Sugarcane molasses based alcohol industry represents one of the largest segments in the Indian chemical industry. The aqueous waste stream left after the recovery of alcohol from the fermented molasses is known in different ways such as spent wash, slope, vinasses, stillage etc., depending upon the distillery unit. The aqueous waste stream is one of the most complex effluents having high biological oxygen demand (BOD) and high chemical oxygen demand (COD). The fermentation of molasses to produce alcohol results in a waste stream having a COD of the order of 1,50,000 - 1,90,000 mg/L. Typically, production of 1 T of 95% alcohol requires about 5.5 T of molasses and produces around 16 m³ of effluent. The waste stream thus produced is difficult to treat. Various primary treatment processes like anaerobic lagooning, incineration, bio-methanation, electro-chemical oxidation etc. are available to treat the waste. Lele et al. have demonstrated the combined process to treat the effluent by thermal pre-treatment followed by wet oxidation with energy recovery.

Presently, bio-gas generation as a primary treatment process is gaining popularity in the waste management of a distillery waste stream because biogas thus generated could be fuel feedstock for cogeneration unit. Typically, 25 Nm³ of biogas is generated per cubic meter of effluent. The residual waste after bio-gas generation is dark in color and exhibits very high COD. Typically, the COD of such a stream could be in the range of 20,000 to 40,000 mg/L. Conventionally, this stream is subjected to secondary treatment, where COD is further reduced by aeration. However, the residual waste after secondary treatment is dark in color and still has COD around 8,000 to 10,000 mg/L. The stringent inland water discharge standards, in years to come, would demand COD to be far less than 200 mg/L and color to be practically nil. The present standards vary depending upon the location and discharge point of stream e.g. discharge in river, sea or on an agricultural land. The stringent environmental regulations for discharge make it desirable to treat the waste by a suitable technology to meet the local discharge standard laid down by pollution control boards of the respective states. Hence, intensive research activities are needed in this area to investigate, evaluate and develop a techno-economically feasible system for secondary treatment of spent wash.

There are many possible ways of making the waste stream after bio-gas generation eco-friendly such as wet oxidation, use of oxidizing agents such as O₃, ozone, hydrogen peroxide and so on. However, wet oxidation seems to be a viable solution to treat the waste. Wet oxidation of distillery waste was reported by Daga et al., and subsequently reviewed by Mishra et al. Wet oxidation (WO) involves oxidation of...
organics and inorganics compounds in water at a temperature between 150-350°C and total pressure ranging from 5 to 15 MPa using air or oxygen. Wet oxidation technology has been found to be effective to treat various industrial effluents. Wet oxidation is capable of treating priority pollutants and also to making the effluent suitable for discharge or recycle. However, capital investment in wet oxidation plant is very high due to high operating temperature, pressure and exotic material of construction for the reactor since the waste stream may contain corrosive constituents like chloride ions. The capital cost can be reduced by concentrating the waste by membrane filtration or adsorption, thereby offering a bright possibility of recovering and recycling the water. The concentrate being less in volume permits a smaller wet oxidation system thereby, gaining an economical advantage.

The waste stream needs a pretreatment for membrane filtration before concentrating the waste to avoid fouling and degradation of the membrane. Hence, the present investigation to treat the waste stream after bio-gas generation has an aim to develop a suitable pretreatment for membrane process and to study the wet oxidation for its discharge. Pretreatment consists of thermal treatment followed by soda-lime treatment. The concentrate stream from membrane containing high COD and color bearing compounds after this treatment can be subjected to wet oxidation. During wet oxidation low molecular weight acids such as formic, acetic acid are formed. Acetic acid is very stable acid towards wet oxidation. Its concentration progressively increases as wet oxidation proceeds. In the present investigation, wet oxidation was studied to make the stream not only suitable for discharge but also to have acetic acid from wet oxidation process. This acid can be recovered by conventional technique. There exists practically no information on such a hybrid process, which consists of pretreatment, membrane and wet oxidation to maximize acetic acid production. In the present study, attention has been focussed on such a study. The actual stream was obtained after bio-gas generation from a progressive sugar mill in Maharashtra.

