

Evaluation of a Novel Bio-oil Hydrotreating Process Integrating Electrochemical H₂ Compression

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In fossil-based refinery and biorefinery applications hydrogen is recovered by pressure swing adsorption and subsequently re-pressurized using mechanical compressors. Electrochemical hydrogen compression is an efficient way of separating and compressing H₂ from a gaseous mixture within a compact device. In this work, a preliminary investigation of the integration of a bio-oil hydroprocessing unit with a complete novel gas polishing and separation unit was conducted. Apart from the electrochemical compressor, this includes a CO methanation reactor and a ZnO bed to remove the contained CO and H₂S impurities of the hydroprocessing reactor outlet and safeguard the trouble-free operation of the electrochemical device. This first assessment revealed that several operating parameters such as the hydrotreating pressure, the gas polishing and separation temperature and the hydrogen recycling ratio limit the possible operating modes of the subsequent units.

1. Introduction

Fast pyrolysis bio-oils can effectively produce biofuels or bio-intermediates that could be readily introduced into existing refinery infrastructures after they undergo hydroprocessing. Pyrolysis bio-oils are complex mixtures containing carbon, oxygen and hydrogen and more than 400 identified oxygenated compounds (Vasilkovova et al., 2014). Their high oxygen content, thermal instability and low miscibility with hydrocarbons make them unsuitable for insertion into existing refinery systems and therefore, require further upgrading (Zhang et al., 2007). Hydrotreating (HDT) is an upgrading process that utilizes hydrogen for the removal of the oxygen heteroatoms and aims at bio-oil's overall oxygen to carbon ratio reduction. Mild-hydrotreatment generally refers to the upgrading / stabilization process conducted at temperatures up to 250 °C (Venderbosch et al., 2010). A large number of reactions is involved in hydroprocessing and the most common are hydrogenation, hydrodeoxygenation (HDO), decarboxylation / decarbonylation (HDC), as well as cracking and hydrocracking. During HDO, the contained oxygen is removed as H₂O, whereas during HDC, oxygen is removed in the form of CO₂ and CO (Mortensen et al., 2011).

The hydroprocessing reactor outlet consists of an organic, an aqueous and a gaseous phase that contains a large excess of unreacted H₂ (Elliott et al., 2009). This H₂ excess is a major issue that hinders the cost-effective application of bio-oil hydrotreating since pressurized H₂ costs can make up a considerable portion of the operational expenditures (Zhang et al., 2013) and therefore, the efficient recovery and recirculation of this unreacted H₂ is crucial for process economics.

The state-of-the-art hydrogen recovery method for industrial-scale chemical and petrochemical applications is pressure swing adsorption (PSA). During PSA, hydrogen contents are selectively adsorbed by a porous solid adsorbent and then desorbed for reuse of the adsorbent. This seemingly simple process demands a sophisticated design of a multi-column adsorption system comprising of a series of cyclic steps (Liu et al., 2009). However, for usage in high-pressure biorefinery applications, an additional downstream compression step is required since the PSA H₂ product is recovered at the same pressure (Liemberger et al., 2017). Conventionally, hydrogen is mechanically compressed in a multi-stage, isentropic compression process that involves moving

parts and requires lubrication (Tzimas et al., 2003). The combination of PSA and mechanical compression is a known technology that has already been studied in several hydrotreating-related modelling works (Atsonios et al., 2018). However, there is a need for alternative, compact and energy-sparing processes.

In this work, an electrochemical hydrogen compressor (EHC) is employed as an alternative way of separating and compressing H_2 from the gaseous mixture that results from the hydrotreater. A major advantage of this new compressor is that it purifies and simultaneously compresses the H_2 at higher pressures within a compact piece of equipment. This implies that the additional compression step when using PSA is not necessary and since the electrochemical compression process is isothermal, less power is required compared to mechanical compression (Onda et al., 2007). The developed EHC model uses basic AspenPlus™ unit operation blocks to represent the main electrochemical operations, whereas voltage, current density and power requirements are externally modelled.

