these two materials.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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CRedit authorship contribution statement

Jorge Bueno Moron: Writing – original draft, Investigation, Formal analysis, Data curation. **Gerard P.M. van Klink:** Writing – review & editing, Supervision, Methodology. **Gert-Jan M. Gruter:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jorge Bueno Moron reports financial support was provided by European Union. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supporting Information. Complete description corresponding to the cellulose analysis of the feedstock tested by Celignis. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wmb.2024.06.006>.

References

- Araiza, J.R., Masuno, N.M., Hirsch-Weil, A.D., Wood, B.A., 2016. Methods for producing 5-(halomethyl)furfural. Patent WO2016149461A1.
- Bergius, F., June 1937. The production of food-stuffs, alcohol and glucose from wood by means of the Bergius-Rheinau process. *Curr. Sci.* 5, 632–637.
- Bergius, F., March 1937. Conversion of wood to carbohydrates. *Ind. Eng. Chem.* 29, 247–253.
- Bilek, M.A., Salem, H.J., Korehei, R., Olson, J.A., 2021. Recycling Paper-Plastic laminate coffee cups using a Single-Disk Refiner: Energy requirements and recovered fiber quality. *Waste Manag.* 136, 104–112.

- Bueno Morón, J., Gruter, G.-J.M., van Klink, G.P.M., 2023. Method of extracting 5-Chloromethylfurfural with an organic solvent from cellulosic fibers and man-made non-cellulosic fibers hydrolysed together with hydrochloric acid. Patent WO2023166122A1, 07 September 2023.
- Bueno Morón, J., Arbore, F., van Klink, G.P.M., Gruter, G.-J.M., 2024. 5-Halomethylfurfural synthesis and industrial preparation routes.
- Bueno Moron, J., van Klink, G., Gruter, G.-J.-M., 2023. Production and downstream integration of 5-(chloromethyl)furfural from lignocellulose. *ACS Sustain. Chem. Eng.* 11, 17492–17509.
- Cherkasov, N., Adams, S.J., Bainbridge, E.G.A., Thornton, J.A.M., 2023. Continuous stirred tank reactors in fine chemical synthesis for efficient mixing, solids-handling, and rapid scale-up. *React. Chem. Eng.* 8, 266–277.
- Eckhart, R., 2021. Recyclability of cartonboard and carton.
- Ernantez Efstathopoulou, K., Barrera, M.M.B., Navacerrada, M.A., January 2017. Textile wastes: state of the art. *J. Textile Sci. Eng.* 07.
- Escobar Gómez, V., Moreno González, C.A.C.M.J., Gata Jaramillo, A.M., 2021. Initial conditioning of used cigarette filters for their recycling as acoustical absorber materials. *Materials* 14 (15), 4161.
- Esmieo, M., Shaklawon, M., Ali Shanab, O., 2018. Feasibility study of cardboard waste recycling.
- European Commission, 2023. Circular economy for textiles: taking responsibility to reduce, reuse and recycle textile waste and boosting markets for used textiles. European Commission, Brussels.
- European Commission, 2023. EU strategy for sustainable and circular textiles. European Commission, Brussels.
- Fashion Revolution, 2023. Fashion Transparency Index 2023. Fashion Revolution.
- Grover, T., Khandual, A., Chatterjee, K.N., Jamdagni, R., 2014. Flame retardants: An overview 61, 29–36.
- Hamada, K., Suzukamo, G., Nagase, T., 1978. German Patent Patent 2745743.
- Haworth, W.N., Jones, W.G.M., 1944. The conversion of sucrose into furan compounds. Part I. 5-Hydroxymethylfurfuraldehyde and some derivatives. *J. Chem. Soc. (Resumed)* 667.
- House of Commons: Environmental Audit Committee, “Disposable Packaging: Coffee Cups,” House of Commons, London, 2019.
- Kawamura, K., Sako, K., Ogata, T., Mine, T., Tanabe, K., 2020. Production of 5-hydroxymethylfurfural by the hydrothermal treatment of cotton fabric wastes using a pilot-plant scale flow reactor. *Bioresource Technol. Reports* 11, 100476.
- Lane, D.R., Mascal, M., Stroeve, P., January 2016. Experimental studies towards optimization of the production of 5-(chloromethyl)furfural (CMF) from glucose in a two-phase reactor. *Renew. Energy* 85, 994–1001.
- 1 ed., 2023. Springer Singapore, p. 150.
- machinedesign, “Engineering a Better Pizza Box,” 4 January 2018. [Online]. Available: <https://www.machinedesign.com/materials/article/21836297/engineering-a-better-pizza-box> (accessed 10 November 2023).
- Marinello, S., Lolli, F., Gamberini, R., Rimini, B., 2020. A second life for cigarette butts? A review of recycling solutions. *J. Hazard. Mater.* 384.
- Mascal, M., September 2015. 5-(Chloromethyl)furfural is the new HMF: functionally equivalent but more practical in terms of its production from biomass. *ChemSusChem* 8, 3391–3395.
- Mascal, M., March 2019. 5-(Chloromethyl)furfural (CMF): A platform for transforming cellulose into commercial products. *ACS Sustain. Chem. Eng.* 7, 5588–5601.
- Mascal, M., Nikitin, E.B., September 2008. Direct, high-yield conversion of cellulose into biofuel. *Angew. Chem.* 120, 8042–8044.
- Mascal, M., Nikitin, E.B., May 2009. Towards the efficient, total glycan utilization of biomass. *ChemSusChem* 2, 423–426.
- Mascal, M., Nikitin, E.B., 2009. Dramatic advancements in the saccharide to 5-(chloromethyl)furfural conversion reaction. *ChemSusChem* 2 (9), 859–861.
- Mascal, M., Nikitin, E.B., February 2010. Co-processing of carbohydrates and lipids in oil crops to produce a hybrid biodiesel. *Energy Fuel* 24, 2170–2171.
- Mascal, M., 2009. High-yield conversion of cellulosic biomass into furanic biofuels and value-added products. Patent US20090234142A1.
- Masuno, M., Bissell, J., Smith, R.L., Higgins, B., Wood, B.A., Foster, M., 2012. Utilizing a multiphase reactor for the conversion of biomass to produce substituted furans.pdf. Patent WO2012170520A1.
- Mccaskey, H.O., Edward Benson, M., 1980. “Fire-resistant laminates”. United States of America Patent EP0050448A1, 08 October 1980.
- Origin Materials, 2023. “Origin Materials Announces Mechanical Completion of Origin 1 Manufacturing Plant,” Origin Materials, 27 January 2023. [Online]. Available: <https://investors.originmaterials.com/news-releases/news-release-details/origin-materials-announces-mechanical-completion-origin-1> (accessed 04 January 2024).
- Origin Materials, 2023. “Origin Materials Announces Commencement of Commercial-Scale Production at Origin 1,” Origin Materials, 11 October 2023. [Online]. Available: <https://investors.originmaterials.com/news-releases/news-release-detail/s/origin-materials-announces-commencement-commercial-scale> (accessed 04 January 2024).
- Ozola, Z.U., Vesere, R., Kalnins, S.N., Blumberga, D., 2019. Paper waste recycling. Circular economy aspects. *Environ. Climate Technol.* 23, 260–273.
- Reynolds, L., 2020. Environment Recycling & Waste: Can Pizza Boxes Be Recycled?, Treehugger [Online]. Available: www.treehugger.com/can-pizza-boxes-be-recycled-5025227 (accessed 10 November 2023).
- Rock, W., 2020. Incorporation of Post-Consumer Pizza Boxes. WestRock CP, LLC.
- Schmidt, H.-P., Wilson, K., 2014. The biochar revolution: transforming agriculture & environment. *Biochar J.* 1, 19–29.
- Soukup-Carne, D., Sanchez Bragagnolo, F., Soleo Funari, C., Esteban, J., 2024. Production and synthetic possibilities of 5-chloromethylfurfural as alternative biobased Furan. *Catalysts* 14 (2), 117.