**Experimental Procedure**

**Materials**

The effluent samples of distillery waste used in the investigation were obtained from a progressive cooperative sugar mill, in the state of Maharashtra, India. The samples were collected after bio-gas generation. Typical analysis is given in Table I. The reagents for analysis and other chemicals were used of A. R. grade and obtained from S. D. Fine Chem. Ltd, Mumbai. Oxygen with a minimum purity of 99.5% was used for wet oxidation and was obtained from Maharashtra Oxygen Ltd., India. A. R. grade ferrous sulfate was used as a catalyst. The flocculents used were of commercial grade, supplied by Pidilite Industries Ltd., Mumbai.

**Analytical procedure**

Chemical oxygen demand (COD) was analyzed by the standard dichromate reflux method described by Snell. Acetic acid formed during wet oxidation was analyzed on gas chromatography unit, Chemito 3865 (manufactured by Toshniwal Instruments Ltd, Mumbai). A glass column packed with Carbopack BD-A 4% and Carbowax 20M was used with FID and operated at an isothermal temperature, 140°C, to analyze the acids. The N₂ carrier gas flow was 40 mL/min, detector and injector temperature was kept at 190°C. The chloride ions were determined by standard titrimetric Volhard's method whereas potassium ion was analyzed by “DIONEX High Performance Ion Chromatography using CS1 column and a post column reactor. The samples were also analyzed for color by Hazen (APHA) method using a standard solution of potassium chloroplatinate and cobalt chloride as well as on UV/VIS spectrometer (Chemito 2100, Toshniwal Instruments Ltd, Mumbai). The light absorbance was measured spectrophotometrically and was used to infer percentage reduction in color.

**Experimental equipment**

Fig. 1 depicts the schematic diagram of the experimental set up. The thermal treatment and wet

| Table 1—Typical Characteristics of distillery waste after bio-gas generation |
|-----------------------------|-----------------------------|
| Contents                  | Concentration               |
| Chemical Oxygen Demand (COD)| 35,000 mg/L                 |
| Color                     | 37,000 Hazen (APHA)         |
| pH                        | ~7.70                       |
| Sp. Gravity               | 0.98 gm/mL                  |
| Total suspended solids (TSS)| 1.371 % (w/v)              |
| Total dissolved solids (TDS)| 3.426 % (w/v)              |
| Cl⁻ ions                  | 7500 mg/L                   |
| K⁺ ions                   | 4800 mg/L                   |

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oxidation experiments were carried out in 2L capacity SS-316 autoclave (Sharad Engineering Works, Mumbai) equipped with a variable pulley driven turbine type impeller and a temperature controller. The reactor has an inner diameter of 102 mm and impeller diameter 52 mm and was equipped with a pressure indicator, a gas sparging tube into the liquid phase beneath the impeller and sample collection outlet with condenser. The reactor was also provided with a rupture disc as well as a non-return valve at the gas inlet. The liquid samples were collected through a chilled condenser-cum-cooler mounted on the reactor. A mechanically agitated glass vessel of 1000 mL volume fitted with a four straight turbine agitator was used for lime and soda treatment.

Procedure

The spent wash after bio-gas generation was thermally treated in the autoclave at 150°C under self pressure for 40 min in the absence of air. It was then filtered at ambient conditions and subjected for soda-lime treatment in a glass reactor. The samples were treated first by lime followed by flocculation at a gentle speed for 20 min and then allowed to settle for 30 min. The sample was filtered and treated with sodium carbonate to remove dissolved calcium.

