Production of HMF from cellulosic biomass: Experimental results and integrated process simulation

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Abstract

Hydroxymethylfurfural (HMF) is one of the most promising biomass derived platform chemicals. It can be synthesized from biomass carbohydrates mainly glucose and fructose via dehydration under acidic conditions. The reaction may be performed either in water, ionic liquids or organic solvents, in particular polar aprotic solvents. In this work the process modelling of a two-step synthesis of HMF from biomass is presented. Starting from hemicellulose-free biomass, the first step includes the hydrolysis of cellulose towards glucose in the presence of H_2SO_4 as catalyst, while in a second step glucose is dehydrated to HMF with the aid of Sn20/Al_2O_3 catalyst. Hydrolysis is performed in aqueous medium, while dehydration of glucose is taking place in a DMSO/H_2O mixture. Overall production of HMF is modelled via the chemical process optimization software, ASPEN Plus™. The optimized process is scaled up at an industrial scale where the heat integration and mass and energy balance calculations are performed.

keywords: HMF, cellulosic biomass, process modelling, experimental

1 Introduction

The gradual depletion of fossil resources and the increasing demand for fuels and chemicals have resulted in the pursuit of alternative technologies and carbon sources. Towards this end lignocellulosic biomass is among the most promising sustainable sources for the production of environmentally friendly bio-fuels and bio-chemicals due to its abundance and chemical structure[1]. Cellulose, the main structural component of biomass, can be hydrolyzed to glucose under acidic conditions and glucose can be subsequently transformed to a variety of high added value chemicals such as 5-hydroxymethylfurfural (HMF)[2, 3]. HMF has been widely recognized as one of the top chemicals of the future chemical industry due to its versatility, as it may be converted to numerous compounds serving as fuels or fuel additives, building blocks for the production of polymeric materials replacing their fossil-based counterparts, etc. [4].

HMF is synthesized through dehydration of glucose or fructose by elimination of three water molecules, in the presence of an acid catalyst. Despite the apparent simplicity of HMF synthesis, the reaction is accompanied by a number of side reactions such as re-hydration of HMF to levulinic acid and formic acid, and cross polymerization to soluble polymers and insoluble humins, which makes HMF production very complicated[5]. A number of mechanisms have been already proposed for the formation of HMF from glucose and there are many studies strongly supporting both the cyclic and acyclic [6] pathways that might include an intermediate isomerization step to fructose prior to dehydration or suggest that the dehydration might proceed directly from glucose. However, polysaccharides and raw biomass are the feedstock that must eventually be used for any commercial unit to economically produce HMF. Different reaction systems have already been investigated for HMF synthesis from glucose or fructose, but few have been examined using cellulose or cellulosic fraction of biomass as the starting material. According to experimental results, the reaction conditions, especially in terms of temperature, solvent and catalyst, affect significantly the product distribution [7]. When the reaction takes place in aqueous media HMF rehydration towards levulinic acid, formic acid and humins are favored. Instead, in the presence of ionic liquids[8], polar protic and aprotic organic solvents [9] or their mixtures with water, these side reactions are being suppressed. Among the various solvents tested, DMSO has proven to be the most effective owing to its ability to stabilize the furanose form of fructose and to catalyze dehydration, resulting in high HMF yields [10]. Current scaled-up processes for the synthesis of 5-HMF rely on fructose as a starting material and employ inorganic acids as catalysts for the dehydration. Fructose is produced mainly via the isomerization of glucose, thus increasing its price. In addition the use of inorganic acids in the process adds to equipment costs and necessary waste treatment processes. Furthermore, the purification and storage of HMF for long periods due to susceptibility to polymerization and rehydration consist a barrier for HMF commercialization. Another challenge is the proneness of HMF to degradation even under mild conditions [11]. Thus, the current study presents experimental yield values of HMF using glucose as feedstock and a heterogeneous catalyst coupled with process modelling results to investigate the feasibility of HMF production process.

Several studies deal with the process modelling of furan monomers production. However, to the best of our knowledge, there are very few studies focusing on the process modelling of HMF production. King [12] presented a simplified model of furfural and HMF production via liquefaction of corn stover. Montarstruc et al [13] investigated and modeled the integration of a furfural biorefinery into a Kraft pulp mill. Marcotullio focused on the modelling of furfural production process [14] via feeding an aqueous solution rich in pentoses at a reactive distillation column where furfural is produced in the presence of NaCl in dilute acid solution as catalyst. Moreover, Agirrezabal-Telleria et al [15], simulated the production of furfural from corncobs with simultaneous N_2 stripping. Patel et al [16] [17] modeled the production of HMF and levulinic acid via a biphasic reactor in presence of homogeneous catalyst, using fructose as feedstock. Martin et al [18], dealt with the modelling and techno-economic evaluation of furfural and Dimethylformamide production from algae and switchgrass with intermediate HMF production. Additionally, Abuschinow et al [19], performed a process modelling and economic analysis on the production of THF from Maleic Acid.

