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Effluent Water Treatment of BTL Process Using Activated Sludge Technique

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ABSTRACT─ Conversion of biomass to liquid fuels (BTL) is an important process which produce significant amount of effluent water. Treatment and reuse of this effluent water will make the process more sustainable and environmental friendly. Activated sludge method was utilized to remove organic pollutants from BTL effluent water in a bench scale experimental system. Investigation of operating parameters showed that 93% removal of organic pollutants was obtained for the feed with COD value of 1500 mg/L in the pH range between 5.5-6 or 7.5-8.
Keywords: BTL effluent water, activated sludge, COD, organic pollutant

Introduction

Energy and water are among the most crucial needs of human to survive. Water scarcity as an outcome of an increase in consumption (by the growth of the world's population) along with the discriminate use of water and mismanagement; have resulted in drought of many part of the world and imminent risk of climate change. Besides, depletion of fossil energy resource and the carbon emission released by the consumption of conventional fuels, have compromised the environment and highlights the importance of energy security and renewable energy[1] Renewable energies have gained attention during the last decades, while some technical and economic challenges have been faced. Improving energy processes by the prospect of sustainability is one of the most important efforts which should be investigated. Synthesis gas (syngas) as main product of biomass gasification process contains mostly hydrogen and carbon monoxide[2 ,1] . Hydrogen can be separated from syngas and purified for electricity generation while syngas can be converted into the liquid fuels via Fischer-Tropsch synthesis (FTS) process3][. FTS process requires a catalyst with a long lifetime, good activity and high selectivity toward liquid products. Cobalt catalyst has been proven as a suitable catalyst for FTS process due to its higher selectivity toward linear hydrocarbons than iron catalyst, and lower cost compared to the ruthenium based catalysts4][. There is a great potential for synthesis gas production through bio-based materials all over the world. Hence, the importance of conversion of biomass to liquid fuels (BTL) process for producing value-added products from biomass derived synthesis gas seems obvious.[5]

As seen in Figure 1, BTL process consists of three steps. First, feedstock enters the process of syngas generation. Next, after syngas treatment, CO and H_2 enter the FTS process. In the presence of cobalt catalyst, syngas is converted to the long-chain hydrocarbons (mostly paraffin) by the general reactions indicated in Equations 1 and 2.

$$CO + 2H_2 \rightarrow (\text{-}CH_2\text{-}) + H_2O \quad (1)$$

$$2CO + H_2 \rightarrow (\text{-}CH_2\text{-}) + CO_2 \quad (2)$$

Products are further upgraded and separated so that condensed effluent at the end of the process can be obtained both from the FTS and from upgrading unit. Water and carbon dioxide are two main by-products of this process. BTL process produces approximately 1.25 barrel of water per one barrel of hydrocarbon products. This water contains organic matters as well as toxic formaldehydes. So, it is necessary to be treated to meet current standards for discharge to environment or re-use for agricultural purposes.