Wet oxidation experiments were carried out by taking the above-pretreated waste of known concentration (600-800 mg/L) in the reactor in a batch mode of operation at near neutral pH. In a typical experiment, a sample was charged into the reactor and heated to the desired temperature. As soon as the desired temperature was reached, a sample was collected through a sample condenser and this was referred to as “zero” time sample for kinetic measurements. In catalytic reaction, a catalyst of known concentration was added while charging the solution in the reactor. As soon as the ‘zero time’ sample of the reaction was collected, oxygen was sparged in the reactor to a predetermined pressure level and maintained at it while, collecting samples for COD and color analysis. The total pressure is the sum of oxygen pressure and vapor pressure. In all experiments, it was ensured that the oxygen was available in far excess than that theoretically required. The experiments were carried out at different temperatures, oxygen pressure and at various catalyst concentrations for the kinetic study. The experimental variation in COD measurement was found to be less that 5%.

Results and Discussion

Pretreatment

The physical and chemical coagulation method is
 generally used for color removal in wastewater. Lime, Ca(OH)$_2$ as an adsorbent is effectively used. However, it is expensive as it results in excess sludge generation and high de-watering and disposal cost. Flocculating agents such as polyelectrolytes can reduce the quantity of lime required for adsorption. In the present study, commercially available polyelectrolyte Magnafloc 1101 was used. Magnafloc 1101 is a lower molecular weight anionic synthetic flocculant and can be effectively operated in wide range of pH 5 - 12.

After thermal treatment and filtration of spent wash at around 30°C, stream was then subjected to lime adsorption. Adsorption was carried out with a flocculant in a glass reactor at a gentle speed of agitation. After allowing the sludge to settle for 30 min, sample, was analyzed for COD and color and studies were carried out for optimization. The concentration of lime was varied from 0 to 5% by w/v and flocculent dosage was given upto 100 ppm (v/v). After removing the sludge, sample was treated with sodium carbonate to remove the dissolved calcium in the form of calcium carbonate, which is detrimental to the membrane process as it contributes to the hardness of water.

Water recovery from such a waste by separation processes like membrane, ion exchange faces serious problems due to the high COD and total dissolved solids (TDS) content. Therefore, it is desired to have a pretreatment to make it amenable for membrane process. The pretreatment described here considerably reduced the COD as well as total dissolved solids (TDS). The characteristics of waste after the treatment are shown in Table 2. However, membrane processes are always associated with the drawback that a concentrated residue remains for disposal and it needs to be treated by a suitable technology before it is discharged. In the present investigation, wet oxidation was chosen to treat the pretreated waste. The concentrate from, the membrane unit is expected to have more or less same chemical compounds. Therefore, pretreated waste stream (after lime treatment) has been taken for wet oxidation study. The objective was not only to treat the waste to make it suitable for discharge but also to maximize acetic acid formation. Acetic acid formed during wet oxidation can be recovered by extraction technique thereby generating wealth from the waste stream.

**Table 2—Pretreatment of distillery waste after bio-gas generation.**

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>COD: 22,000 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>Colour: 27, 300 Hazen</td>
</tr>
<tr>
<td>Time</td>
<td>TDS: 1.52% (w/v)</td>
</tr>
</tbody>
</table>

*Fig. 2* — Performance of catalytic and non-catalytic wet oxidation (Temperature, 210°C; O$_2$ pressure, 0.69 MPa; FeSO$_4$, 9.6234 x10$^{-4}$ kmol.m$^{-3}$)

*Fig. 3* — Kinetic plot for non-catalytic wet oxidation at different temperature and oxygen pressure