The electrochemical compressor requires several specifications for its input, especially the H_2S and CO contents have to be previously reduced. A zinc oxide bed and a methanation reactor are interpolated before the electrochemical compressor for H_2S and CO removal, respectively. The scope of this work is to present a first assessment of a bio-oil hydroprocessing unit that assimilates a novel hydrogen recirculation and compression concept, which has not been previously studied. The first modelling approach of the system is presented, as well as a preliminary investigation of key operating parameters that affect the overall system performance.

2. Process description and modelling methodology

2.1 Overview

A simplified process flow diagram with the major components of the entire proposed novel scheme is shown in Figure 1. A sulphided hydroprocessing catalyst is used, which can justify any observed discrepancies around the hydroprocessing reactor due to the release of H_2S in the product streams. In order to perform the electrochemical hydrogen separation, CO and H_2S have to be removed by integrating two conditioning steps including Sulphur removal and CO methanation. The integration of the overall scheme is the main focus of this work.

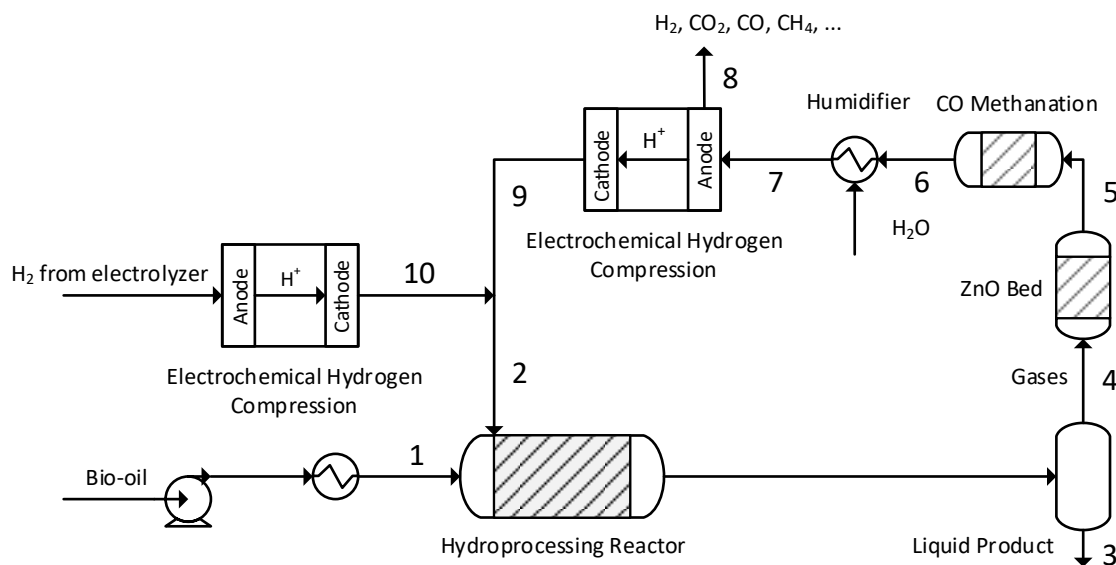


Figure 1: Flowsheet of the novel bio-oil hydroprocessing unit and the separation of gaseous products.

The operation of each unit imposes certain limitations on the operation of the subsequent units. Therefore, certain parameters have to be taken into consideration for the efficient operation of the entire flowsheet:

- EHC temperature: higher operating temperature is preferable since activation and Ohmic losses are lower (Figure 2).
- HDT reactor pressure: higher HDT pressure requires higher EHC pressure ratios and therefore, higher H_2 back diffusion losses are observed (Figure 3).
- The operating temperature of the CO -Methanation reactor and ZnO bed: CO and H_2S equilibrium concentrations must comply with the tolerance levels of the EHC system (Figures 4 and 5).

- Amount of recycled H₂: CO Methanation consumes H₂ and therefore, less of the latter can be recirculated and more make-up H₂ is required.
- H₂ Recycling Ratio: the maximum H₂ recycling ratio is limited by the back-diffusion of H₂.

