High-rate anaerobic-aerobic biological treatment of a wastewater from a Fischer-Tropsch process

M. Beccari*, M. Majone*, D. Dionisi*, A. Donadio*, E. N. D'Addario**, and R. Sbardellati**

* Sapienza University of Rome, Dept of Chemistry, P.le A. Moro 5, 00185 Rome, Italy
** Eni S.p.A, Refining and Marketing Division, via E. Ramarini 32, 00016 Monterotondo, Italy

This study investigates the anaerobic-aerobic treatment of an industrial wastewater from a Fischer-Tropsch process. The considered synthetic wastewater has an overall concentration of 28 gCOD/L, mainly due to alcohols. The continuous anaerobic process was studied in a fixed-bed reactor under mesophilic conditions (35°C). Gradual start-up, starting from 3.4 gCOD/L/day, was used in order to overcome potential inhibition from long-chain alcohols (>C6). Then, the process was operated successfully by feeding with the wastewater, with neither pretreatment nor dilution, up to an organic load rate of 20 gCOD/L/day (hydraulic retention time 1.4 days). 96% COD removal and full conversion of removed COD into methane was obtained (about one third coming from hydrogenophilic methanogenesis). By considering a potential of 200 tCOD/day to be treated, that would also correspond to a net production of electric energy of about $8*10^7$ kWh/year. The effluent of the anaerobic reactor contained only acetic and propionic acids, that were easily removed under aerobic conditions.

1. Introduction

This paper is aimed to study the anaerobic continuous treatment of a high-strength industrial wastewater from hydrocarbon liquefaction by Fischer-Tropsch process. The considered wastewater is characterised by a high COD content (28 gCOD/L) and by a high organic load (200 tCOD/day). Anaerobic treatment is therefore the desired treatment option for the considered wastewater.

However, most of the wastewater COD (85%) is due to alcohols with different chain length (from methanol to decanol) and literature data on anaerobic treatability of alcohol-containing wastewaters are scarce. Moreover, most of these studies only consider short-chain alcohols. Han et al. (2005) studied the UASB treatment of a wastewater mainly composed of volatile fatty acids and ethanol, obtaining high conversion into methane up to organic loading of 13 gCOD/L/day; with similar substrates, O'Flaherty et al. (1998) also obtained almost complete COD removal; C3 and C4 alcohols were successfully treated in an hybrid (fixed bed-suspended biomass) reactor (Henry et al., 1996). On the other hand, long-chain alcohols are much less studied and there are some evidences that they can inhibit bacterial activity (Carlsen et al., 1991).

A previous study by this research group (Dionisi et al., 2007) has investigated the anaerobic treatment of the considered wastewater by batch tests. It has been shown that the long-chain alcohols (from 6 to 10 C atoms) strongly inhibit the anaerobic

metabolism, both of acetogenic and methanogenic microorganisms. However, biomass activity resumed after long adaptation (about 20 days).
On the basis of the previous investigation, the present study was aimed to investigate the performance of a continuous packed-bed anaerobic bioreactor fed with the considered wastewater. In order to overcome inhibition from long chain alcohols, appropriate start up was performed starting from low organic load and by using modified feed (diluted with no or less long-chain alcohols). Then, the organic load and long-chain alcohol concentration were progressively increased, while monitoring reactor performance in terms of COD removal, methane production, and effluent concentration of the main substances. The maximum methanogenic activity of the microorganisms grown in the reactor was also measured through batch tests.

2. Materials and methods

2.1 Wastewater

Based on typical composition of aqueous waste streams generated from the liquefaction of hydrocarbons with the Fischer-Tropsch process, a synthetic wastewater was prepared. Main components of the wastewater were alcohols (84.8% as COD). Other components of the wastewater include acids (10.7% as COD) and hydrocarbons (4.5% as COD). The complete wastewater composition has been previously reported (Dionisi et al., 2007).