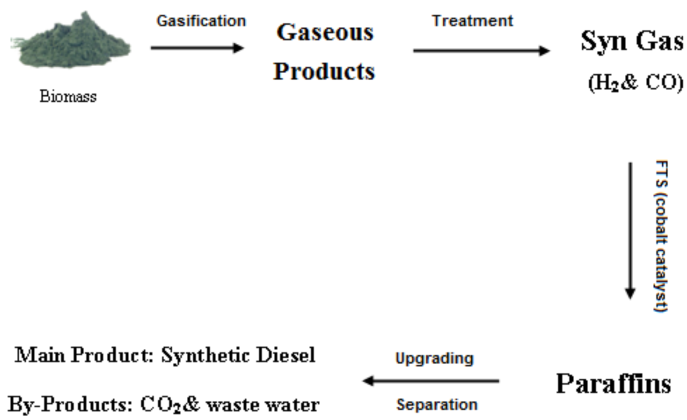

Figure 1. Schematic of biomass to liquid fuels process

There are different technologies have been used for waste water treatment including chemical treatment, membrane processes, evaporation, activated carbon adsorption etc. 6]7 ,[. Most of the produced hydrocarbons in petroleum industry can be treated by some of the micro-organisms via a biological process into H_2O and $CO_2$8][. The rate of the biological treatment of hydrocarbons is depended on various parameters including temperature, PH, Salinity, heavy metal concentration, type of hydrocarbon and the concentration of hydrocarbon and nutrients9][. Hence, these parameters should be efficiently controlled to gain a high performance treatment. In aerobic biological treatment, oxygen is needed for converting hydrocarbons into CO_2 and H_2O10][. Furthermore, lack of nutrients in biological treatment inhabits the process. The amount of this nutrient should be sustained; otherwise, these nutrients should be added into the system. Normally, there is a considerable amount of formaldehydes (HCHO) in the BTL effluent which is toxic and makes a disturbance in the growth of microorganism. In this case, there are some bacteria which consume formaldehydes as a feed. The main species of this bacteria are Methylotrophs Type I, Type II Methylotrophs, and M.Methanica.[11] Active sludge process is the most common method for treatment of petroleum waste water. In this method, a bulk layer of microorganisms is formed to aerobic stabilization of waste materials. This study aims to treat the effluent water of BTL process via activated sludge method for regaining considerable amount of water for agricultural application by removing the toxic materials and aerobic degradation of hydrocarbons (mostly alcohols) in the effluent water. The main aim of this study is treatment of BTL process effluent water to reuse it in agriculture and irrigation. The importance of such technologies for Iran, as a country with the high risk of aridity, seems noticeable and urgent.

Materials and Methods

1. BTL effluent water characteristics

The properties of BTL effluent water using cobalt catalyst are shown on Table 1. According to this table, the effluent water contains considerable amounts of methanol. Furthermore, it can be expected that trace amount of cobalt will be present in the form of suspended particles which may be separated physically by API and DFI units. Also, there are also some hydrocarbons remained in the water. As mentioned in Table 1, methanol as an alcohol is the major component in the BTL effluent water.

Table 1. Characteristics of BTL effluent water

Component description	Mass flow rate	Units
Methanol	0.245	wt %
Ethanol	0.005	wt %
n-Propanol	2.75	ppm
n-Butanol	5.25	ppb
Aldehydes and Ketones	<0.1	wt %
Total organic acids	<0.1	wt %
oil	300-1000	ppm
Temperature	40	ºC
Molecular weight	18.035	kg/kmol
pH	7	-

2. Activated sludge setup

For testing the treatment performance of the BTL effluent water, a bench scale experimental system was used (Figure 2) with the following specifications: an aeration tank with volume of 24 L, a sedimentation tank with the volume of 12 L, central diffusive aeration system, an internal effluent water tank with the volume of 110 L, a tank for separation of oil from effluent water with the volume of 4.5 L, and a nutrient tank with the volume of 7 L. First, for running the system, 15 L of sludge was poured into the tank. Next, for increasing the microbial layer, methanol, nitrogen, phosphorus etc., were added in the batch condition. Then, BTL effluent water was artificially made considering the characteristics of the actual wastewater. After removing the oil fraction in IGF separation tank, it was added to the internal tank and flowed with a low flow rate to the sludge tank. This process took 14 days and the flow rate was increased step by step to reach its ultimate level. Noting that formaldehyde was added even with the lower flow rate to avoid damaging the microbial layer. For supplying nutrients, Diammonium phosphate ($(NH_4)_2HPO_4$) and urea (CH_4N_2O) were dissolved in deionized water in a separate tank and injected into the aeration tank7][. Discharging waste water from aeration tank enters the sedimentation tank where the sludge is settled and the treated water is extracted from the surface layer. The settled sludge is pumped back by the air lift system to the aeration tank in order to sustain the concentration of microorganisms. Overall process of activated sludge treatment is shown in Figure 2. Regular measurements were done during the system operation for gathering data and screening the process.

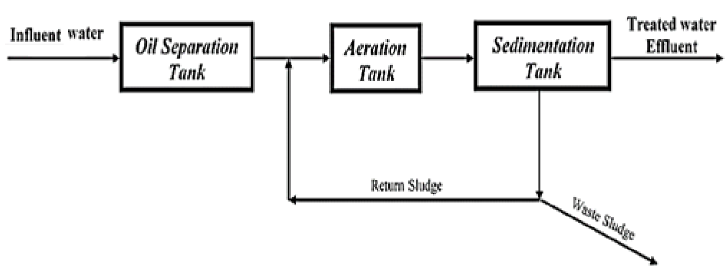

Figure 2. Schematic of BTL effluent water treatment process

3. Measurements and analysis

COD is the amount of the oxygen needed for total oxidation of organic and inorganic compounds in the sample into H_2O and CO_2. COD test can be done in much less time than BOD (Approximately 2 h) and it can be applied for different wastewaters. Closed Reflux Calorimetric method was employed for COD test in this work [12]. In this method, organic matters in the sample are oxidized by boiling solution of H_2SO_4 and $K_2Cr_2O_7$, which are the strong oxidation agents and digestion takes place in two hours. Meantime, the $HgSO_4$ and $AgSO_4$ are used as a digestive solution while $AgSO_4$ has a catalytic effect and $HgSO_4$ deactivates the nitrite and chloride ions to prevent their harmful effect within the treatment as equations 3 and 4.