Based on the experimental results obtained in the present study, the process for HMF production from cellulosic biomass is modelled in detail using ASPEN plus™, a market-leading chemical process optimization software. The process modelling of HMF production is described starting from the biomass feedstock until the production of the bio-chemical. Optimized simulation for the process is performed by applying the experimental results of the project and upscaling them at an industrial scale. After the modelling of the process (see Figure 1), the identification of the heat and power demands was held and the corresponding heat integration was performed. Heat recovery optimization was also performed for best energy exploitation, resulting in improved energy efficiency of the simulated plant. Moreover, mass and energy balance calculations were performed.

2 Experimental

2.1 Materials

Concentrated sulfuric acid (H_2SO_4) (95-97%), anhydrous Dimethylsulfoxide (DMSO) and $SnCl_2.2H_2O$ were obtained from Sigma Aldrich and were used as received. γ-Al_2O_3 was purchased from Saint-Gobain NorPro (Germany). A hemicellulose-free biomass feed originating from Almond shell after pretreatment with H_2SO_4, was used in all experiments of the current study. The biomass sample consisted of 4.65 wt.% hemicellulose, 40.48 wt.% cellulose and 53.05 wt.% lignin as determined by the NREL/TP-510-42618 method .

2.2 Catalyst synthesis and characterization

The catalyst applied for the glucose dehydration to HMF consisted of 20 wt.% Sn on γ-Al_2O_3, denoted as Sn20/γ-Al_2O_3 and was prepared by wet impregnation followed by drying at 100 ^oC. The catalyst was characterized by X-ray fluorescence analyses, N_2 adsorption/desorption measurements, X-ray diffraction and FT-IR coupled with pyridine adsorption.

2.3 Biomass hydrolysis to produce glucose

Hydrolysis of hemicellulose-free biomass into glucose was implemented in a batch, stirred, autoclave reactor (C-276 Parr Inst., USA). In a typical experiment, a sample of biomass (10 wt. %) in 0.75% H_2SO_4 (500 g) was charged into the reactor and heated to 175^oC for 60 min. After completion of the reaction, the reactor was cooled rapidly, and the liquid product was separated by vacuum filtration. The remaining solid denoted as biotar, was recovered, dried and analysed further in view of assessing its potential as a solid fuel.

2.4 Glucose dehydration and recovery of HMF

Glucose-rich solution produced from biomass hydrolysis was used as feedstock for glucose dehydration to HMF. The reaction was carried out in a batch, stirred, autoclave reactor (C-276 Parr Inst., USA) under N_2. The glucose-rich solution was slightly condensed by evaporation to increase the glucose concentration and afterwards was mixed with DMSO to obtain a 80%DMSO/20%H_2O solution. After addition of Sn20/γ-Al_2O_3 catalyst (glucose/catalyst 1/1) the mixture was loaded into the reactor and heated to 150^{o}C for 60min. Upon completion of the reaction, the reactor was cooled rapidly, and the liquid product was recovered by vacuum filtration. Afterwards, the HMF-rich liquid product was subjected to liquid-liquid extraction with dichloromethane (DCM) for the separation and recovery of HMF.

2.5 Product Analysis

The liquid products from both reactions were analyzed by Ion Chromatography (ICS-5000, Dionex, USA). The quantification was based on external calibration, using standard solutions of sugars and sugar alcohols (sorbitol, mannitol, rhamnose, arabinose, galactose, glucose, mannose, fructose and xylose), hydroxylmethylfurfural (HMF) and organic acids (formic, acetic, glycolic, lactic, levulinic, propionic and butyric acid). The analysis of sugars was performed using a CarboPac PA1 (5 μm, 4 x 250 mm) column and precolumn (5 μm, 4 x 30 mm) connected to a pulsed amperometric detector (PAD). The analysis of the organic acids was performed on a AS-15 (5 μm, 4 x 250 mm) column and pre-column (5 μm, 4 x 30 mm) connected to a conductivity detector (CD).

The characterization of the retrieved biotar (unreacted solids) included determination of its composition by the NREL/TP-510-42618 method, ultimate and proximate analysis and heating value measurement. The ultimate (CHNS) analysis was accomplished by the use of a Perkin Elmer Series II instrument, the proximate analysis was performed using thermogravimetric analyzer (ELTRA THERMOSTEP) and the calorific value of the samples was determined by means of PARR 6400 calorimeter.

3 Process description and model methodology

In this section, the description of the HMF production plant studied in this paper is presented, along with the operation principles and the main physical and chemical mechanisms that take place in each process step, starting from the hemicellulose-free biomass up to the production, recovery and purification of the final products. Thus, HMF production is split in three main processes: cellulose hydrolysis, HMF synthesis and HMF recovery.

The overview of the proposed HMF production process is depicted in Figure 1.