2.2 Reactor

The anaerobic reactor was a fixed-bed biofilm reactor, with a working volume of 1 L. The biomass was grown on Anox-Kaldnes KMT-k1supports. Above the packed bed, space was left for effluent clarification and gas separation. The liquid effluent was recirculated through an internal heat exchanger, in order to maintain the desired temperature (35 °C) and a high degree of axial mixing. The reactor was inoculated with sludge from the anaerobic digester of a municipal wastewater treatment plant and maintained under batch conditions until biofilm developed. Then, a continuous organic load of 3.4 gCOD/L/day was applied, by using a diluted modified wastewater without long-chain alcohols in the feed. Then, the influent flow-rate was gradually increased and the long-chain alcohols were gradually added to the feed, first at 1:8 dilution (organic load rates 6 and 12 gCOD/L/day), then without any dilution (organic load rates 13.5 and 20 gCOD/L/day). The reactor was regularly sampled for effluent and gas-phase composition. During the run at 13.5 gCOD/L/day, batch tests were carried out by switching the feed off and spiking the desired susbstrate (acetic acid, propionic acid, methanol or hydrogen). Time profiles of the added substrate and of the produced methane were then collected.

2.3 Analytical methods

Gas-chromatography was used for methane determination (stationary phase 1% SP1000 on 60/80 Carbopack B, FID, column temperature 80°C) as well as for alcohols (stationary phase 4% Carbowax 20M on Carbopack B-DA, FID, column temperature: 80°C 4 min, from 80 to 220°C at 12°C/min, 220°C 10 min). Hydrogen was analysed through gas chromatography (molecular sieve column 2 m x 2 mm at 105 °C, reduction

gas detector, RGD). Acids were analysed through HPLC (column SupelcoGel C-610H, photodiode array detector).

3. Results and discussion

3.1 Performance of the anaerobic reactor

The time evolution of the performance of the reactor during the run (approximately 1 year) is presented in Figure 1, while average values of the measured parameters are shown in Table 1.

After the adaptation period at the lowest organic load (3.4 gCOD/L/day) with no long chain alcohols, the organic load was increased to 6 and 12 gCOD/L/day by using modified wastewater (long chain alcohols diluted 1:8). Reactor performance was characterised by a progressive increase of residual acetic and propionic acids in the effluent (other compounds were never detected). However, methane was the main product at both organic load rates, corresponding to an average of 61% and 74% of influent COD, respectively. Then, the unmodified wastewater was used and the organic load rate slightly increased (from 12 to 13.5 gCOD/L/day, due to the increased concentration of long chain alcohols). Two distinct phases could be observed 13.5 gCOD/L/day. In the first phase (days 140-225), the performance of the reactor closely matches that of the previous runs (6 and 12 gCOD/L/d), characterised by increasing effluent COD values at increasing organic load rates. Overall effluent concentrations of acetic plus propionic acid were approximately 6.5 gCOD/L, corresponding to a 77% COD removal. The removed COD was all converted to methane. At day 225 the feed to the reactor was switched off, in order to carry out batch tests (next paragraph). After the feed was switched on again, the performance of the reactor was significantly improved: indeed, the liquid-phase effluent COD was quite lower (at 0.63 g/L as average value) and virtually all the influent COD was converted into to methane. The improved performance of the reactor can likely be explained with an increased adaptation of the biomass to the inhibiting substances, i.e. the long-chain alcohols. Because long-chain alcohols were never detected in the effluent, it is likely that they were initially adsorbed in the biofilm within the reactor, because of an organic load higher than removal rate from the slowly acclimating biomass; during the no-feed phase the biomass removed the residual long-chain alcohols, thus removing any inhibition, while also becoming able to remove them at higher rates. Hydrogen concentration in the reactor basically followed acetic and propionic acids in the effluent, so showing similar effects of organic load rate and long chain alcohols on activity of acetoclastic and hydrogenophilic methanogens. However, hydrogen was always very low (below $2*10^{-4}$ mg/L), that indicates a high activity of the hydrogenophilic methanogens.

At the final tested operating conditions, 20 gCOD/L/day, the complete removal of the influent COD was confirmed, with complete conversion to methane.

With regard to final treatment of the residual COD from the anaerobic reactor, batch tests (data not reported) have confirmed that it is readily biodegradable under aerobic conditions, with high removal rates and with no inhibiting effect on biomass metabolism.