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The wet oxidation experiments were carried out in the temperature range of 180-225°C using O$_2$ partial pressures between 0.414-1.38 MPa. The initial concentration of waste was 600-800 mg/L of COD. This ensured that the system is free from mass transfer limitation.
During wet oxidation, formation of highly refractory lower molecular weight carboxylic acids like formic, acetic, glyoxalic, oxalic etc takes place\textsuperscript{10}. The oxidation of lower molecular weight acids is the rate controlling step in wet oxidation and severe oxidation conditions are required to destroy them. However, if a desirable quantity of acetic acid in a wet oxidation unit is produced by a suitable catalyst, which can easily be recovered by the conventional extraction process, then valuable chemicals can be recovered. Thus wealth can be obtained from waste. In the present investigation, cheaply and readily available homogeneous ferrous sulfate catalyst in the form of FeSO\textsubscript{4} was chosen to study the performance of the wet oxidation process and also to observe acetic acid formation. The sulfate ions are more docile than chloride ions in the presence of oxygen towards material of construction hence ferrous sulfate was preferred to chloride as a catalyst. The residual iron after wet oxidation can be removed from the aqueous stream by conventional techniques e.g. precipitation as hydroxide.

**Kinetic study** — Wet oxidation is a gas-liquid reaction involving various transport processes that take place in series. Since oxygen has higher diffusivity in gas phase and lower solubility in water, the gas-phase mass transfer resistance is negligible in the operating temperature range of 180-225°C. In the preliminary experiments at higher temperature 240°C, the rate of oxidation was found to be independent of the impeller speed between 6.7-13.6 rps also indicating the absence of liquid-side mass transfer resistance\textsuperscript{16}. All subsequent experiments were carried at the impeller speed of 13.6 rps. Since the concentrations of waste in aqueous solutions were very low, COD ~ 800-900 mg/L, the solubility of oxygen in water was estimated from the data published by Crammer\textsuperscript{17}. The destruction of organics via wet oxidation technique is known to be a combination of various free radical reactions\textsuperscript{18-20}. The wet oxidation reaction scheme for any organic compound can be represented as,

\[
\text{Organic substrate} + O_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(1)}
\]

\[
\text{(COD)}
\]

\[
\text{low molecular weight acids (formic, acetic etc.)}
\]

The destruction of COD to CO\textsubscript{2} and H\textsubscript{2}O could be a combination of various reactions. Thus, in wet oxidation, the reaction would exhibit different kinetic behaviour, namely the fast oxidation of organic substrate to CO\textsubscript{2}, and acids, in parallel followed by the slower oxidation of low molecular weight compounds formed such as acetic acid to CO\textsubscript{2}. The kinetics of acids mineralizing to CO\textsubscript{2} is very much influenced by the presence of other species and thus modeling of wet oxidation becomes too complex. Each species exhibits its own influence and also exhibits different kinetics of mineralizing to CO\textsubscript{2}. However, for ease of design, a lumped or global kinetics of COD destruction to CO\textsubscript{2} and H\textsubscript{2}O is considered. Thus to make modeling approach more
meaningful and process environmental engineer friendly, the following series reaction is proposed as the lumped model.

\[
\text{(COD)}_{\text{waste stream}} \xrightarrow{k_1} \text{(COD)}_{\text{lower mol wt compounds}} \xrightarrow{k_2} \text{CO}_2 + \text{H}_2\text{O} \quad \ldots (2)
\]

The knowledge of kinetics of both steps is essential for one may employ biological treatment after the first fast step of COD reduction or complete oxidation is desired. Order with respect to oxygen could depend on the contribution of the various free radical reactions involving O\(_2\). The kinetic data for catalytic and non-catalytic wet oxidation reactions were interpreted as studied earlier\(^{21}\) and the rate equations obtained.

