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Chemical Engineering Journal 136 (2008) 14–24

Chemical Engineering Journal

www.elsevier.com/locate/cej

Effluent treatment for alcohol distillery: Catalytic thermal pretreatment (catalytic thermolysis) with energy recovery

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Received 27 May 2006; received in revised form 31 January 2007; accepted 3 March 2007

Abstract

The sugarcane molasses-fed distillery wastewater (DWW) has very high biochemical and chemical oxygen demand (BOD and COD) and has to be treated to meet the regulatory discharge standards and to recover its energy content. The catalytic thermal pretreatment (or catalytic thermolysis, CT) is a novel pretreatment process to recover the majority of its energy content with consequent COD and BOD removal. The present paper deals with the CT of DWW using CuO catalyst. Experiments were conducted in a 1 dm^3 stainless steel pressure reactor in a batch mode in the temperature range of 100–140 °C and corresponding autogenous pressure with CuO mass loading in the range of 2–5 kg/m^3. The initial pH (pH_0) is found to have profound impact on the efficiency of thermolysis in COD removal and the optimum pH_0 is found to be 2. At 140 °C with 3 kg/m^3 catalyst loading and pH_0 2, a maximum of 60% COD could be reduced. The CT process follows a two step mechanism: each step obeys the first order reaction kinetics with respect to COD and a fractional order 0.37 and 0.29 with respect to catalyst mass loading for the first and second steps, respectively. The CT process results in the formation of settleable solid residue and the slurry obtained after the thermolysis exhibited very good filtration characteristics. At 140 °C and pH_0 2, the solid residue had a C:H atomic ratio of 1:1.08 with a heating value of 21.77 MJ/kg. The residue can be used as a fuel in the combustion furnaces and the ash obtained can be blended with organic manure and used in agriculture/horticulture.

Keywords: Catalytic thermal pretreatment; Catalytic thermolysis; Charred residue; Distillery wastewater; Distillery spent wash; Energy recovery

1. 1.Introduction

The fermentation of cane sugar molasses in distilleries to produce ethyl alcohol is a very large agro-based chemical industry in India and South America. The fermentation broth containing 6–8% alcohol by volume is distilled to recover alcohol. The aqueous waste stream emanating from the distilleries is known in different ways as distillery spent wash (DSW), distillery wastewater (DWW), slope, stillage, vinasse, etc., depending upon the distillery unit. The distilleries generate 12–17 m^3 of wastewater per m^3 of alcohol produced. This wastewater has very high chemical oxygen demand (COD) (60–200 kg/m^3) and biochemical oxygen demand (BOD) (25–75 kg/m^3). The presence of high concentrations of carbohydrates, reducing sugars, dissolved lignin, proteins, alcohols, waxes, etc. impart high COD and BOD to the DWW. Amongst various treatment processes suggested for the treatment of DSW, anaerobic microbial digestion, concentration of the effluent through multi-effect evaporators followed by incineration, wet oxidation (WO) and coagulation–flocculation are found to be most promising. Anaerobic digestion has the advantage of very high efficiency of energy recovery in the form of methane-rich (∼70%) gas with 80–90% BOD removal and ∼70% COD removal efficiency [1,2]. However, the effluent from the anaerobic digestion plant (biodigester) normally has high BOD (∼5–7 kg/m^3) and COD (∼30–45 kg/m^3). Due to very stringent effluent discharge standards for COD and BOD ($COD < 0.10\ kg/m^3$ and $BOD < 0.03\ kg/m^3$ for surface waters; and $COD < 0.3\ kg/m^3$ and $BOD < 0.10\ kg/m^3$ for sewers) [3], the biodigester effluent is to be treated further. Apart from polluting the soil and the receiving water bodies, the typical odor emanating from the distilleries creates serious environmental nuisance to several square kilometer area around it. Aerobic treatment of the bio-digester effluent (BDE) is resorted to by most of the distilleries in India. In China, a large number of distilleries use multiple effect evaporators to concentrate the effluents followed by incineration to recover most of the energy content

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doi:10.1016/j.cej.2007.03.006

Nomenclature

A	filtration area (m^2)
AGR	atmospheric pressure glass reactor
BOD	biochemical oxygen demand (kg/m^3)
C	concentration of slurry (kg/m^3)
$C_A(t)$	concentration of organic substrate at any time(t) expressed as (COD) in kg/m^3
C_{A0}	initial concentration of organic substrate expressed as (COD_0) (kg/m^3)
C_w	catalyst (CuO) mass loading (kg/m^3)
COD	chemical oxygen demand (kg/m^3)
COD_0	chemical oxygen demand of the original effluent (DWW) (kg/m^3)
E	apparent activation energy (kJ/mol)
k	specific first-order reaction rate constant (min^{-1})
k_n	specific nth order reaction rate constant
k_1	first-order reaction rate constant for the fast thermolysis reaction step (min^{-1})
k_2	first-order reaction rate constant for the slow thermolysis reaction step (min^{-1})
m	reaction order with respect to catalyst mass loading (C_w)
n	reaction order with respect to organic substrate concentration (COD)
pH_f	final pH of DWW
pH_0	initial pH of DWW
R	universal gas constant, 8.314 J/(mol K)
R_m	filter medium resistance (m^{-1})
SSR	Stainless Steel (SS-316) Reactor
t	time (s)
t_h	transient heating time (pre-heating time) (min/h)
t_R	treatment time (min (or h))
T	temperature (°C)
TOC	total organic carbon (kg/m^3)
w	catalyst
X_A	conversion of organic substrate, $1 - (C_A(t)/C_{A0}) = 1 - ((COD)/(COD)_0)$

Greek letters

α	average cake resistance (m/kg)
β	intersect value represented by Eq. (13)
μ	viscosity of the filtrate (Pa S)

in the form of high pressure steam. However, this method has still not found acceptance in the distilleries in India despite the fact that this is the well accepted technology for chemical and energy recovery in integrated kraft pulp and paper mills. In this scenario, other treatment methods like coagulation–flocculation [4], ozonation and/or WO [5–8] and thermolysis followed by membrane separation may be the alternatives to conventional aerobic treatment.

The WO process employs high pressure and high temperature conditions, high pressure oxidants (air or oxygen) and high pressure equipment (autoclave/continuous reactor) and accessories [5,6]. These requirements make the process capital-intensive. The WO severity can be reduced by using catalysts [7,8]. Non-catalytic thermal pretreatment (hydrolysis or thermolysis) of DWW has been reported by some investigators [5,8–10]. Catalytic wet oxidation (CWO) of the DWW using mixed oxides and zeolite based catalysts at temperatures 200–250 °C and pressure 0.5–2.5 MPa could reduce its total organic carbon (TOC) from 22.5 to 6–10 kg/m^3 in a short contact time of 10 min [8]. In a typical run, about 57% COD reduction was obtained using non-catalytic and anoxic thermolysis, while about 73 and 82% COD reduction could be obtained during non-catalytic and catalytic wet oxidation (CWO). Chaudhari et al. [10] have recently shown that the CT of the BDE from a DWW treatment plant at moderate temperature of 140 °C and autogenous pressure with 3 kg/m^3 of CuO reduces the severity of the process considerably and that the COD of the effluent is reduced by about 70% and the BOD by about 83%. The initial pH (pH_0) of the effluent has tremendous impact on the thermolysis with pH_0 1 giving the maximum COD reduction. The separation of the insoluble compounds in the form of solid residue reduces the COD of the filtrate/supernatant substantially. Oxic treatment (WO) results in the oxidation of its components [5]. It has also been observed that the process of thermolysis is influenced by the presence of catalysts (homogeneous as well as heterogeneous) [11].