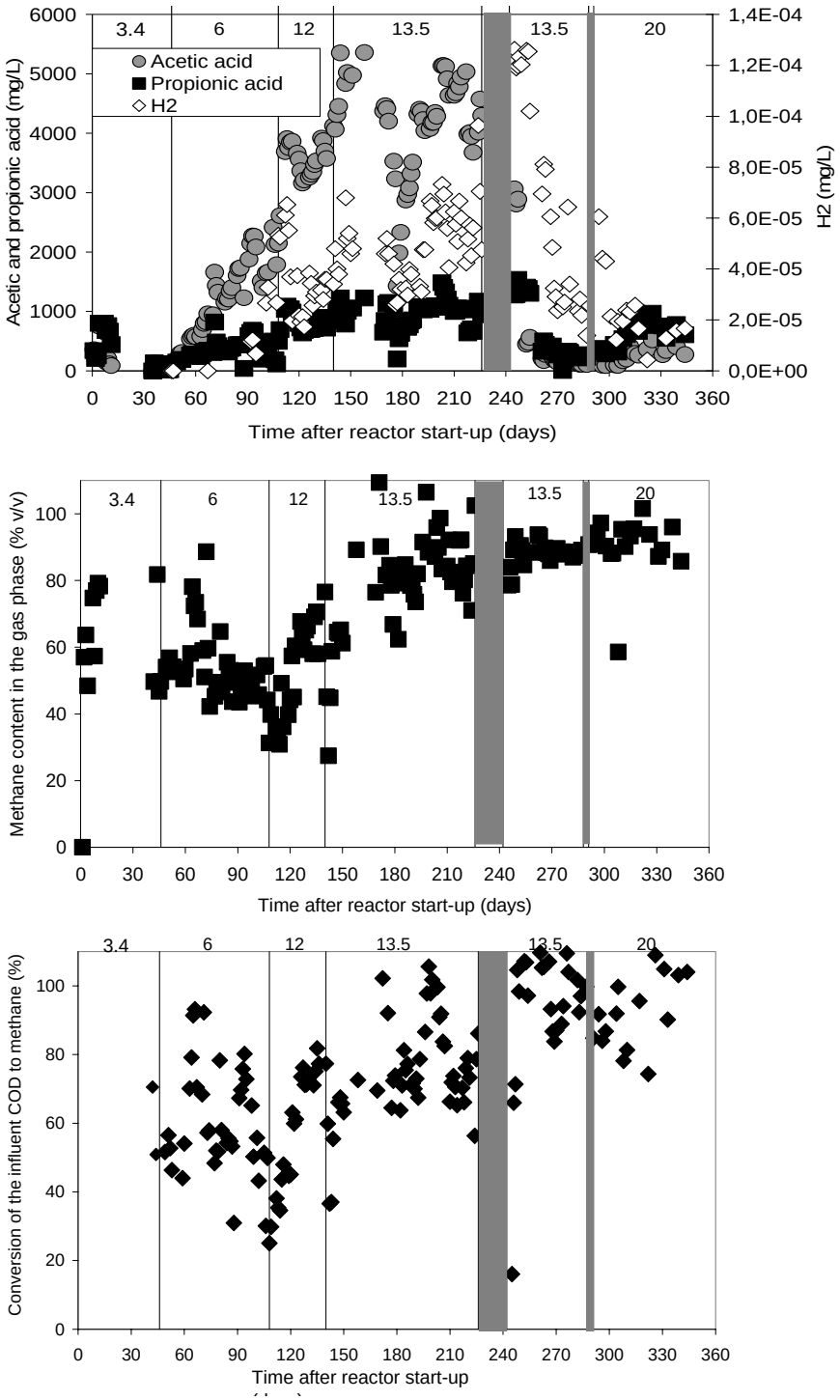

Figure 1. Time profiles of the main measured parameters during reactor operation (grey columns indicate that usual feed was interrupted and batch tests performed)

Table 1. Summary of the average performance of the anaerobic reactor at steady-state