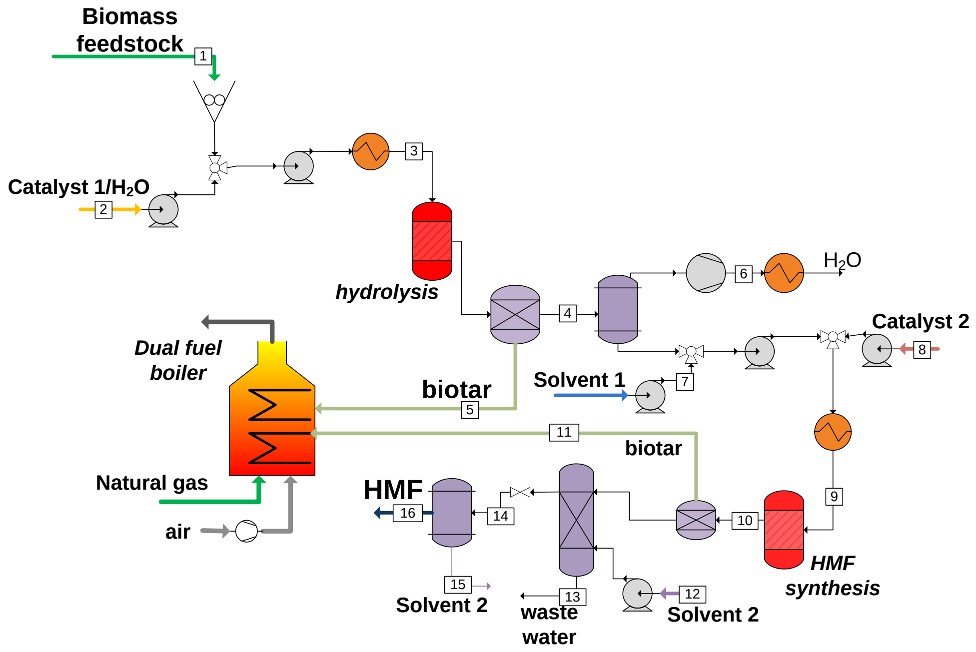

Figure 1. Overview of HMF production process from cellulosic biomass

Initially, biomass undergoes size reduction down to 0.3-1.0 mm [20] in a grinder. The particles are mixed with diluted acid catalyst (H_2SO_4), preheated and introduced to a first hydrolysis reactor and heated to the desired temperature. In the hydrolysis reactor, the cellulose part of the biomass is mainly converted into C6 monosacharides (primarily glucose) and other byproducts. Afterwards, the hydrolysate stream is submitted to HMF synthesis whereas the unreacted solid fraction, mainly lignin, including possibly formed humins, are retrieved as bio-tar, separated and forwarded for combustion. The hydrolysate stream, rich in glucose, firstly undergoes an evaporation step in order to increase the concentration of glucose, during which mainly water and some acids are also evaporated and forwarded for compression in order to recover heat through its cooling. The glucose-rich stream is added to a DMSO solvent stream for facilitating the selective synthesis of HMF yields (as opposed to using only H_2O as a solvent). The latter stream is introduced into the HMF reactor in the presence of the proposed solid catalyst. In the reactor, most of the glucose is dehydrated into HMF with the simultaneous production of byproducts and humins. After the HMF reactor, humins are separated and forwarded for combustion, along with the rest of the biotar from the hydrolysis step in order to cover the energy demands of the process. Furthermore, the HMF stream is forwarded for separation and purification. The produced HMF stream firstly undergoes liquid-liquid extraction with DCM. Mainly HMF is transferred into the organic circuit whereas the raffinate is treated as wastewater. The loaded organic solvent is then introduced to a three flash separation step at vacuum conditions where most of the HMF is purified and the solvent is separated and recovered. Through these processes, HMF is recovered as the final product.

3.1 Process Modelling

The process modelling was carried out using the simulation tool ASPEN plus™ [21]. Furthermore, NRTL property method was used as it is recommended for such processes from literature [14, 22-24]. The process modelling is based on actual lab-scale experimental results. Via simulation, the upscaling of the process was conducted with the determination of mass balances and identification of the energy demands of the processes.

The composition of the biomass that was used both for the experiments and the modelling, is presented in **Table 1**:

Table 1. Feedstock (hemicellulose-free biomass) composition (ash free-dry basis)

Cellulose	40.48%
Hemicellulose	4.65%
Lignin	53.05%
Unidentified	1.82%
Higher Heating Value (dry basis)	19.88 MJ/kg

For the purposes of modelling, the inserted biomass is modeled with the above characteristics at dry basis and ash free conditions. Finally, the feedstock capacity is assumed to be 1500 kg/h of biomass.

3.1.1 Cellulose Hydrolysis

For the cellulose hydrolysis process, water is added to the solid feedstock until the water to solid ratio is equal to 9, in the presence of 0.75%wt. H_2SO_4 as a catalyst. During hydrolysis, the cellulose part of the biomass is hydrolyzed into C6 monosacharides, mainly glucose. Along with glucose, other byproducts as organic acids (acetic, levullinic, formic acids etc.), HMF, xylose, mannose and levoglucosan are produced. The products that could not be identified, were assumed to be humins during the process modelling. The humins were modeled with the formula $C_{12}H_8O$ in order to fulfil the elemental and mass balance of the model. For the purpose of the modelling, humins are treated as solids and submitted to combustion [25] along with the rest unreacted biomass. The specifications of Cellulose hydrolysis are shown in **Table 2.**

Table 2. Cellulose Hydrolysis Specifications

Catalyst: H_2SO_4	0.75 wt%
H_2O/biomass	9
Temperature	175 °C
Pressure	8.2 bar

After the cellulose hydrolysis, the solid fraction (biotar) is filtered from the rest of the hydrolysate. The biotar is separated and forwarded also for combustion.