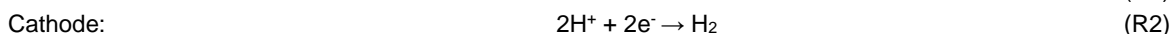
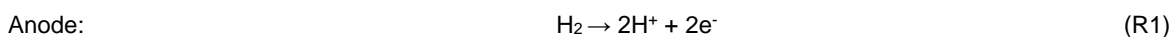
The following sections present the developed models and discuss their contribution in the operation of the integrated system.

2.2 Mild-hydrotreating

The pyrolysis bio-oil feed contains high oxygen and water content and requires further upgrading in order to be used as biofuel or to be co-processed into existing refinery infrastructures. Therefore, it is fed to the hydroprocessing reactor with high excess of hydrogen. The yields of each product phase is based on the work conducted by Venderbosch et al. (2010). The hydroprocessing reactor is represented by an AspenPlus™ RYield reactor and the atomic and total mass balances are evaluated in AspenPlus™ Fortran calculator blocks. The upgraded oil and aqueous phase compositions are calculated by ensuring that the inlet and outlet mass balances are in agreement.

2.3 Electrochemical Hydrogen Purification and Compression

The electrochemical hydrogen compression is an alternative process to mechanical compression and/or mechanical purification. The operating principle is simple: A humid gaseous mixture containing H₂ is fed to the anode catalyst layer, at low pressure. Once a potential difference is applied, the hydrogen oxidation reaction occurs (HOR) and H₂ is oxidized to protons H⁺ (R1). The membrane is only hydrogen permeable and therefore, the other gases act as diluents that do not affect the system's operation. Protons travel through the membrane and are reduced to molecular H₂, by the hydrogen evolution reaction (HER) (R2).



Compression occurs using a back-pressure valve. It is apparent that this device can be used at three different configurations based on the desired function: a) H₂ compression, b) H₂ recovery from a gaseous mixture, c) separation and subsequent compression of the recovered H₂. In this case, after the two gas polishing steps, the gaseous stream enters the electrochemical compressor for hydrogen recovery and subsequent compression. In addition, an electrochemical compressor is used to compress the additional H₂, which is assumed to be produced by H₂O electrolysis.

Several operating parameters and losses have to be taken into consideration for the EHC operation. The compression process is isothermal and Faradaic, which implies that the moles of compressed H₂ are proportional to the applied current, whereas compression power requirements are dictated by Nernst's equation. The irreversibilities of the system include the resistance of the protons travelling through the membrane (Ohmic losses) and the activation requirements of the anode and cathode reactions (activation losses). Figure 2 illustrates the polarization curves under different operating temperature. Operation at the highest possible temperature is preferable since Ohmic and activation losses are lower. In addition, for proper system function and to reduce the Ohmic losses, the membrane needs to be adequately humidified. Therefore, a humidifier was placed before the EHC entrance (Figure 1) to saturate the inlet gaseous mixture.

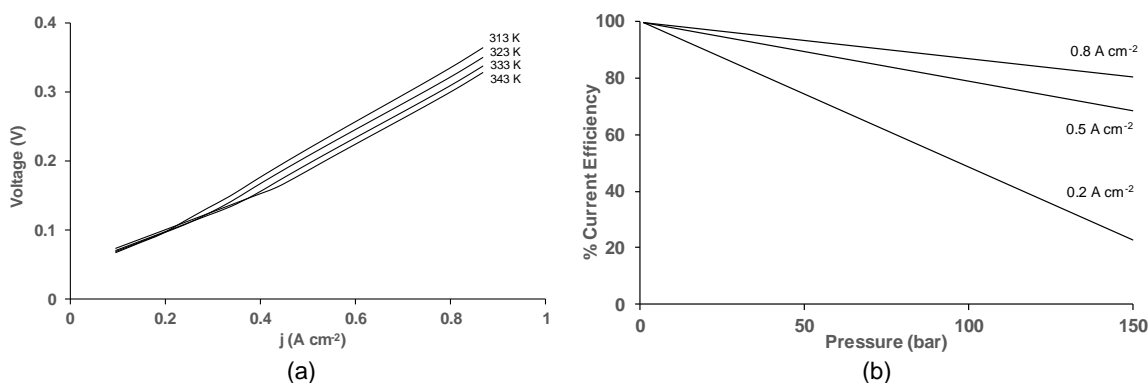


Figure 2: (a) Current - Voltage curves under different operating temperature. (b) Back diffusion losses expressed in current efficiency terms