	Organic load rate (gCOD/L/day)				
	6	12	13.5 (first phase)	13.5 (second phase)	20
Gas Phase					
Overall gas production (L/d)	2.51	4.89	4.28	5.20	7.80
Methane content (%, v/v)	52	63	88	89	89
Methane production (L/d)	1.28	3.14	3.76	4.62	7.00
Conversion of influent COD to methane (%)	61	74	78	98	98
Liquid phase (g/L)					
Acetic acid	1.67	3.61	4.46	0.17	0.25
Propionic acid	0.4	0.83	1.04	0.29	0.61
Butanoic acid	0	0	0.042	0	0
Pentanoic acid	0	0	0	0	0
Hexanoic acid	0	0	0	0	0
Methanol	0	0	0.045	0	0
Ethanol	0	0	0	0	0
Propanol	0	0	0	0	0
Butanol	0	0	0	0	0
Pentanol	0	0	0	0	0
Hexanol	0	0	0	0	0
Hepthanol	0	0	0	0	0
Overall solubile COD in the liquid effluent (gCOD/L)	2.39	5.11	6.54	0.63	1.2
Overall COD removal (%)	89	78	75	97	96

3.2 Batch tests and mass balance

Batch tests were carried out with acetate, propionate, methanol and hydrogen in the reactor, in order to calculate their maximal removal rates during the run at 13.5 gCOD/L/day (at the end of each of the two phases),. As a typical example, Figure 2 shows the test with methanol, carried out during the first phase of the run. It is evident that methanol is completely and directly converted to methane at high rate (about 3.5 gCOD/L/day). This finding is also relevant because it shows that other possible methanol metabolisms, such as the conversion to acetic acid (Batstone et al., 2002), were not important for the biomass grown in the reactor.

With regard to acetic acid removal rate (data not shown), batch tests confirmed that its removal rate was much higher in the second phase of the run (approximately 15 gCOD/L/day), than in the first phase (approx. 3 gCOD/L/day). The test with hydrogen (data not shown) also confirmed the quite high activity of hydrogenophilic

methanogens (about 5.6 gCOD/L/day). Maximal conversion rates of selected compounds under batch conditions can be compared with the actual conversion rates in the reactor under usual conditions (Table 2). The latter have been estimated from mass balance in the reactor, by assuming a set of conversion reactions for all compounds in the feed, as reported in Table 3 (Dionisi et al. 2001).

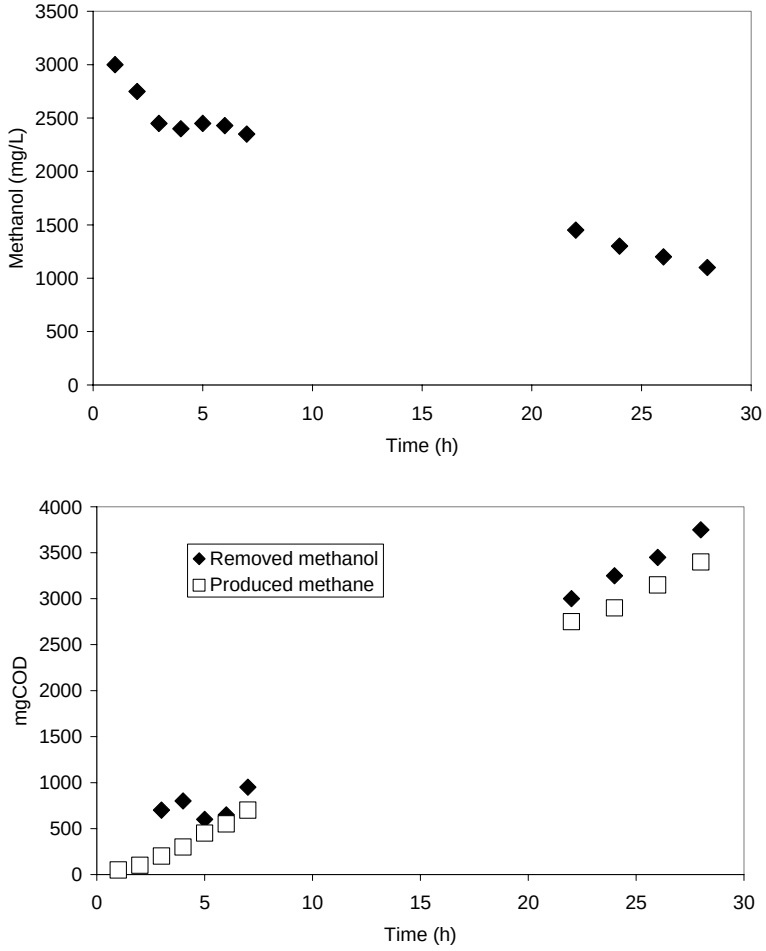

Figure 2. Batch test with methanol (organic load rate 13.5 gCOD/L/day, first phase)