The objective of the present work is to explore the efficiency of the CT process in the reduction of COD of the distillery spent wash (DSW or DWW). Since Cu-based compounds (viz. CuO, $CuSO_4$) have been found to be very effective in the WO of many recalcitrant and refractory pollutants in aqueous streams [7,11–15], CuO has been used as the catalyst in the present study. The anoxic CT was performed at temperatures in the range of 100–140 °C and the corresponding autogenous pressures. The kinetics of the COD reduction, the filtration characteristics of the residue, and the fixation of copper in the residue and its leaching into the filtrate have also been examined and reported in this study.

2. Experiment

2.1. Materials and catalyst preparation

The distillery wastewater was obtained from Sir Sadi Lal Chemicals and Distillery Ltd., Pilkhani, UP (India). Typical analysis of the effluent, before and after thermal treatment, is presented in Table 1. Laboratory reagent (LR) and analytical reagent (AR) grade chemicals obtained from S.D. Fine Chemicals Ltd., Mumbai (India) were used in the experiments and the analysis. AR grade ethyl alcohol was obtained from Hongu Industries Corporation, China. The CuO catalyst was prepared in the laboratory from cupric nitrate by alkali precipitation followed by drying and calcination. To prepare 10 g CuO catalyst, 30.40 mg/l copper nitrate solution was prepared in distilled water and liquid ammonia was added to the solution gradually (drop by drop) while stirring the solution at a constant speed. The resultant precipitate was washed thoroughly with distilled water and then it was dried in an oven at 105 °C for 18 h. The dried matter was calcined in a furnace at 400 °C for 4 h. The calcined solid

Table 1
Typical composition of distillery wastewater

Parameters	DWW	DWW after thermolysis
COD	108,400	43,300
BOD	48,000	4630
Organic carbon	13,212	7980
Inorganic carbon	8928	4000
Total carbon	22,240	11,980
Reduced carbohydrates	65,100	24,610
Dissolved lignin	18,700	11,800
Protein	11,520	42
NH_4-N	861	303
Organic nitrogen	1010	340
Total Kjeldahl nitrogen (TKN)	1871	643
PO_4^-	220	180
K^{++}	7650	1560
SO_4^-	4940	3140
Cl^-	6500	5640
Fe^{++}	28	20
Ca^{++}	2200	360
Cu	26	199
Total dissolved solids (TDS)	68,182	50,140
Total suspended solids (TSS)	16,357	4070
pH	4.0	2.19
Color	Blackish brown	Orange

Note: all the values except pH, are in mg/dm^3.

was ground in a laboratory grinder and sieved. The solid particles with an average size of 220 μm were used in the experiments.

2.2. Experimental set up and procedure

The thermolysis experiments were performed in a 0.5 dm^3 atmospheric pressure glass reactor (AGR) as well as in a 1 dm^3 high pressure stainless steel (SS-316) reactor (SSR) The AGR was equipped with a vertical condenser. The SSR was equipped with electrical heating, temperature indicator-cum-controller, liquid sampling port, pressure indicator, and a cooling coil. The reactor contents were agitated using a magnetic stirrer (the stirring speed can not be determined but the intensity of stirring can be varied). After the start of an experimental run at a desired temperature, the effluent samples were withdrawn from the reactor at definite time intervals. The samples were filtered and the filtrate was analyzed for its COD value [16]. Each COD run was repeated twice to check the reproducibility of the results. Any run with a deviation of more than 3% was further repeated to check its reliability. The effect of such variables as pH_0 (1–10), temperature (T = 100–140 °C) and catalyst mass loading (C_w = 2–5 kg/m^3) on the COD removal efficiency was studied.

The experiments at atmospheric pressure and up to 100 °C were carried out in the AGR, whereas high temperature (100–140 °C) and autogenous pressure experiments were carried out in the SSR. The autogenous pressures of the solution at 100, 120, 130 and 140 °C were, respectively, 2.8, 5.1, 7.2 and 8.6 bar as against the vapour pressure of water which were 1, 2, 2.7 and 3.6 bar at the corresponding temperatures [17]. This pressure enhancement is due to the presence of organic matter in the effluent. The effluent was pre-heated from the ambient temperature to the treatment temperature: the pre-heating period (t_h) varying with the treatment temperature. The time of start of treatment was considered as the 'zero time' when the treatment temperature was attained due to preheating of the wastewater from its ambient temperature. All the experimental runs in the SSR were carried out for the treatment time, t_R = 6 h. The AGR was used to optimize the pH_0 of the effluent that gave the best performance for the CT. The treated effluent was filtered/centrifuged and the solid residue was dried in an oven at 105 °C until its weight became constant. The oven-dried residue was analyzed for its C, H, N, S, ash content and heating value.

2.3. Analytical procedure

Chemical oxygen demand (COD) was determined by the standard dichromate reflux method [16]. BOD of a sample was determined by incubating the seed sample for 3 days at 27 °C [3]. The chloride content was determined by standard titrimetric Volhard method [18]. The elemental (CHNS) analysis was done using an elemental analyzer (Elementar, model Vario EL III, Germany). The ash content was evaluated by combustion in a muffle furnace at 925 °C for 7 min. The specific energy of the residue was determined by using the standard bomb calorimeter [19]. The amounts of metal ions leached out in the solution and those fixed in the solid residue were determined by using an atomic absorption spectrometer (AAS) GBC, model Avanta, The residue obtained was dried and dissolved in aquarezia (1/3 concentrated nitric acid and 2/3 concentrated hydrochloric acid) while heating at about 80 °C. After suitable dilution of the solution with double-distilled water, the Cu content was determined by the AAS. The protein content of the DWW was determined by the Bradford method [20]. The reduced carbohydrates concentration was estimated by Fehling's method [21]. Organic nitrogen and ammoniacal nitrogen were determined by using the standard Kjeldahl method [16] and the Nesslerization method [16] using spectrometer (Hatch, model DR/4000U). Sulphates and phosphates were determined by using standard methods [16]. The lignin content was determined by using the modified Klason method [22], by replacing sulphuric acid with hydrochloric acid. The lower carboxylic acids (viz. formic acid and acetic acid) and ethyl alcohol were determined by using the gas chromatograph (Model HP 5890, FID detector) with HP 20 M capillary column. The injection temperature was 200 °C and the detector temperature was maintained at 250 °C. AR grade formic acid, acetic acid and ethyl alcohol were used as reference compounds. Inorganic carbon, organic carbon and total carbon were estimated using the total carbon analyzer (Shimadzu, Model TOC-V_{CSN}).