3.1.2 HMF Synthesis

The filtered hydrolysate is submitted to HMF synthesis. Prior to the HMF reactor, the stream is processed through an evaporation step in order to increase the glucose concentration of the stream so as to improve the HMF yields. During evaporation, mainly water and some of the acids are extracted. The vapor is forwarded for compression, afterwards it is cooled and part of the released heat is recovered. The evaporation step occurs until glucose has a concentration of 7.8%wt. Moreover, DMSO solvent is inserted so as to obtain a solution of 20%-80%wt water-DMSO for improved HMF yields. After the addition of DMSO, the stream enters the HMF synthesis reactor with the presence of a Sn20-γ-Al_2O_3 solid catalyst in a ratio of catalyst/glucose: 1/1 wt. During the dehydration of glucose into HMF, the byproducts produced include mannose, fructose, acetic acid, lactic acid, formic acid and glycolic acid while the conversion of glucose is 82.46%. Likewise, in HMF synthesis, for simulation reasons, the rest of the unidentified products are assumed to be humins as described in cellulose hydrolysis. The HMF synthesis specifications are shown in **Table 3**.

Table 3. HMF Synthesis Specifications

H_2O-DMSO	20%-80%
Solid Catalyst ratio: Sn20-γ-Al_2O_3 /Glucose	1/1 (wt)
Temperature	150 °C
Pressure	8.2 bar

After HMF synthesis, the humins are separated from the stream. They are considered as biotar and introduced together with the unreacted biomass of the previous process step for combustion.

3.1.3 HMF Recovery

The produced stream requires purification for the separation of 5-HMF from the rest of the products. To this end, the stream goes through a liquid-liquid extraction step where HMF is extracted with DCM (dichloromethane). An input of 1/10/1 of solution/CH_2Cl_2/H_2O is used. The liquid-liquid extraction takes place under atmospheric conditions where HMF, along with DCM, is separated with a 98% recovery assumed in the model.

Moreover, a further separation step is modeled where the extracted HMF is purified and separated, mainly from DCM. For that purpose, a three stage separation step is modeled where three flash tanks, operating at vacuum conditions, recovering the HMF nearly at 96.5% purity. The flash tanks heat the stream at temperatures lower than 80 °C so as HMF is not degraded. The flash tanks specifications are shown in **Table 4**. After the flash tanks, HMF is recovered as the final product of the whole process.

Table 4. HMF Separation Specifications

	Flash Tank 1	Flash Tank 2	Flash Tank 3
Temperature	40 °C	45 °C	75 °C
Pressure	1 bar	0.8 bar	0.1 bar

3.2 Heat Integration

A boiler is considered for the heat demands coverage. However, since the high temperature heat demands (those that cannot be covered through effective recovery from another exothermic source) cannot be covered totally by the retrieved biotar heat content, the use of additional external heat source in the form of fuel is required. In this study, the external fuel is considered to be natural gas (molar composition: 92.0 % CH4, 5.0% C2H6, 3.0% C3H8, LHV: 45 MJ/kg).

The steam boiler configuration is demonstrated in **Figure 2**. It consists of two water/steam circuits: one for the heat provision at the first step of cellulose treatment process (both preheating and reactor heat duty 202^{o}C/ 16 bar) and one for the rich in glucose solution preheating before the HMF synthesis reactor (180^{o}C/ 10 bar). The boiler is atmospheric, air blown and the quantity of the oxidizing medium flow rate is determined by the desired oxygen concentration at the flue gases (5%).

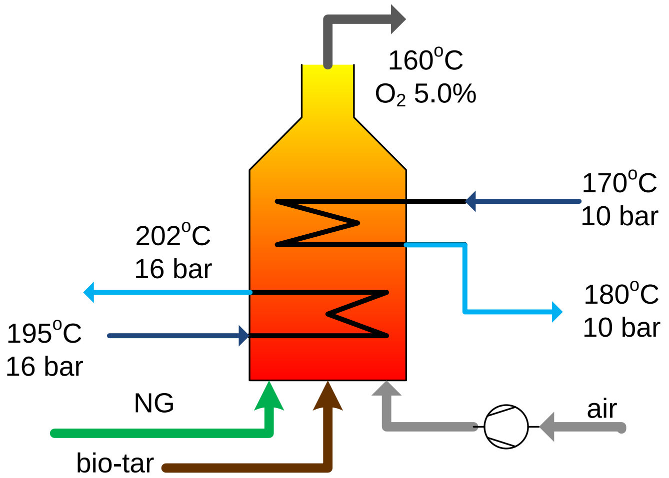

Figure 2. Dual fuel boiler for high temperature heat coverage

4 Results and discussion

4.1 Lab-scale Experimental Results

The scope of the paper is to present the process modelling results for the synthesis of HMF from actual biomass, therefore only a brief description of the experimental work is provided. Further details on the obtained experimental results will be presented in a subsequent publication.