It was observed that in non-catalytic oxidation at \(225^\circ\text{C}\) and at 0.69 MPa oxygen pressure; about 70% COD reduction was achieved within 120 min. The color reduction was found to be more than 95%. Catalytic oxidation using ferrous sulfate (FeSO\(_4\)) was studied in the temperature range of 180 - 210\(^\circ\text{C}\) and oxygen partial pressure range of 0.414 - 1.38 MPa. Catalyst loading was varied in the range of 1.9247 \(\times\) \(10^{-5}\) to 9.6234 \(\times\) \(10^{-4}\) kmol m\(^{-3}\). At a catalyst loading of 9.6234 \(\times\) \(10^{-4}\) kmol m\(^{-3}\), maximum COD reduction of 60% with about 95% colour removal was achieved at 180\(^\circ\text{C}\) in 120 min at 0.69 MPa oxygen pressure. A comparative study of catalytic and non-catalytic oxygen at similar conditions can be seen in Fig. 2. It clearly indicates that the performance of wet oxidation is enhanced in the presence of Fe\(^{2+}/\text{Fe}^{3+}\) as catalyst. It was observed that use of Fe\(^{2+}\) or Fe\(^{3+}\) did not make any noticeable effect in the COD reduction. The effect was studied with an equivalent amount of iron as ferric sulfate.

Over the entire temperature range studied, the reaction was found to obey first order kinetics with respect to COD though other orders were also tried. The reaction kinetics could be well explained by order with respect to substrate as one. Kinetic plots for non-catalytic and catalytic oxidation are shown in Figs 3 and 4, respectively, indicating the two step mechanism. The Arrhenius plot showing ln \(k\) vs \(1/T\) is exhibited in Figs 5 and 6. The energy of activation for the first and second step was found to be 65.74 kJ mol\(^{-1}\) and 8.45 kJ mol\(^{-1}\), respectively, for non-catalytic oxidation. In case of catalytic oxidation, similar kinetics was observed and activation energy was found to be 33.06 kJ mol\(^{-1}\) and 30.6 kJ mol\(^{-1}\) for the first and second steps, respectively. Based on the above experimental findings, the global rate equation for non-catalytic wet oxidation was developed and given below:

**Kinetic equations**

**Non catalytic oxidation of distillery waste:**
(Temperature; 200-225\(^\circ\text{C}\), O\(_2\) pressure; 0.69 MPa, pH \(\sim\)7)

First step

\[
r_1 = -\frac{d(\text{COD})}{dt} = 8.25 \times 10^4 \exp\left[-\frac{7945}{T}\right]([\text{COD}][\text{O}_2])^{1.45} \ldots (3a)
\]

Second step

\[
r_2 = -\frac{d(\text{COD})}{dt} = 0.002 \exp\left[-\frac{1024}{T}\right]([\text{COD}][\text{O}_2])^{1.45} \ldots (3b)
\]

**The catalytic oxidation of distillery waste:**
(Temperature; 180-210\(^\circ\text{C}\), O\(_2\) pressure; 0.69 MPa, Catalyst FeSO\(_4\); 1.9247 \(\times\) \(10^{-5}\) - 9.6234 \(\times\) \(10^{-4}\) kmol m\(^{-3}\); pH \(\sim\)7)

First step

\[
r_1 = -\frac{d(\text{COD})}{dt} = 3.1 \times 10^4 \exp\left[-\frac{3996}{T}\right][\text{COD}][\text{O}_2]^{1.45} [\text{FeSO}_4]^{1.46} \ldots (4a)
\]
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Fig. 7 - Acetic acid formation in catalytic wet oxidation
(02 pressure, 0.69 MPa; Catalyst FeSO4, 9.6234x10^-4 kmol.m^-3, HQ, hydroquinone, 55 mg/L).

Second step

\[ r_2 = \frac{d(COD)}{dt} \]

= 20.35 \exp\left(\frac{-3697}{T}\right)[COD][O_2]^{0.78}[FeSO_4]^{0.17} \quad \ldots (4b)

Wet oxidation efficiency with respect to COD and color destruction increased with increase in temperature, oxygen partial pressure and catalytic loading. Potassium and chloride ions remain same throughout the experiments. The lower dependency of destruction of COD on the catalyst concentration (Eq. 4-b) indicates ineffectiveness of the catalyst in destroying COD due to low molecular weight acids.