Another important loss at high pressure ratios is H₂ back-diffusion. Due to the pressure difference between anode and cathode, molecular H₂ flows from the high-pressure cathode back to the low-pressure anode. This results in lower Faradaic efficiency, which indicates that the actual compressed H₂ flow does not correspond to the theoretical flow. Figure 3 illustrates these efficiency losses at different current densities and cathode pressure, where current efficiency refers to the actual compressed H₂ flow compared to the theoretical flow dictated by Faraday's law. A detailed presentation of the model equations, as well as, detailed description of the occurring EHC phenomena can be found in the work of Bampaou et al. (2018).

2.4 Gas conditioning steps

Before the EHC system, the HDO off-gases require conditioning due to the inhibiting behaviour of the CO and H₂S components. The contained H₂S is attributed to the use of a sulphided hydroprocessing catalyst, and apart from its corrosive and toxic properties, it needs to be removed due to its poisonous behaviour at the catalyst and membrane of the EHC (Mohtadi et al., 2003). Therefore, an extremely low S content is required before entering the electrochemical separation system. To ensure long-term performance of EHC, it is suggested that hydrogen sulphide levels should be in the order of ppb (in this case up to 10 ppb) (EG&G Technical Services, 2004). A deep sulphur removal process is H₂S adsorption using a zinc oxide bed, where S is removed in the form of ZnS (R3) (Novochinskii et al., 2004). However, when a certain amount of water is present in the feed, sulphur cannot be reduced to less than 100 ppb (Li and King, 2006).



In addition, several ppm of CO can poison the Pt catalyst and membrane of the electrochemical compressor and must be separated from the gaseous mixture (Ibeh et al., 2007). CO Selective Methanation is a CO removal process that requires no additional reagents. In addition, the produced methane can be later combusted to support other endothermic reactions of the process or reformed to produce additional hydrogen (Snytnikov et al., 2016). To avoid deterioration of cell performance, it is recommended to keep CO levels under 10 ppm (Qi et al., 2001). During the CO-methanation process, CO is hydrogenated to form CH₄ and H₂O (R4) usually at temperatures 200 – 300 °C and ambient pressure. However, due to the carbon dioxide content of the gaseous mixture, additional side reactions occur, such as carbon dioxide methanation (R5) and the reverse water-gas shift reaction (R6). These reactions consume H₂ and therefore, lower amount of H₂ can be actually recycled back to the hydroprocessing unit.

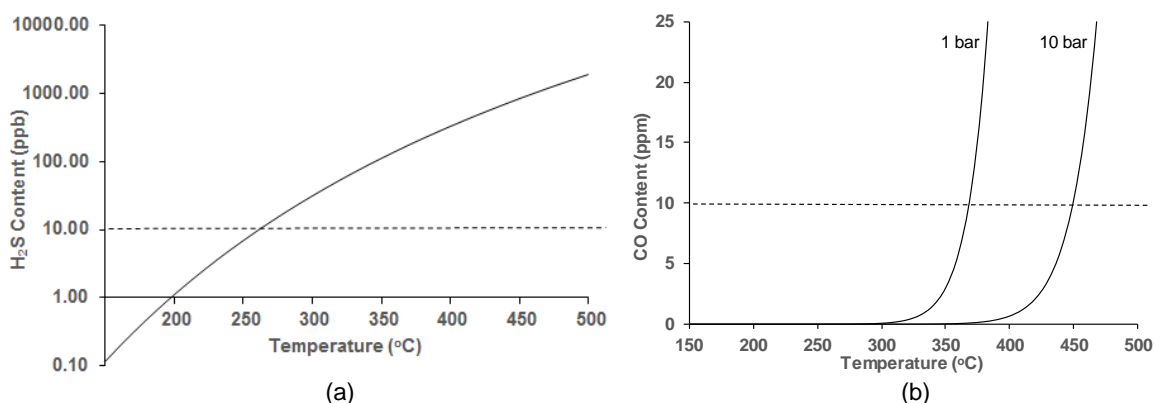


Figure 3: (a) H₂S equilibrium concentration and amount tolerated by EHC.. (b) CO equilibrium concentration and amount tolerated by EHC