In order to define the experimental conditions at lab scale, the initial experiments were performed with microcrystalline cellulose for the 1st step and standard glucose for the 2nd step. Microcrystalline cellulose (6 wt. %) was treated with different homogeneous and heterogeneous catalysts under set conditions. Among the different catalysts tested, H_2SO_4 resulted in the highest glucose yield and selectivity. A brief optimization of H_2SO_4 concentration, reaction time and temperature indicated that 175°C for 60min of reaction time were an acceptable compromise between glucose yield and selectivity and by-products formation. Under these conditions, cellulose conversion was 74% and the glucose selectivity was 50.5 wt %.

The second reaction step consisted of the conversion of glucose to HMF, using as a catalyst Sn20-γ-Al_2O_3 in 80% DMSO-20% H_2O as reaction media. The use of an aprotic solvent was decided considering four main factors (i) that Lewis acid catalysts are deactivated in aqueous solutions [26], (ii) DMSO itself solvates the glucose molecules and stabilizes the furanoic form of glucose, (iii) DMSO is a good dehydration medium acting as a donor/acceptor of lone pairs from its oxygen and sulphur atoms respectively [10, 27] and that (iv) DMSO solvates the HMF carbonyl and stabilizes HMF preventing its further conversion [28]. On the other hand, Sn was selected as the active metal since previous reports [29-31] have demonstrated that it displays the highest activity in sugars chemistry due to its capability to activate the carbonyl groups. Using the selected catalyst, the reaction conditions were optimized in terms of catalyst concentration, reaction time and temperature aiming to the highest HMF yield. The identified optimum reaction conditions were at 150°C for 60min at a glucose to catalyst ratio 1/1, resulting in glucose conversion of 99.5 wt. % at 27.5 wt. % yield in 5-HMF.

The application of the above conditions on hemicellulose-free biomass sample resulted in somewhat improved yield for glucose, probably due to the lower crystallinity of cellulose in the treated biomass, as compared to the microcrystalline cellulose. Consequently, the initial hydrolysis step resulted in cellulose-based glucose yield and selectivity 43.1 and 60.5 wt. % respectively. Using this solution, after addition of DMSO, the HMF yield and selectivity was 20.6 and 25.0 wt. % respectively.

The detailed experimental results obtained from the hemicellulose-free biomass presented in Tables 5-7 were used as input for the process modelling and upscaling of HMF production. **Table 5** presents the detailed composition of the solution resulting from the 1st hydrolysis step.

Table 5. Cellulose (in hemicellulose free biomass) Hydrolysis Experimental Results

Conversion Cellulose	71.43%
Mass Yields (biomass based wt %)	
Glucose	17.44%
HMF	0.88%
Mannitol	0.07%
Levoglucosan	0.54%
Xylose	0.31%
Mannose	0.33%
Fructose	0.10%
Galactose	0.004%
glycolic acid	0.03%
Acetic acid	1.11%
Lactic acid	0.08%
Formic acid	2.07%
Propionic acid	0.08%
Levulinic acid	4.86%
Lignin	53.05%
Unreacted hemicellulose	0.02%
Humins	7.47%

Furthermore, **Table 6** presents the product yields obtained during 2nd step of dehydration of the glucose-rich solution form the 1st step, into HMF.

Table 6. HMF Synthesis Experimental Results (starting from hemicellulose free biomass)

Conversion Glucose	82.46%
Mass Yields (glucose-based wt%)	
HMF	20.64%
Levoglucosan	0.11%
Mannose	0.11%
Fructose	0.12%
Glycolic acid	0.46%
Acetic acid	1.54%
Lactic acid	14.39%
Formic acid	6.99%
Levulinic acid	15.97%
Humins	22.12%

Finally, **Table 7** presents the composition and heating value of the unreacted biomass and humins which are extracted from the processes and are considered as biotar.

Table 7. Biotar specifications

C (% d.b)	63.7
H (% d.b)	5.46
N (% d.b)	0.15
O (% d.b)	30.29
S (% d.b)	0.3
ash (% d.b)	0.1
HHV (% d.b.)	24.75 MJ/kg

All the above experimental results were considered as input to the process modelling. The yields were used to model the reactions occurring in these processes and calculate the mass balance of the system. In addition, the specifications of biotar were used in order to perform the heat integration and energy balance of the whole process as biotar is consumed to cover the energy demands of the plant.

4.2 Process simulation results

4.2.1 Mass Balance

As aforementioned, the whole HMF production process was modelled based on the experimental results and upscaled via the process modelling tool ASPEN plus™. **Figure 3** demonstrates the main mass results of the HMF process. It is an overview of the mass flow across the different processes. The hemicellulose-free biomass feedstock (originated from almond shells) has a 1500 kg/hr flow rate. The final product (HMF) is recovered at 54.0 kg/hr, nearly 3.6% of the initial biomass with a 96.5% purity and 98% recovery. From the first reaction step, around 77.1% of the initial biomass is retrieved as unreacted solids (mostly lignin and unreacted cellulose and hemicellulose) and undetected compounds that are considered as humins for the sake of modelling procedure. At the second reaction step, 5.9% of the total biomass feedstock is not detected among the products and in order to satisfy the mass balance, the worst case scenario is adopted considering it as humins. Hence, around 83% of the starting biomass is considered as biotar and forwarded for combustion in order to cover the energy demands of the process. It should be underlined that this fraction may be less in case of a better mass balance closure can be accomplished. Finally, nearly 13% of the inserted biomass is converted into by-products which are separated after the HMF separation process as waste water and after the evaporation step as vapors.