Acetic acid formation — Wet oxidation of the organic substrate forms low molecular weight acids such as acetic acid. The acetic acid formed is one of the major intermediates in wet oxidation. Experiments were carried out to maximize acetic acid formation so as to recover the acetic acid as wealth from waste, since acetic acid is a valuable byproduct.

Trace amounts of acetic acid were observed in non-catalytic oxidation. However, in catalytic oxidation at 225°C and 9.6234x10^-4 kmol m^-3 FeSO4, formation of 30 ppm acetic acid took place after 20 min and it became steady at around 40 ppm after 60 min. This explained that the catalytic and non-catalytic process of wet oxidation follow different paths. The profile of acetic acid formation at different conditions is shown in Fig. 7. It was observed that during catalytic oxidation, acetic acid concentration increased with increasing temperature showing a maximum of 80 ppm at 240°C. However, to further enhance acetic acid formation, a trace amount of hydroquinone was added. It is well known that the presence of a redox catalyst like Fe(II) – Fe(III) is well suited for the system ‘quinone = hydroquinone’. Oxidation of hydroquinone provides H2O2 which further reacts with Fe(II) producing strong OH• radicals for oxidation as shown below.

\[ 2Fe^{2+} + 1/2O_2 \rightarrow 2Fe^{3+} + O^2^- \quad \ldots (5) \]

\[ RH + OH^- \rightarrow H_2O + R^- \quad \ldots (9) \]

\[ RH + HO_2^- \rightarrow H_2O_2 + R^* \quad \ldots (10) \]

In a typical experiment at 225°C in presence of 55 ppm of hydroquinone, a sharp increase in acetic acid level was observed. The amount of acid increased almost twice otherwise at similar conditions is shown Fig. 7. The acid thus produced can be recovered by conventional liquid-liquid extraction technique. Thus wet oxidation offers a bright possibility of not
only to making waste streams suitable for discharge but also recovering the value-added product like acetic acid from the waste stream. Also, as expected, addition of hydroquinone showed a marked enhancement in initial COD reduction rate due to availability of more free radicals. The results are compared in Fig. 8.

Conclusion
The pretreatment of distillery spent wash after biogas generation consisting of thermal treatment at 150°C under pressure in absence of air followed by sodalime can considerably reduce the COD and TDS load. The waste after pretreatment achieved 40% COD and 30% colour reduction.

The wet oxidation of pretreated waste was successfully employed to treat distillery effluent for its suitable discharge. Wet oxidation of distillery waste is effective in the removal of colour and COD. More that 95% of colour can be removed by wet oxidation at 225°C and 0.69 MPa oxygen partial pressure for 2 h with COD 70% reduction. A homogeneous catalyst ferrous sulfate is found to be suitable for wet oxidation, which reduces the severe conditions of wet oxidation. Catalytic wet oxidation with FeSO₄ increases acetic acid formation. With moderate temperature and oxygen partial pressure, the acetic acid formation can be still increased by addition of hydroquinone (−5% (w/w) of COD) taking advantage of higher COD reduction rates.

The wet oxidation of distillery waste was found to proceed with two distinct steps. The predicted global rate equations based on dilute waste were found to be useful and were applicable for the actual waste.

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The author A D Dhale is grateful to the University Grants Commission (UGC), Government of India, New Delhi, for awarding the Senior Research Fellowship.

Nomenclature
COD = chemical oxygen demand, mg/L  
BOD = biological oxygen demand, mg/L  
TDS = Total dissolved solids

TSS = Total suspended solids

\[ [O_2] \] = oxygen concentration, kmol.m⁻³

\[ r \] = rate of oxidation reaction with respect to COD reduction, mg/L.s

\[ T \] = Temperature, K

\[ [COD]_0 \] = initial COD, mg/L

\[ [COD]_t \] = COD (mg/L) at time “t” (s)  

\[ t \] = time, s

References