- Stora Enso, 2022. New developments challenge a common myth - Paper cups can and should be recycled across Europe, Stora Enso, 25 March 2022. [Online]. Available: <https://www.storaenso.com/en/newsroom/news/2022/3/paper-cups-can-and-should-be-recycled-across-europe> (accessed 14 November 2023).
- Szmant, H.H., Chundury, D.D., May 1981. The preparation of 5-chloromethylfurfuraldehyde from high fructose corn syrup and other carbohydrates. *J. Chem. Technol. Biotechnol.* 31, 205–212.
- Titirici, M.-M., Antonietti, M., Thomas, A., 2006. A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach. *Chem. Mater.* 18 (16), 3808–3812.
- van Putten, R.-J., Waal, J.C., de Jong, E., Rasrendra, C.B., Heeres, H.J., de Vries, J., February 2013. Hydroxymethylfurfural, A versatile platform chemical made from renewable resources. *Chem. Rev.* 113.
- van Zandvoort, I., Wang, Y., Rasrendra, C.B., van Eck, E.R.H., Buijninx, P.C.A., Heeres, H.J., Weckhuysen, B.M., 2013. Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. *ChemSusChem* 6 (9), 1745–1758.
- Vanapalli, K.R., Sharma, H.B., Anand, S., Ranjan, V.P., Singh, H., Dubey, B.K., Mohanty, B., 2023. Cigarettes butt littering: The story of the world's most littered item from the perspective of pollution, remedial actions, and policy measures. *J. Hazard. Mater.* 453, 131387.
- Venkatesan, S., Afroz, M., Navaratnam, S., Gravina, R., 2023. Circular-economy-based approach to utilizing cardboard in sustainable building construction. *Buildings* 13 (1).
- Villanueva, A., Wenzel, H., 2007. Paper waste – Recycling, incineration or landfilling? A review of existing life cycle assessments. *Waste Manag.* 27, S29–S46.
- Zhu, L., Fu, X., Hu, Y., Hu, C., 2020. Controlling the reaction networks for efficient conversion of glucose into 5-hydroxymethylfurfural. *ChemSusChem* 13, 4812–4832.