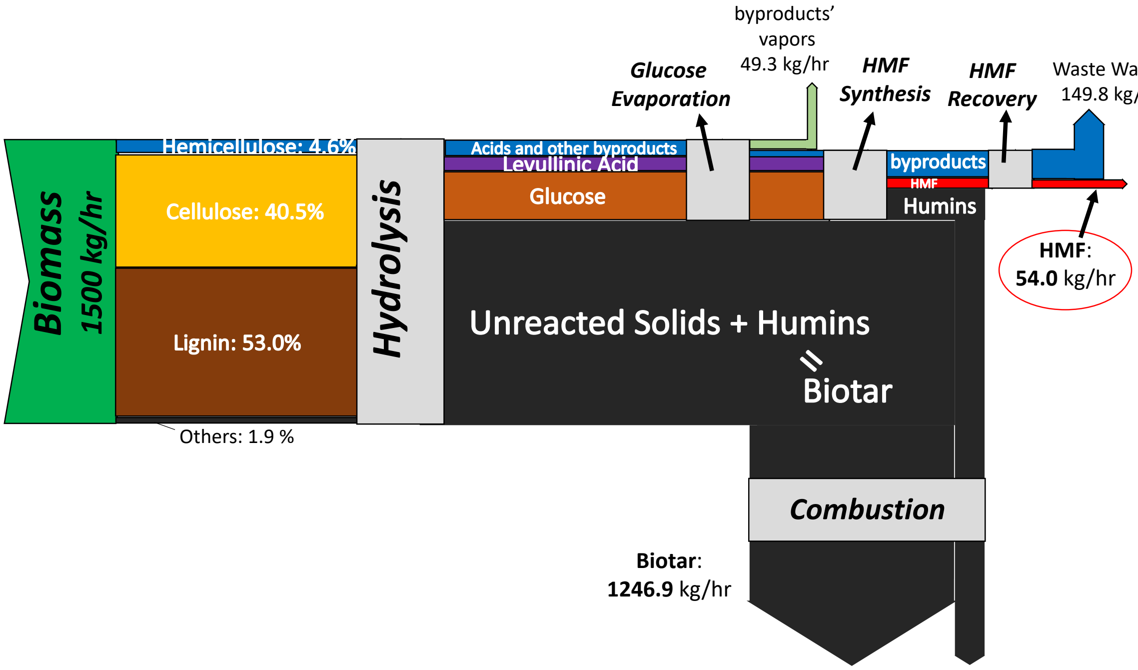

Figure 3. Mass balance overview of HMF process

Moreover, **Table 8** presents the stream results of the corresponding streams of the whole HMF production process as described in **Figure 1**. The mass results from the runs of the process modelling are depicted for each stream and expressed in kg/s. For each stream, the mass fraction of each component is presented along with its operational conditions (temperature and pressure).

Table 8. Stream results for HMF production section (see **Figure 1**)

stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
m (kg/s)	0.42	3.78	4.20	3.90	0.30	2.96	3.73	0.07	4.73	4.73	0.05	50.72	9.65	45.66	0.02
T (^{o}C)	25.0	25.0	170.0	175.0	175.0	158.2	25.0	25.0	150.0	150.0	30.0	25.0	25.0	40.0	75.0
p (bar)	1.0	1.0	8.2	8.2	8.2	1.6	1.0	15.2	8.2	8.2	8.2	1.0	1.0	0.1	0.1
mass fraction															
Acetic acid				1.2E-03		1.3E-03			1.6E-04	2.4E-04			9.1E-05	5.4E-06	7.9E-05
CH_2Cl_2												9.1E-01	5.3E-02	9.9E-01	2.2E-02
DMSO							1.0		7.9E-01	7.9E-01			3.9E-01	1.9E-07	1.2E-03
Unidentified	1.8E-02		1.8E-03												
Formic acid				2.2E-03		2.5E-03			2.5E-04	1.1E-03			5.0E-04	4.9E-06	1.5E-06
Fructose				1.1E-04		1.7E-17			8.8E-05	1.9E-05			9.1E-06	9.5E-24	2.1E-07
Glucose				1.9E-02		5.0E-15			1.5E-02	2.7E-03			1.3E-03	6.0E-21	8.9E-05
Glycolic acid				3.2E-05		1.9E-06			2.5E-05	7.1E-05			3.4E-05	4.4E-08	1.8E-04
H_2O		9.9E-01	8.9E-01	9.6E-01		1.0E+00			1.7E-01	1.7E-01		9.1E-02	5.5E-01	1.5E-03	5.5E-05
H_2SO_4		7.4E-03	6.7E-03	7.2E-03		7.1E-06			5.9E-03	5.9E-03			2.9E-03	1.0E-09	3.3E-03
HMF				9.4E-04		1.2E-05			7.7E-04	3.2E-03			2.3E-05	6.6E-06	9.6E-01
Lactic acid				8.6E-05		3.5E-06			6.8E-05	2.2E-03			1.1E-03	2.0E-07	3.7E-03
Levoglucosan				5.8E-04		1.4E-08			4.8E-04	2.4E-05			4.3E-06	1.9E-11	4.8E-03
Levullinic acid				5.2E-03		6.9E-04			3.8E-03	2.5E-03			1.2E-03	1.2E-08	6.2E-04
Mannitol				7.5E-05		1.8E-12			6.2E-05						
Mannose				3.5E-04		9.5E-17			2.9E-04	1.7E-05			8.4E-06	3.8E-23	5.7E-07
Propionic acid				8.6E-05		9.2E-05			1.3E-05						
SnAl								1.0	1.5E-02	1.5E-02					
Xylose				3.3E-04		7.9E-13			2.7E-04						
Cellulose	4.0E-01		4.0E-02		1.6E-01										
Humins					1.0E-01					9.7E-03	1.0				
Lignin	5.3E-01		5.3E-02		7.4E-01										
Xylan	4.7E-02		4.6E-03		2.8E-04										