3. Results and discussion

3.1. Effect of initial pH (pH_0)

The CT of the diluted DWW, with and without catalyst, was carried out in the AGR equipped with a condenser at the top, at 100 °C and atmospheric pressure. pH_0 of the DWW batch was adjusted between 1 and 10 with either 0.1 M sulfuric acid or liquid ammonia and the treatment was carried out for t_R = 3 h. The

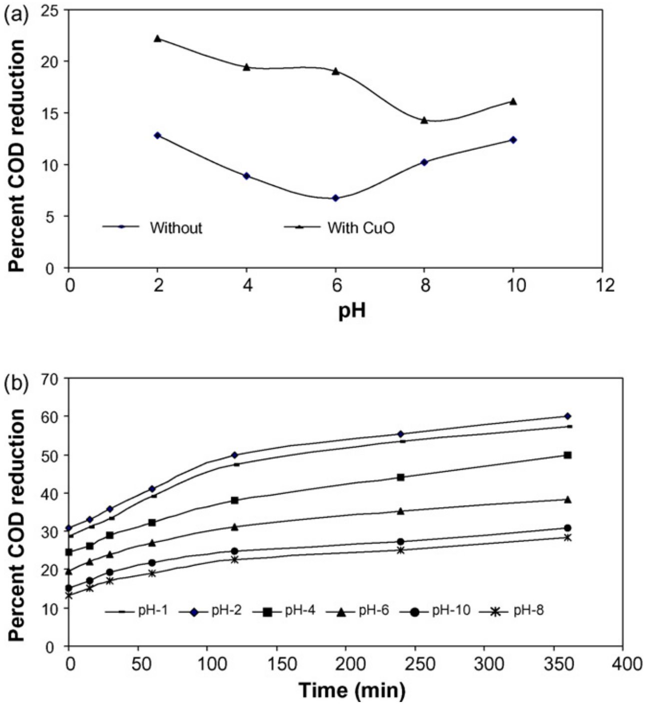

Fig. 1. Effect of pH on COD reduction of DWW during thermolysis. (a) $T = 100\,^{\circ}\mathrm{C}$, $P = 1$ atm, $\mathrm{COD}_0 = 17.5\,\mathrm{kg/m^3}$, $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$, $t_\mathrm{R} = 3$ h, and (b) $T = 140\,^{\circ}\mathrm{C}$, P = autogenous pressure, $\mathrm{COD}_0 = 108.4\,\mathrm{kg/m^3}$, $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$.

results for COD reduction due to thermolysis, with and without catalyst, are shown in Fig. 1(a). As the pH is increased, the COD reduction decreases with a minima at about pH_0 6 (without catalyst), and at about pH_0 8 (with the catalyst). Maximum COD reduction is found at pH_0 2 in the pH_0 range 2–8. The COD reductions, with and without catalyst, are 22% and 12.5%, respectively. In all these runs the initial COD (COD_0) was kept at $17.5\,\mathrm{kg/m^3}$ and $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$. At higher temperatures (up to 140 °C) and effluent autogeneous pressures, the experiments were performed in the SSR. Similar trend of COD reduction is observed at higher temperatures also. Contrary to the findings of several authors [23–25], the effect of the reactor wall on the thermolysis of the DWW was notobserved. Fig. 1(b) presents the results for COD reduction for DWW ($\mathrm{COD}_0 = 108.4\,\mathrm{kg/m^3}$) with $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$ at different treatment times, t_R at 140 °C and autogeneous pressure with pH_0 as the parameter. It is found that pH_0 2 is the best for the thermolysis. It is also seen that the COD reduction is quite fast during the transient preheating period (t_h) and the initial 2 h pretreatment time (t_R) and, thereafter, the COD reduction proceeds very slowly. During preheating periods of the wastewater from the ambient temperature to the treatment temperature, thermal degradation/precipitation occurs. The t_h increases with an increase in the treatment temperature, T. The t_h required for raising the temperature of the reactor and the reactor contents from the ambient temperature to the treatment temperatures were, respectively, 24 min for 100 °C, 30 min for 120 °C, 33 min for 130 °C and 37 min for 140 °C. The COD reduction during the preheating period for the treatment temperature of 140 °C at different initial pH were as follows: 28% (pH_0 1), 30% (pH_0 2), 25% (pH_0 4), 19% (pH_0 6), 13% (pH_0 8) and 15% (pH_0 10). These values are shown at the ordinate at zero time (i.e., $t_\mathrm{R} = 0$). Substantial COD reduction is found during the transient heating period.

Thermolysis is a complex process with various reactions/complexations taking place which result in the removal of complex organic molecules in the form of metal complexed solid residue. During this process, it is anticipated that the pH of the solution undergoes continuous change. At the end of the thermolysis, the final pH ($\mathrm{pH_f}$) may be different than pH_0. The $\mathrm{pH_f}$ were found to be 1.24, 2.26, 4.26, 4.70, 5.15 and 8.67, respectively, against the pH_0 values of 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0. The $\mathrm{pH_f}$ of the effluent with pH_0 2 after $t_\mathrm{R} = 6$ h is found to be 2.28.

The role of pH_0 on the CWO of DWW (or DSW) has not been dealt with by the previous investigators [5,6,8,10]. It has, however been reported that the thermal pre-treatment of the biodigester effluent at 150 °C can reduce its COD by about 37% and its dissolved solids by about 44% with $\mathrm{pH}_0 > 8$. Lele et al. [9] have shown that the pH_0 1 gives the maximum COD reduction during non-catalytic thermal pre-treatment of DWW at 230 °C and autogenous pressure. They reported minimum COD reduction at pH_0 7. Chowdhury and Ross [7] have shown the effect of initial acidity on the wet oxidation of strong wastewaters. Lignin and carbohydrates contain a number of reactive groups including hydroxyl groups, which generally react at pH 0–2 and pH 6–8 [22]. The presence of CuO in heterogeneous and homogeneous forms may catalyze these functional groups to react and form solid metal complex. However, more experimentation is required to unravel the complexity of the complexation process due to pH variation.