Table 2 shows the good agreement between the actual rates as estimated from Table 3 and reactor mass balance with the maximal rates as determined from batch tests. Indeed, at 13.5 gCOD/L/day, maximal rates were always quite higher than estimated from mass balance in the mixed reactor (where kinetics was limited by the low substrate concentration). The only exception was acetic acid which batch removal rate during the I phase was slightly lower than estimated from mass balance. Such discrepancy confirms the fluctuating profile of acetic acid and its tendency to increase in the effluent. On the other hand, during the second phase the batch removal rate is quite higher than required from mass balance, in agreement with the observed better

performance of the reactor. By combining batch tests results during the run at 13.5 gCOD/L/day and mass balance, it was anticipated that the reactor could be operated up to 20 gCOD/L/day with no loss of performance. This was indeed confirmed during the last reactor run. Finally, it is noteworthy the important role of hydrogenophilic methanogens to the overall methane production (about one third at both 13.5, II phase, and 20 gCOD/L/day)

Table 2. Comparison of maximal rates from batch tests and estimated actual rates from reactor mass balance (all the rates are in gCOD/L/day); n.a. data not available.

	Maximal rates from batch tests		Estimated rates from mass balance in the continuous reactor		
	run at 13.5 gCOD/L/day		run at 13.5 gCOD/L/day		run at 20 gCOD/L/day
Compound	I phase	II phase	I phase	II phase	
Acetic acid	3.15	15.9	4.03	6.53	9.40
Methanol	3.54	n.a.	1.71	1.71	2.54
Hydrogen	5.64	n.a.	4.02	4.24	6.10
Overall COD	12.3	25.0	9.76	12.48	18.0

Table 3. Scheme of the possible anaerobic reactions of the main wastewater components. 1) Thauer et al., 1977; 2) Eichler and Schink, 1985; 3) Batstone et al., 2001

Substrate	**Reaction**
Methanol[1]	$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$
Ethanol[2]	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$
Propanol[2]	$CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 2H_2$
Butanol[2]	$CH_3CH_2CH_2CH_2OH + H_2O \rightarrow CH_3CH_2CH_2COOH + 2H_2$
Pentanol[2]	$CH_3CH_2CH_2CH_2CH_2OH + H_2O \rightarrow CH_3CH_2CH_2CH_2COOH + 2H_2$
Propionic acid[3]	$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$
Butanoic acid[3]	$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$
Pentanoic acid[3]	$CH_3CH_2CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 3H_2 + CO_2$
Acetic acid[3]	$CH_3COOH \rightarrow CH_4 + CO_2$
Hydrogen[3]	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

4. Conclusions

The present study showed that the considered wastewater, characterised by a high organic load and by high concentrations of potentially inhibiting substances (long-chain alcohols), could be successfully treated under anaerobic conditions in a high rate packed bed biofilm. In particular, after appropriate start up, the reactor was operated up to 20 gCOD/L/day organic load rate, by removing most of the COD (96%) and transforming it into methane. This applied organic load rate is among the highest reported in the literature for fixed-bed biofilm reactors.

Under the estimated overall load of 200 tCOD/day, methane produced in the anaerobic reactor could provide, through typical cogeneration, a net electric power of 9 MW (or $8*10^7$ kWh/year), in addition to the power required by the anaerobic reactor. Moreover,

based on mass balance and batch tests it was estimated that about one third of overall methane production was due to hydrogen production from alcohols and propionic acid fermentation and to simultaneous hydrogenophilic methanogenesis. Thus, as a perspective, the process could be also interesting for hydrogen production, provided that methanogenesis is appropriately inhibited.
The residual effluent COD from the anaerobic reactor was composed only of acetic and propionic acids, and was readily biodegradable under aerobic conditions. Thus, this study showed that a combined anaerobic-aerobic process, with both stages operated at high organic load rates, is suitable for the treatment of the considered wastewater.

3. Acknowledgments

This research was carried out under the contract 122/2006 between the Department of Chemistry and Enitecnologie S.p.A (now Eni S.p.A). The kind assistance of ACEA-ATO2 staff at the “Roma Nord” WWTP is gratefully acknowledged.

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