4.2.2 Energy Balance

The calculation of the heat balance along the process is necessary in order to identify all the heating and cooling sources. **Figure 4** presents the heat demands and rejected/excess heat at the temperature level that is required or released. The hydrolysis process is the most heat demanding reaction process compared to the HMF synthesis. The low enthalpy heat for HMF purification at the three-step flash separators cannot be totally provided by the excess heat at the evaporator (between the two reactors). Moreover, the use of heat provided from the steam boiler would increase considerably the fuel consumption. Hence, a heat pump unit is introduced using the rejected heat at the HMF condensation as the cold tank of the system. The selected refrigerant is R134a. For the design of the heat pump unit is considered a minimum temperature approach 3^{o}C at the evaporator and 5^{o}C at the condenser and 70% isentropic efficiency of the compressor. According to the operating temperatures of HMF purification at the first flash (40^{o}C) and of the HMF condenser (25 ^{o}C) the pressure ratio of the heat pump is 1.91 and the coefficient of performance (COP) is calculated at 8.73.

From the above, it can be concluded that although the use of solvents DMSO and DCM improve the yields and recovery of HMF, nonetheless, they increase the heat demands of the whole process in separating them from the final product.

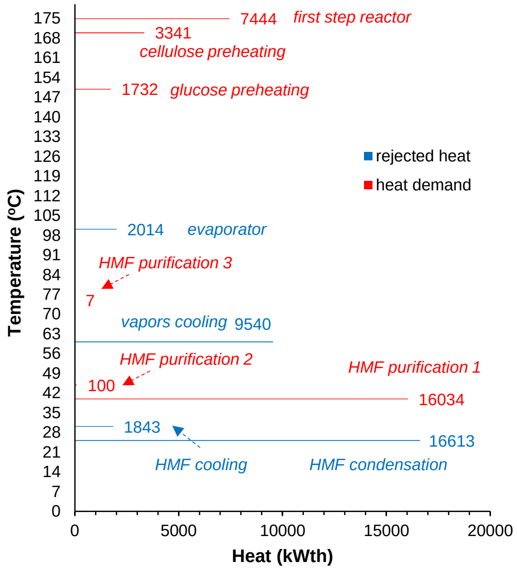

Figure 4. Heat demands and rejected/excess heat for the HMF synthesis process

The natural gas flow rate was calculated at 0.085 kg/s and 6.21 kg/s of steam totally was generated. The heat content of retrieved bio-tar is 8.7 MWth on a HHV basis from 0.35 kg/s biotar.

As far as the cooling system is concerned, excess heat that cannot be utilized is removed from the process by means of cooling water (CW). The total amount of heat that is rejected is 12.6 MW. The cooling water inlet temperature is set at 15 ^{o}C and the flow rate is determined by the maximum temperature increase after the cooling process, ΔT_{max}=10^{o}C. Also, a CW pump is considered that boosts the CW pressure by 5 atm. The simulation run reveals that the total required flow rate of the CW is 238.3 kg/s.

The power consumptions are shown in **Table 9**. Most of the required power is consumed by the compressor and pumps in the HMF synthesis section and the heat pumps at the HMF purification section. The total electricity consumptions are 1266.1 kWe.

Table 9. Power consumptions distribution

Section/ component	**kWe**
grinder	4.2
air blowers	32.1
water pumps (heating system)	2.6
cooling water pumps and vapors compressor	137.5
HMF production pumps	333.6
heat pumps	756.2
total consumptions	1266.1

The energy flow (Sankey) diagram of the whole process is presented in **Figure 5**.