3.2. *Effect of temperature*

The experiments were conducted in the temperature range of 100–140 °C and at the corresponding autogenous pressure, pH_0 2 and $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$ for $t_\mathrm{R} = 6$ h. The COD_0 of the DWW was $108.4\,\mathrm{kg/m^3}$. The COD reduction with, t_R at different temperatures as shown in Fig. 2, seems to be a two step process-the first step during the initial period (up to 2 h) being faster than the slower second step. At 140 °C, 30% COD reduction is obtained during t_h and another 19% reduction is obtained during the next 2 h (t_R). Further treatment for additional 4 h (i.e. at $t_\mathrm{R} = 6$ h) gives

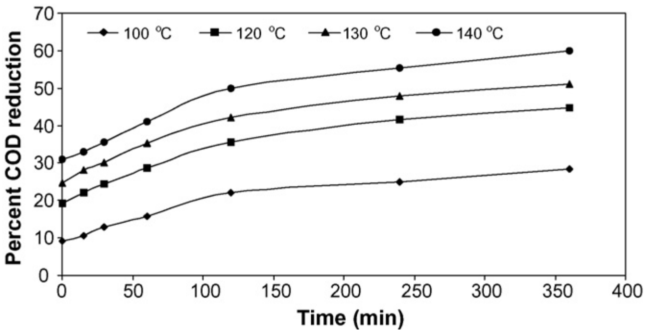

Fig. 2. Effect of temperature on the reduction of COD with time during catalytic thermolysis of DWW. $\mathrm{COD}_0 = 108.4\,\mathrm{kg/m^3}$, pH_0 2, $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$, P = autogenous pressure.

only ∼11% increment in COD reduction. During the transient heating period, t_h, the COD gets reduced by 9.5, 19.5, 25 and 30% at $t_R = 0$ and $T = 100$, 120, 130 and 140 °C, respectively as shown in Fig. 2 by the points on the ordinate. During the transient heating and the first step of thermolysis, precipitation and thermal degradation of organic molecules take place. The large molecules of organic matter break into smaller molecules, which along with catalytic complexation and carbon sequestration lead to carbon-enriched solid residue formation. The thermolysis of the smaller molecules, thereafter, appears to be relatively difficult as shown by the relatively much slower second step. The solid residue has good settling characteristics. As will be shown later, this charred residue has much higher atomic C:H ratio than either the distillery wastewater or the filtrate of the treated wastewater. Gaseous products having pungent and foul smell are also formed, which escape when the valve is opened after the cooling of the reactor. The gases may consist of methane and/or nitrogenous and sulfurous compounds. However these components have not been identified due to difficulty in sampling. The cleavage of the complex molecules present in water and the deposition of the insoluble charred residue leads to the reduction in the COD of the treated wastewater. With an increase in temperature, the pressure of the reaction also increases correspondingly. At $T = 100$, 120, 130, 140 °C, respectively, the COD reduction is found to be 28.3, 44.6, 51.2 and 60.1% after $t_R = 6$ h.

The characteristics of the solid residue obtained after filtration are presented in Table 2. With an increase in T, the amount of residue increases, with 28.71 kg/m^3 obtained at 140 °C. This amount is equivalent to ∼60% convertible COD. The increase in COD reduction due only to residue (char) formation is noteworthy: ∼28% at 100 °C and ∼60% at 140 °C. The C, H, N, S contents of the residue also increase with temperature, whereas the ash content remains more or less constant. The heating value of the residue also increases from ∼17.6 to ∼21.7 MJ/kg as T is increased from 100 to 140 °C.

3.3. Effect of catalyst mass loading, C_w

The thermolysis reaction was also performed with C_w in the range of 2–5 kg/m^3 at 130 °C in order to see the effect of C_w on the COD reduction. The COD reduction was found to increase mildly with an increase in C_w. The increase being ∼8.4% from 45.75% at $C_w = 2$ kg/m^3 to ∼57.4% at $C_w = 5$ kg/m^3 as seen from Fig. 3. It may also be seen that the rate of COD reduction is more when C_w is increased from 2 to 4 kg/m^3. At $C_w > 4$ kg/m^3, the COD reduction does not increase significantly.

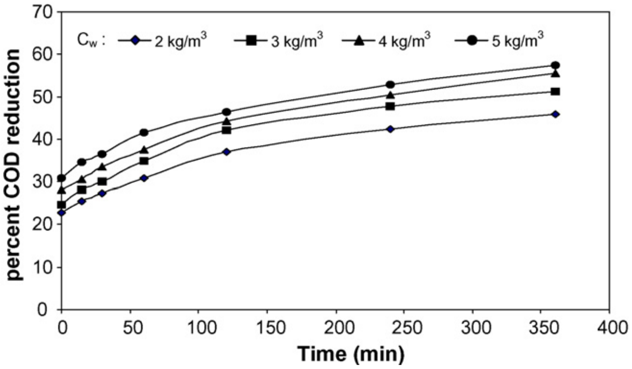

Fig. 3. Effect of catalyst mass loading on the reduction of COD with time during catalytic thermolysis of DWW. $COD_0 = 108.4$ kg/m^3, pH_0 2, $T = 130$ °C, P = autogenous pressure.

3.4. Catalytic thermolysis

The compositional analyses of DWW and the treated DWW after thermolysis at 140 °C, pH_0 2 and $C_w = 3.0$ kg/m^3 are shown in Table 1. It is found that the DWW consists of various components like reduced carbohydrates, proteins, lignin, minerals, etc. Lele et al. [9] have reported the absence of lignin in the DWW while Belkacemi et al. [10] reported the presence of large amount of lignin in timothy grass based spent wash. The carbohydrates contain hydroxyl and carbonyl groups in their molecular structure while the lignin contains hydroxyl and methoxyl groups and a carbonyl group. At low pH (acidic condition) and elevated temperature, carbohydrate undergoes hydrolysis [26]. Lignin undergoes polymerisation and condensation [22]. It is reported that the catalytic thermolysis generates highly reducing soluble and insoluble materials through Mailard reaction [10] along with the insoluble material formed by the reaction between soluble lignin, sugars and proteins [27].

The complexation reactions results in residue formation where as the fragmentation of the large complex molecules leads to the formation of smaller molecules. Due to the formation of insoluble particles (residue), and slight gasification of sulfurans and nitrogenous compounds and the organic matter, C, H, N, COD and BOD of the effluent decreases. From Table 1, it can be seen that the quantity of total carbon, carbohydrates, lignin, proteins and inorganics like sulphates, chlorides, phosphates, nitrogen, etc. reduced in the effluent after CT. This resulted in ∼60% COD reduction and ∼90% BOD reduction of the original DWW at 140 °C and pH_0 2. The COD/BOD ratio also increased from the initial 2.25–9.35 after thermolysis. Thus, the residual 40% (43.3 kg/m^3) COD and 10% (4.63 kg/m^3) BOD have to be

Table 2
Characteristics of the solid residue obtained from catalytic thermolysis at different treatment temperatures (pH_0 2, $t_R = 6$ h)

Temperature (°C)	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)	Total (%)	Solid residue (kg/m^3)	Convertible COD (%)	Heating value (MJ/kg)
100	42.10	3.50	2.70	3.11	29.47	19.12	100	18.1	28.3	17.56
120	44.36	3.70	2.88	3.32	27.71	18.03	100	20.53	44.62	19.21
130	45.21	4.11	3.06	3.67	27.31	16.67	100	23.33	51.2	19.86
140	47.07	4.22	3.77	3.71	14.44	19.78	100	28.71	60.1	21.77

further treated by such methods as WO/membrane separation to meet the statutory discharge standards. As has been shown by Garg et al. [28], the residual copper (199 mg/dm^3) present in the treated wastewater may be sufficient for the CWO process.