The H₂S removal and CO methanation processes are simulated using the REquil AspenPlus™ reactor model, which calculates the equilibrium products concentration at certain reaction conditions. Figures 4 and 5 show the H₂S and CO equilibrium concentration at the reactors' outlet stream. The maximum H₂S and CO concentrations that can be tolerated are shown as dashed lines in Figures 4 and 5, respectively. Figure 5 illustrates the influence of the reactor pressure on potential CO concentration reduction. In this work, 10 bar was chosen as the operating pressure in order to reduce the additional compression work requirements of the EHC.

3. Results and discussion

Table 1 presents the basic characteristics of the streams for hydroprocessing conducted at $P = 50$ bar and 50 % hydrogen recycling ratio. The gaseous stream exiting the CO methanation reactor (Stream 8) is humidified before entering the EHC system due to the need for proper humidification of the EHC membrane. The recirculated H_2 (Stream 9), as well as the fresh H_2 (Stream 10), are water-saturated due to the utilization of a humid membrane. The anode outlet stream (Stream 9) is not recirculated due to the compromise of recirculating only 50 % of the contained H_2 . However, it contains a significant amount of CH_4 , which could be later used for reforming and producing additional H_2 or for combustion to support the heat demands of the process.

Table 1 Stream table of the hydroprocessing unit and separation of gaseous products.

Stream Number	1	2	3	4	5	6	7	8	9	10
Stream Name	Bio-oil	H_2 Feed	Liquid Product	Product Gases	CO-MET Inlet	CO-MET Outlet	EHC Feed	Anode Outlet	H_2 Recycle	Fresh H_2
Total flow (kg/h)	100	1.11	99.85	1.29	1.28	1.28	6.43	1.00	0.29	0.82
Temperature (K)	398	343	498	498	473	473	424	343	343	343
Pressure (bar)	50	50	50	50	10	10	10	10	50	50
Mass fraction %										
Gases	-	100	-	100	100	100	100	100	100	100
H_2O	-	5.22	-	-	0.83	8.13	81.73	7.39	5.22	5.22
H_2	-	94.78	-	44.61	44.94	43.1	8.57	16.78	94.78	94.78
CO	-	-	-	2.82	2.84	trace	trace	trace	-	-
CO_2	-	-	-	6.64	6.69	trace	trace	trace	-	-
CH_4	-	-	-	44.38	44.70	48.77	9.70	71.23	-	-
H_2S	-	-	-	1.55	trace	trace	trace	trace	-	-
Liquids	100*	-	100**	-	-	-	-	-	-	-

*Composition (dry wt. %): Bio-oil: C: 55.3, H: 6.8, O: 37.9, H_2O : 23.9

**Composition (dry wt. %): a) Upgraded oil (49.5 %): C: 70.61, H: 8.34, O: 21.05, H_2O : 7.7, b) Aqueous phase (50.5 %): C: 14.02, H: 10.48, O: 75.5, H_2O : 62.1

At the cathode exit, however, there is additional liquid water, due to water movements inside the membrane, which is not illustrated in Table 1. This water needs proper management to prevent accumulation at the cathode department.

4. Conclusions

This work studies the integration of a bio-oil hydroprocessing unit with an electrochemical hydrogen compressor for efficient purification and pressurization of the unreacted H_2 . Crucial parameters that affect the operation of the overall system are the hydrotreating pressure, the EHC operating temperature, the CO methanation and ZnO bed temperature, and the amount of recycled H_2 . An indicative stream table is presented for the case of hydroprocessing at 50 bar and 50 % H_2 recycling. CO methanation consumes H_2 and therefore, the amount of hydrogen that can be recycled to the hydroprocessing reactor is limited. Operation at higher pressures is feasible, however, additional back-diffusion losses have to be taken into consideration. These losses can be countered by operating at higher H_2 recycling ratios or using modified membranes. A more detailed analysis of these operating parameters for different hydroprocessing and recycling cases, as well as the combination of mechanical and electrochemical compression will be the main focus of future work.

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