$$HgSO_4 + 2NO_2^- \rightarrow Hg(NO_2)_2 + SO_4^{2-} \qquad (3)$$

$$HgSO_4 + 2Cl^- \rightarrow HgCl_2 \downarrow + SO_4^{2-} \qquad (4)$$

Regarding the aforementioned descriptions, 2.5 mL of effluent water sample was refluxed in oven at 150 ˚C in the presence of 0.5 mL of digestion solution and 3.5 Ml of H_2SO_4 and $AgSO_4$ inside the tube with a plastic capping and metallic ring. After two hours, the solution turned out of the oven and after reaching the room temperature and settling the sediments, the COD was measured by a Spectra photometric method. pH was measured using standard methods (APHA, 2005). Efficiency of microorganisms performance was calculated through following equation:

$$\text{Microorganism efficiency (\%)} = \frac{\text{Inlet COD} - \text{Outlet COD}}{\text{Inlet COD}} \times 100$$

pH measurements were done by a standard pH meter. In order to test the mixed liquor suspended solids (MLSS) a well-mixed sample was filtered through a weighed standard glass-fiber filter. The residue left on the filter was dried to a constant weight at a temperature between 103 °C and 105 °C. The increase in weight of the filter represents the total suspended solids of the sample. Mixed liquor volatile suspended solids (MLVSS) values were determined through burning off the organic fraction of the MLSS at 550°C that left behind the inorganic fraction of the mixed liquor, the weight of which was then subtracted from the MLSS to obtain a better estimate of the organic compounds. Formaldehyde content of samples was determined by chromatography/mass spectrometry (GC/MS, Agilent Technology (HP)).

Results and Discussion

1. COD analysis of activated sludge

In order to evaluate the effect of microorganisms on the treatment of BTL effluent water, COD measurements were done through the above-mentioned procedure. The feeds with different amount of COD were treated under the same condition to investigate capability of microorganisms in elimination of various amounts of organic pollutants. As seen in Figure 3, although all the feeds exhibit significant reduction in COD, feeds with the COD values of 600 (Feed 5) show highest microorganisms efficiency. Hence, these feeds could be more suitable for activated sludge treatment of BTL effluent water.

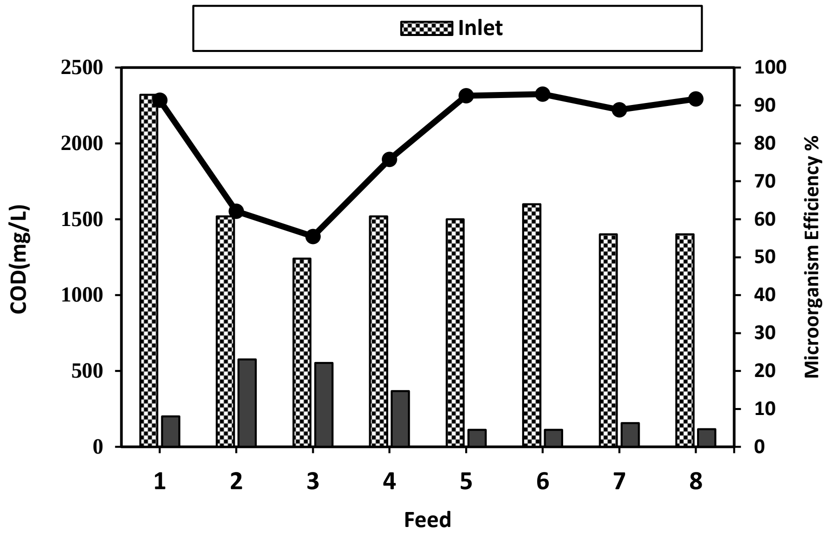

Figure 3. variations of COD and microorganism efficiency

2. Effect of pH

In order to determine the pH range for the best performance of microorganisms, feed with different pH values was treated. Figure 4 displays outlet COD variation in different pH values of BTL effluent water. Accordingly, the lowest amounts of COD were obtained in the pH range between 5.5 -6 and 7-8, which means that microorganism, have the best performance in slightly acidic or basic media. Moreover, as another evidence for the best performance of microorganisms in these pH ranges, formaldehyde content in outlets was studied. As seen in table 2 effluent of the feed 5 has the lowest amount of formaldehyde.