It is reported that during CWO of phenol using copper oxide mounted on activated carbon as a catalyst, the leaching of the active substance (CuO) is responsible for the catalyst deactivation [29]. It was also shown that the deactivation of the catalyst during CWO was unrelated to low pH but was associated with the formation of CWO intermediates. The study of thermolysis cum wet oxidation of alcohol distillery wastewater with mature timothy grass as the substrate for alcohol fermentation showed the loss of activity of Cu–NaY catalyst due to leaching of Cu cation [8]. The thermolysis is an anoxic process. After reaction, the majority of CuO gets transferred into the solid residue, and its recovery is difficult. Thus there is a catalyst loss, but no conclusive statement can be made about the deactivation of the catalyst.

Table 3 presents the comparison of the data for the pretreatment of DWW by different investigators. It is seen that the COD reduction at moderate temperature (140 °C) is comparatively higher than that of non-catalytic pre-treatment at a higher temperature (160 °C) and corresponding autogenous pressure [5,9]. The results show the efficacy of CT over that of the non-catalytic thermal pretreatment of DWW. Thus the CT process reduces the severity of the operating conditions considerably while giving comparable COD reduction efficiency.

3.5. Kinetics of thermolysis

The thermolysis process can be represented as

$$\text{complex organic matter} \xrightarrow[+\text{heat}+\text{H}_2\text{O}]{+\text{catalyst}} \text{solid residue} + \text{smaller organic molecules} + \text{water} + \text{gas} \qquad (1)$$

This reaction (1) can be written as a simple reaction:

$$A \xrightarrow[+\text{H}_2\text{O}+\text{heat}]{\text{catalyst}} B + C + D \qquad (2)$$

where A represents the host of complex organics, B the solid residue, C the smaller organic molecules and D the gas. Gas formation is too little and is, therefore, ignored. As will be shown later, C_w affects the reaction rate and the extent of COD reduction. The kinetics of CT may be represented by a simple power law rate equation:

$$-\frac{\mathrm{d}C_\text{A}}{\mathrm{d}t} = k_n C_\text{A}^n C_\text{w}^m \qquad (3)$$

where n and m are the reaction order with respect to COD and the catalyst loading, respectively, and k_n is the reaction rate constant. As observed in this study, the majority of the catalyst gets complexed with the solid residue and the residual copper is present in the solution. From the mechanistic point of view, the representation of the complex formation and COD reduction cannot be made completely to our satisfaction at present. Since the catalyst is not lost during thermolysis, the power law model seems to adequately represent the global kinetics of thermolysis.

For constant and optimum C_w, Eq. (3) reduces to

$$-\frac{\mathrm{d}C_\text{A}}{\mathrm{d}t} = kC_\text{A}^n \qquad (4)$$

where

$$k = k_n C_\text{w}^m \qquad (5)$$

Taking lumped organics to be represented by the COD of the DWW, C_A may be written as (COD), and Eq. (4) may be written as

$$-\frac{\mathrm{d(COD)}}{\mathrm{d}t} = k(\text{COD})^n \qquad (6)$$

Figs. 2 and 3 show that the COD reduction is fast during the initial reaction period. Later on, the reaction becomes slow.

Table 3

Comparison of results of different investigators on the treatment of sugarcane molasses based DWW

Investigators	Substrate	Treatment conditions and observations					
		Catalyst	Initial pH	Time (h)	Temperature (°C)	Pressure (bar)	% COD/TOC reduction
Daga et al. [5]	Distillery wastewater	Nil	4.5	6	230	Self Pr.	54
	$\text{COD}_0 = 60–100\ \text{kg/m}^3$		4.5	6	160	Self Pr.	35
Lele et al. [9]	Distillery wastewater	Nil	4.5	2	250	77	63.0
	$\text{COD}_0 = 108\ \text{kg/m}^3$		4.5	2	160	20	27.8
Belkacemi et al.[a] [10]	Distillery wastewater $\text{TOC}_0 = 22{,}500$	Nil		0.17	240	Self Pr.	57
Chaudhari et al. (present work)	Distillery wastewater	CuO	2.0	6	140	8.6	60
	$\text{COD}_0 = 108.4\ \text{kg/m}^3$	(3 kg/m^3)	2.0	2	140	8.6	51
			4.0	6	140	8.6	50
			4.0	2	140	8.6	38
Chaudhari et al. (unpublished)	Distillery wastewater	CuO		12	100	1.0	45
	$\text{COD}_0 = 34\ \text{kg/m}^3$	(3 kg/m^3)		2	100	1.0	13

[a] Wastewater from mature Timothy grass-based alcohol plant.

Thus the COD reduction is a two step process. This two step process manifests for all treatment temperatures and pH_0. Since the plot of COD reduction versus time is not linear, it is not a zero order reaction as reported by Lele et al. [9] for non-catalytic thermal pretreatment of DWW. Daga et al. [5] have reported first order kinetics for hydrolysis (thermolysis) of DWW. Belkacemi et al. [10] also reported first order (TOC removal) kinetics for thermolysis and wet oxidation of high-strength mature timothy grass-based alcohol distillery liquors. Based on the previous studies and the nature of the curve (COD reduction versus time) obtained in the present work, the process can be represented adequately by the first order reaction. Thus, Eq. (6) may be written as

$$-\frac{\mathrm{d(COD)}}{\mathrm{d}t} = k(\mathrm{COD}) \tag{7}$$

Integration of Eq. (7) gives

$$-\ln(1-X) = kt \tag{8}$$

where

$$X = 1 - \frac{(\mathrm{COD})}{(\mathrm{COD_0})}$$

The specific rate constant k can, thus, be estimated by plotting $[-\ln(1-X)]$ against treatment time, t. Fig. 4(a) show the plot of $[-\ln(1-X)]$ versus t for the experimental runs at pH_0 2 with $C_w = 3\,\mathrm{kg/m^3}$ for the treatment of DWW having $COD_0 = 108.4\,\mathrm{kg/m^3}$, at different T. This figure also shows a two-step reaction mechanism: the data being represented by two simple straight lines. Thus, both the steps can be represented by first order kinetics with respect to COD. Table 4 presents the values of rate constants k_1 and k_2, and the ratio k_1/k_2 as determined for different reaction temperatures. It is found that as the temperature is increased from 100 to 140 °C, the rate constant increases by more than 100% for both the steps. Further, the first step is found to be about three times faster than the second step, although, the increase in the rate of reaction with temperature in the second step is more than that in the first step.