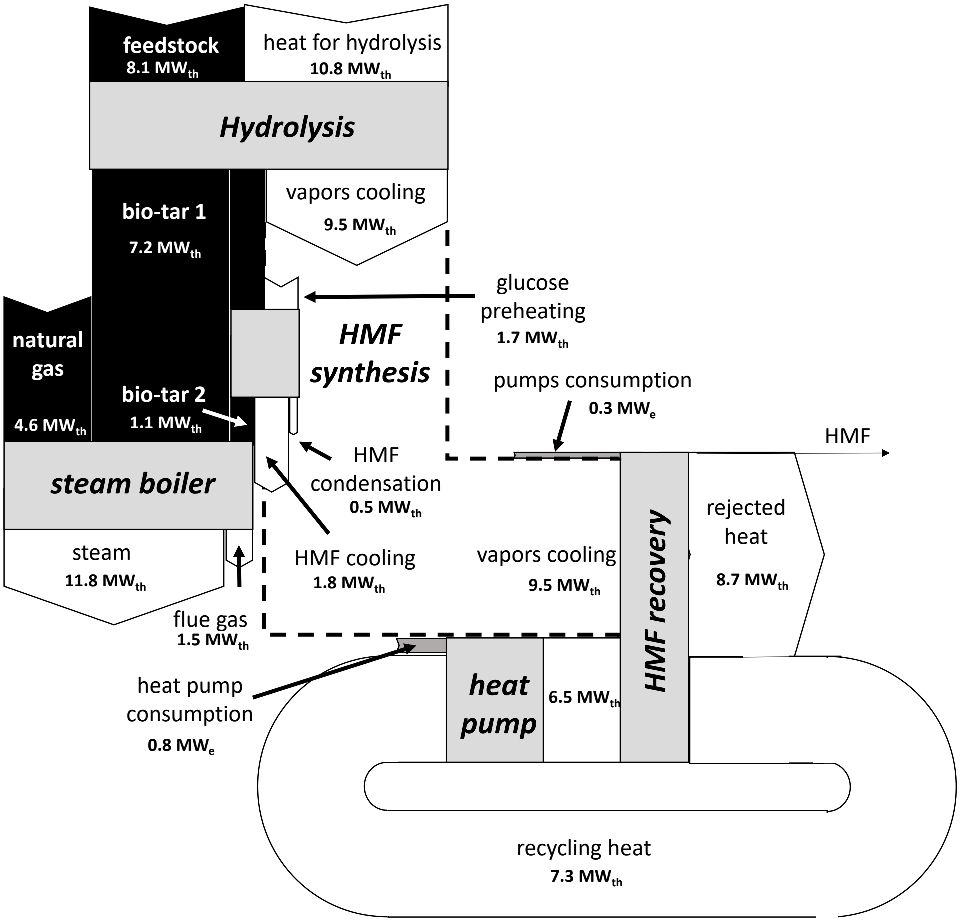

Figure 5. Sankey diagram of the HMF production plant: with black color are the streams that carry chemical energy, with white the heat streams and with grey the power streams

5 Conclusions

The current paper addresses the production of the versatile chemical HMF, from hemicellulose- free biomass. Firstly, experimental data of a two-step process for the production of HMF from actual biomass were obtained. Based on the experimental results, the initial step of glucose production from cellulose hydrolysis, using hemicellulose-free biomass as feedstock, maybe performed in an aqueous solution, in the presence of H_2SO_4 as a catalyst, at 175^{o}C for 60min. Regarding the dehydration of glucose into HMF, the optimum conditions were found to be at 150 ^{o}C for 60min in the presence of solid catalyst Sn20/γ-Al_2O_3 and with the addition of the aprotic solvent DMSO until a solution of glucose in 80%DMSO/20%H_2O is achieved.

Based on these experimental results, the upscaling at industrial level and modelling of the HMF production was performed via the ASPEN plus™ simulation tool. Around 3.6% of the inserted hemicellulose-free biomass was converted into HMF and around 13% were converted into various byproducts. Taking into account that only the cellulose content is available for HMF synthesis, the overall cellulose-based product yield of HMF is 8%. The unreacted biomass along with the produced humins were considered as biotar and forwarded for combustion to cover the energy demands of the whole process. In addition to the process modelling, the optimum heat integration was performed and the energy balance of the system was calculated. The energy system of the whole process consists of a dual fuel boiler where external fuel (natural gas) and biotar is consumed in order to cover the heat demands of the process. The total electricity demands of the process was calculated at 1.2 MWe whereas the heat demands at 26.1 MWth.

From the synergy of experimental procedure and process modelling, it was revealed that the production of a valuable compound from cellulosic biomass such as HMF can be accomplished through a new value chain. However, since this is approach is presented for first time, various aspects can be taken into consideration for further improvement of the process. The large yields of byproducts could be either reduced by the development of more efficient catalysts or part of them such as lactic acid and levulinic acid could be also recovered. The fine tuning of the operational parameters should be accomplished with respect to the reduction of heat and power demands. A techno-economic study of the proposed HMF production plant is essential for the evaluation of the method where also the lignin valorization pathway could be further investigated.

6 List of Abbreviations

COP	Coefficient of performance
CW	Cooling water
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
FF	Furfural
HHV	Higher heating value
HMF	5-Hydroxymethylfurfural
NG	Natural Gas
PSA	Pressure Swing Adsorption
ST	Steam Turbine
THF	Tetrahydrofuran

7 Nomenclature

$\dot{m}$	Mass flow, kg/s
p	Pressure, abr
T	Temperature, ^{o}C
Q_{th}	Heat load, MW_{th}
Q_e	Power load, MW_e
HHV	Heating Value, MJ/kg

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