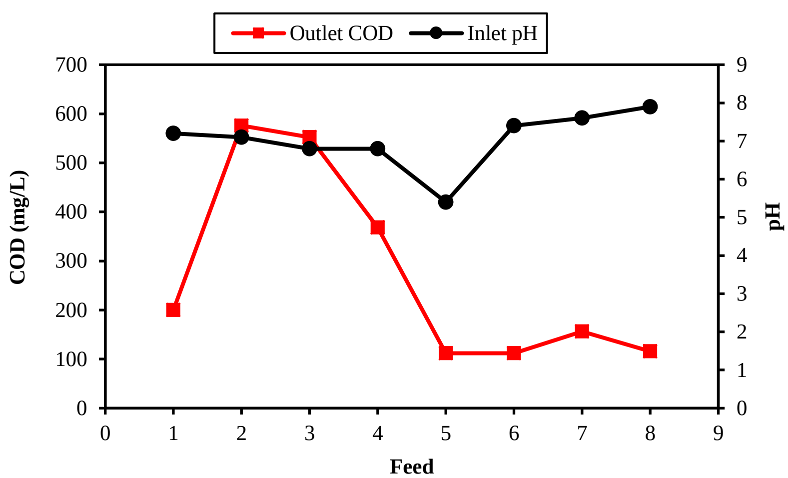

Figure 4. Outlet COD variation in different pH

Table 2: HCHO variation with pH (each feed has 100 (mg/L) formaldehyde)

Feed #	1	2	3	4	5	6	7	8
HCHO (mg/L)	1.5	1.05	0.9	0.23	0.2	0.25	0.27	0.7
pH	7.2	7.1	6.9	6.8	5.4	7.4	7.6	7.9

3. MLSS and MLVSS measurements

MLSS testing measures the total concentration of mixed liquor suspended (non-soluble) solids in the aeration basin of an activated sludge system. The mixed liquor suspended solids (MLSS) data is critical in determining the operational behavior and solids inventory of the system and it is used to determine the time for waste and/or recycle sludge. Mixed liquor volatile suspended solids (MLVSS) test may be performed in order to determine the concentration of volatile suspended solids in the aeration basin of an activated sludge system. Mixed liquor volatile suspended solids data is critical in determining the operational behavior and biological inventory of the system. The difference between MLSS and MLVSS values is the representative of organic pollutants. Eliminating organic pollutants leads to a decrease in the aforementioned discrepancy. According to the Figure 5 effluents of 4, 5, and 6 have the maximum overlap for MLSS and MLVSS values which indicates that in these effluents almost all of the organic pollutants were removed.

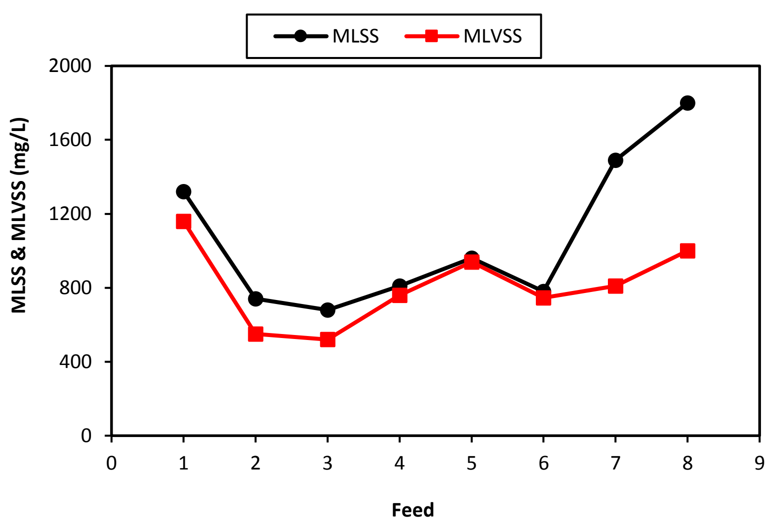

Figure 5. MLSS and MLVSS variation with Feed

Conclusion

In this work, capability of activated sludge method for treatment of BTL effluent water was studied. The effects of some impressive parameters such as COD, pH, MLSS, and MLVSS on the process efficiency were investigated. According to the results, activated sludge displayed a good performance by showing approximately 93% reduction in COD in slightly acidic or basic media (pH= 5.5-6 or 7.5-8). These encouraging results suggest that activated sludge method possesses great potential for elimination of organic pollutant from BTL effluent water.

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