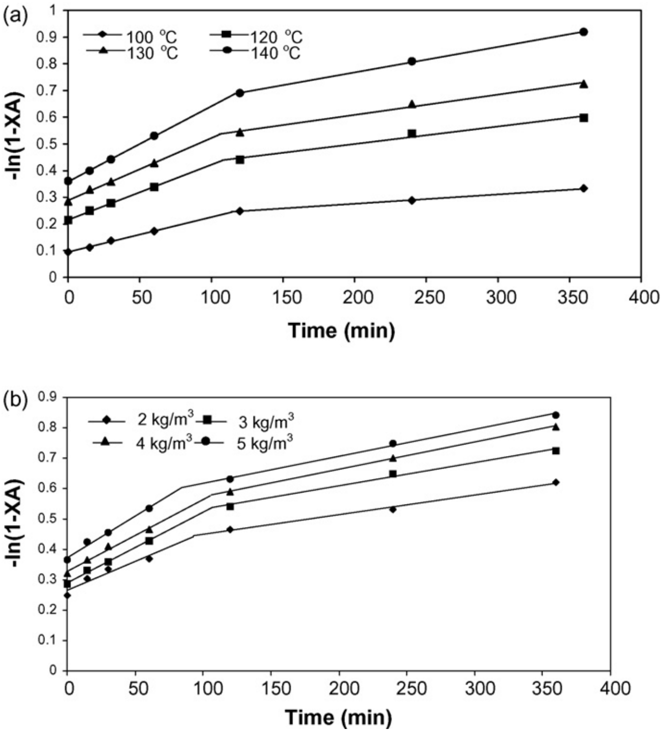

Fig. 4. (a) First order kinetics for catalytic thermolysis of DWW with respect to organic substrate. $COD_0 = 108.4\,\mathrm{kg/m^3}$, pH_0 2.0, $C_w = 3\,\mathrm{kg/m^3}$, P = self pressure. (b) First order kinetics for catalytic thermolysis of DWW with respect to organic substrate for different CuO catalyst mass loading. $COD_0 = 108.4\,\mathrm{kg/m^3}$, pH_0 2.0, $T = 130\,^\circ\mathrm{C}$, P = self pressure.

The effect of catalyst mass loading on the reaction rate constant was also studied at 130 °C.

Eq. (5) may be written as

$$\ln k = \ln k_n + m \ln C_w \tag{9}$$

Thus, if the plot of $\ln k$ versus $\ln C_w$ gives a straight line, the order of reaction, m for each of the reaction steps may be determined. Fig. 4(b) presents a plot for $[-\ln(1-X)]$ against t at different C_w.

The values of k_1 and k_2 for the first and second steps, respectively are given in Table 4. It is seen that the ratio, k_1/k_2, increases, although feebly, with an increase in C_w. Fig. 5 presents the plot of $\ln k$ against $\ln C_w$ for the first and second steps of the reaction. Eq. (9) is found to satisfactorily and adequately represent the experimental data. The order of reaction, m, with respect to catalyst loading is found to be 0.367 and 0.290 for the first and second step, respectively.

The activation energy and the frequency factor may be determined by Arrhenius equation as

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{10}$$

where T is in K, E is the activation energy and k_0 is the frequency factor.

Thus, a plot of $\ln k$ against $1/T$ (Fig. 6) should give the frequency factor and the activation energy. The activation energy, E for the first and second steps is found to be 24.2 and 29 kJ/mol, respectively. The corresponding values of the frequency factor are 3.25 and 4.76 $\mathrm{min^{-1}}$, respectively.

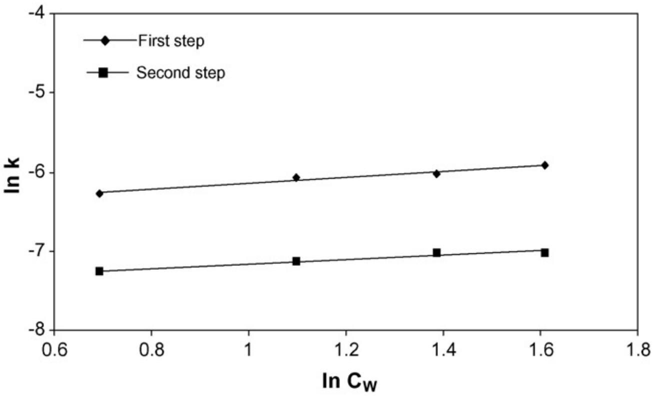

Fig. 5. Effect of concentration of CuO catalyst loading on reaction rate constant for catalytic thermolysis of DWW.

Table 4
First order rate constant (k) for the first and second reaction steps during catalytic thermolysis

Rate constant at different temperatures ($C_w = 3\,kg/m^3$)				Rate constant at different catalyst concentrations ($T = 130\,°C$)			
Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2	C_w ($kg\,m^{-3}$)	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2
100	0.0013	0.0004	3.25	2	0.0019	0.0007	2.71
120	0.0021	0.0007	3.0	3	0.0023	0.0008	2.875
130	0.0023	0.0008	2.87	4	0.0024	0.0009	2.89
140	0.0028	0.0010	2.8	5	0.0027	0.0009	3.0

The kinetic equation for the catalytic thermolysis process of the distillery wastewater in the temperature range of 100–140 °C and the corresponding autogenous pressure and with C_w in the range of 2–5 kg/m^3 and at an initial pH$_0$ 2 are, thus, given as

- first step

$$r_1 = -\left(\frac{d(COD)}{dt}\right) = 3.246 \exp\left[-\frac{2910}{T}\right] [COD]\,[C_w]^{0.367} \qquad (11)$$

- second step

$$r_2 = -\left(\frac{d(COD)}{dt}\right) = 4.766 \exp\left[-\frac{3490}{T}\right] [COD]\,[C_w]^{0.29} \qquad (12)$$

3.6. Filterability study

The filtration characteristics of the slurry obtained after the thermolysis of the DWW were studied on an ordinary filter paper (zerohaze Grade-A, pore size 7–11 μm, obtained from S.D. Fine Chemicals Ltd., Mumbai). This filter paper was supported on a ceramic Bueckner funnel. Since the pH of the solution is found to have profound effect on the filtration characteristics, the pH of the slurry was adjusted between 1 and 10. The filtration resistances for the filter media as well as filter cake were obtained using the following equation [30]:

$$\frac{dt}{dV} = k_c V + \beta \qquad (13)$$

where $k_c = c\alpha\mu/A^2(-\Delta p)$; $\beta = \mu R_m/A(-\Delta p)$.

A plot of dt/dV versus V with pH as the parameter is presented in Fig. 7. The values of k_c and β have been determined from the slope and intercept of the plot. The viscosity of the filtrate was determined at room temperature (18 °C) using Ostwald capillary viscometer. The α and R_m were estimated from k_c and β and these are presented in Table 5. It can be seen that the values of the medium resistance and the cake resistance for the filtration of the treated wastewater are the highest at pH$_0$ 10 and lowest at pH$_0$ 1, with the values at pH$_0$ 1 and pH$_0$ 2 being almost similar. This shows that the filterability of the slurry is maximum at pH$_0$ 1–2, and as the pH$_0$ of the wastewater is raised, the filterability deteriorates. The viscosity of the filtrate increases feebly with an increase in the pH$_0$ of the effluent. Thus, its effect on the filterability is found to be insignificant.

The values of specific cake resistance were in the range of 2–23 × 10^9. This range is somewhat similar to that reported by Chaudhari et al. [11] for BDE and Lele et al. [9] for DWW. Typical values of specific cake resistances for different sludges are given by Barnes et al. [31]. These values are 4–12 × 10^{13} m/kg for the activated sludge, 3–30 × 10^{13} m/kg for the digester sludge, 3–10 × 10^{11} m/kg for the conditioned primary sludge and 2–20 × 10^{11} m/kg for conditioned digested sludge. Thus, the specific cake resistance for DWW sludge is at least an order of magnitude lower than that for the conditioned primary and the digested sludges. Therefore, the DWW sludge

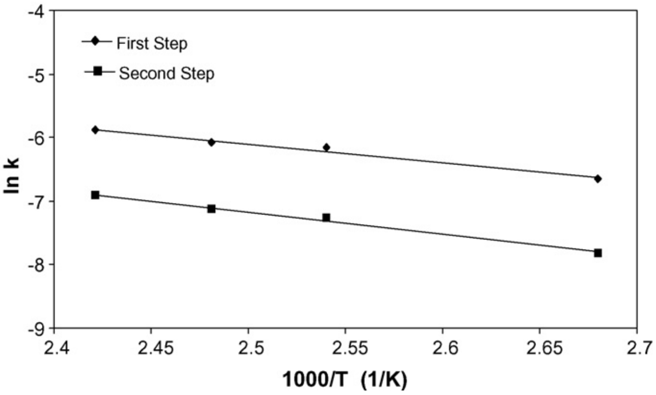

Fig. 6. Arrhenius plot for catalytic thermolysis of DWW.

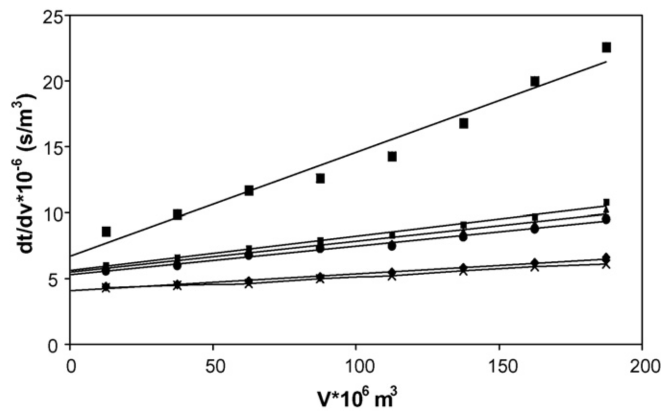

Fig. 7. Effect of pH on the filterability of DWW after thermolysis. $T = 140\,°C$, P = autogenous pressure, COD$_0$ = 108.4 kg/m^3, $C_w = 3\,kg/m^3$.

Table 5
Filterability of the treated wastewater (at $t = 140\,^{\circ}$C, $t_R = 6$ h, P = autogenous pressure)

Initial pH	k_c ($\times 10^{-12}$ s/m^6)	β ($\times^{10-6}$ s/m^3)	C (kg/m^3)	μ ($\times 10^3$ Pa S)	α ($\times 10^{-9}$ m/kg)	R_m ($\times 10^{-9}$ m^{-1})
1	0.0109	4.061	28.43	1.026	2.22	3.70
2	0.0128	4.086	28.71	1.084	2.61	3.51
4	0.0218	5.286	23.27	1.112	4.16	4.44
6	0.0235	5.473	19.81	1.177	5.99	4.35
8	0.0261	5.598	18.92	1.212	6.76	4.32
10	0.0788	6.682	17.7	1.150	23.0	5.43

has much better filterability than the municipal sludges. It may be realized that the fermentation conditions for ethanol production and the environmental and operating conditions prevailing within the biodigester also affect the filterability. It is alsoknown that the specific cake resistance for the filtration of the fermentation broth in mycelial fermentation decreases with decreasing pH under acidic conditions [32].

3.7. Analysis of the filtrate

The wastewater treated at 140 °C for 6 h (t_R) was filtered and some of the physical and chemical characteristics of the filtrate are listed in Table 6. It is observed that the filtrate contains dissolved copper. The specific gravity of wastewater is found to increase as the initial pH of the DWW is raised from 4 to 10. It is also observed that the final pH (pH_f) of the initially acidic liquor (upto pH_0 4) increases after the treatment and, thereafter, the pH_f of the treated wastewater decreases. The chromatographic analysis of the filtrate of the wastewater treated at pH_0 2, showed the absence of the lower carboxylic acids (formic acid and acetic acid). This means that the COD reduction during the thermolysis of DWW does not lead to the formation of carboxylic acids. Since the pH_f of the treated effluent at 140 °C and pH_0 2 is 2.28, the treated effluent is to be neutralized before being discharged into surface water bodies or the sewers. However, the thermolysis step is only the pre-treatment step and the pretreated effluent has to be treated further to meet the effluent standards for being discharged into sewers or receiving water bodies.

The studies on WO of the thermally treated biodigester effluent (effluent from the bio-methanation reactor of the distillery wastewater treatment plant) shows substantial increase in the final pH of the thermally treated effluent (from pH_0 1.5 to pH_f 4.35) [11]. With the nature of effluents (biodigester effluent and spent wash (DWW)) being similar, the thermally pre-treated spent wash (DWW) may be subjected to CWO and the pH severity of the process is expected to get reduced. The filtrate of the treated wastewater at pH_0 2, 140 °C and $t_R = 6$ h, contains ~199 mg/dm^3 of copper, which can work as a catalyst in the successive WO process.

Table 6
Analysis of the filtrate obtained after catalytic thermolysis at different pH_0 (and at $T = 140\,^{\circ}$C, $t_R = 6$ h, $COD_0 = 108.4$ kg/m^3)

Initial pH (pH_0)	Final pH (pH_f)	Color	Specific gravity[a]	COD (kg/m^3)	Dissolved copper concentration (mg/dm^3)
1	1.24	Orange	1.119	46.22	233
2	2.28	Orange	1.113	43.30	199
4	4.26	Black	1.109	54.40	138
6	4.70	Black	1.110	66.85	129
8	5.15	Black	1.113	77.73	127
10	8.67	Black	1.114	75.01	291

Viscosity of water at 18 °C = 1.059 Pa S. Specific gravity of water at 18 °C = 1.087.

[a] Determined at ambient temperature (18 °C).

Table 7
Analysis of the residue obtained after thermolysis (at $T = 140\,^{\circ}$C, $t_R = 6$ h)

	Initial pH					
	1	2	4	6	8	10
Weight of residue (kg/m^3)	28.43	28.71	23.27	19.81	18.92	17.7
Color	Black	Black	Black	Black	Brown	Greenish brown
Nature	Fine free flowing powder	Fine free flowing powder	Fine free flowing powder	Fine free flowing Powder	Fine sticky powder	1–2 mm granules
Approx. drying period (h)	3.0	3.0	4.0	4.5	6.0	10.0
Specific energy (MJ/kg)	19.95	21.77	19.44	18.20	17.26	17.08
% convertible COD	57.3	60.1	49.81	38.2	28.3	30.8
% energy recovery[a]	38.15	42.17	30.51	24.57	22.17	20.58
% Cu (by weight)	8.02	7.89	9.77	12.22	13.28	11.59

[a] Percent energy recovery = (specific energy × mass)$_{\text{residue}}$/(specific energy × mass)$_{\text{DWW}}$.

3.8. Analysis of the residue

The solid residue obtained after filtration was dried in an oven at 105 °C until its weight became constant. Its composition and some of its physical properties are presented in Table 7. It is found that the colour of the residue remains black upto pH_0 6 and then turns brown to greenish brown at pH_0 8 and 10, respectively. The residue obtained from lower pH_0 treatment shows free-flowing powder property, while the residue from the higher pH_0 treatment shows sticky character, and the solid particles show granular structure. It is also found that the drying period for the residue increases with an increase in the pH_0 of the wastewater for CT. It is also seen that at pH_0 2, the maximum energy recovery of ∼42% with a corresponding COD reduction (∼60%) and the highest specific energy (∼21.8 MJ/kg) are obtained through the residue formation. This specific energy (21.8 MJ/kg) is marginally less than that reported by Lele et al. [9] for the charred residue (22.7 MJ/kg) obtained after non-catalytic thermolysis of DWW and greater than that reported by Chaudhari et al. [11] for the charred residue (17.9 MJ/kg) obtained after CT of the biodigester effluent (BDE). The lower specific energy than that of Lele et al. [9] is because of the treatment at lower temperature and pressure and the presence of CuO in the residue. The higher specific energy than that of BDE [10] may be attributed to the presence of more carbon and hydrogen in DWW than that in BDE, which have been transported to the charred residue. The charred residue is found to be free flowing and easily grindable in comparison to BDE charred residue [11].

3.9. Material balance for copper

Copper is a heavy metal and the permissible copper concentration in discharge wastewater is 3 mg/dm^3 [3]. In order to test the accuracy of the analysis using AAS, copper material balance was made for the DWW, residue and the filtrate. The material balance for Cu was satisfied within the permissible range of error as seen from Table 8. The residue, however, shows high copper retention. This copper will get transferred to the ash if the residue is used as a fuel. The ash can be blended with the organic manure and be used as copper-rich nutrient for agriculture and horticulture.

3.10. Overall material balance

The distillery wastewater, residue and the final filtrate were dried and analyzed for C, H, N, S and the ash. The composition of the effluent, filtrate and the charred residue obtained from a typical run (140 °C, pH_0 2) are given in Table 9. The overall material balance as well as component material balance are found to be well satisfied. It may be seen that the sum of the ash

Table 8
Material balance for copper

Temperature (°C)	Initial pH_0	Cu in residue mg/dm^3	Cu in filtrate mg/dm^3	Total Cu (filtrate + residue) mg/dm^3	% error
100	2	2340	230	2570	2.16
120	2	2320	280	2600	1.03
130	2	2310	297	2607	0.76
140	2	2320	199	2519	4.11
140	1	2315	233	2548	2.97
140	4	2348	203	2551	2.89
140	6	2390	129	2519	4.11
140	8	2410	127	2537	3.42
140	10	2311	291	2602	0.76

Cu used as catalyst = 3 g/dm^3; amount of wastewater = 0.3 dm^3; weight of CuO = 0.9 g/0.3 dm^3; weight of Cu = 0.788 g/0.3 dm^3; initial concentration of Cu in the DWW = 0.788 g/0.3 dm^3 = 2.627 g/dm^3 = 2627 ppm (w/v). % error = [(initial Cu concentration in the DWW − total Cu concentration from the filtrate and the residue)/(initial concentration in the DWW)] × 100.

Table 9
Composition of DWW, filtrate and residue (T = 140 °C, pH 2, C_w = 3 kg/m^3)

	Total solid (%)	C	H	N	S	O[a]	Ash	Total
Dry basis composition (%)								
DWW	8.45	34.76	5.87	3.0	3.8	29.91	22.66	100.0
Filtrate	5.42	27.57	5.03	3.06	4.74	32.94	26.66	100.0
Charred residue	100	47.07	4.22	3.77	3.71	21.45	19.78	100.0

	Total solid (%)	C (×10^3 kg)	H (×10^3 kg)	N (×10^3 × kg)	S (×10^3 kg)	Ash (×10^3 kg)	C:H atomic ratio
Material balance (bases: 10^{-3} m^3)							
DWW	84.54	29.39	4.96	2.54	3.21	19.15	1:2.03
Filtrate	54.21	14.96	2.72	1.66	2.29	14.45	1:2.18
Charred residue	28.71	13.51	1.21	1.08	1.06	5.67	1:1.08
Total of filtrate and residue	82.92	28.47	3.93	2.74	3.35	20.12	
% error	1.91	3.13	20.76	7.87	4.36	5.06	

[a] Oxygen (O) was calculated by the balance of CHNSO ash to 100.

content for the filtrate and the residue is more than that for the distillery wastewater. However, it may be noted that the residue also contains copper in it and this increase may be attributed to it. The error in the balance is found to be less than ±8% except for the hydrogen. The high value of error in the hydrogen and nitrogen balance may be attributed to the formation of some hydrogenous and nitrogenous gases, which are formed during the thermolysis process and escape when the lid of the autoclave is opened.

4. Conclusions

The thermolysis is found to be an effective process for the treatment of DWW. Treatment at 140 °C with $C_\mathrm{w} = 3\,\mathrm{kg/m^3}$ and pH_0 2 results in a maximum of 60% COD removal, mainly due to formation of insoluble and settleable solid residue.

The CT process using CuO as a catalyst is found to very effective as the reaction rate constant and the extent of COD reduction at moderate temperatures (130–140 °C) and autogenous pressures (7–8 bar) are found to be comparable to that reported by other workers through non-catalytic thermolysis, at considerably higher temperatures (200–250 °C) and autogenous pressures (70–80 bar).

The kinetics of thermolysis of DWW shows a two step mechanism: the first step being much faster than the second step. Each step obeys the first order reaction kinetics with respect to COD and a fractional order 0.37 and 0.29 with respect to catalyst mass loading for the first and second steps, respectively.

The CT process produces settleable and insoluble solid residue. The solid residue obtained at 140 °C and pH_0 2, has a C:H atomic ratio of 1:1.08 and a heating value of 21.77 MJ/kg. The slurry obtained after the thermolysis has very good filtration characteristics. The residue can be used as a fuel in the combustion furnaces to recover its energy content and the ash containing Cu may be blended with organic manure and used as a nutrient-rich manure in agriculture and horticulture.

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