NEW PROCESS FOR PRODUCTION OF BIO-DIESEL FROM VEGETABLE OIL

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ABSTRACT

Low-cost, high-capacity processes for the conversion of biomass into fuels and chemicals are essential for expanding the utilization of carbon neutral processes, reducing dependency on fossil fuel resources, and increasing rural income.

The quality of bio-oils can be improved by the partial or total elimination of the oxygenated functionalities present. Two main deoxygenation methods have been studied for this purpose. The first comprises bio-oil cracking over solid acid catalysts at atmospheric pressure, resulting in simultaneous dehydrationdecarboxylation. The other utilizes typical hydrotreating conditions, high hydrogen pressures in combination with conventional catalysts, for the hydrogenation of unsaturated groups and hydrogenation-hydrocracking of large molecules.

Although hydrotreating is extremely effective, techno-economic analyses reveal its economics to be unfavorable for the production of the fuel-type products it affords. If renewable hydrogen is readily available, then this may not be such a disadvantage; however, this approach is unsuited for the distributed stabilization/upgrading of pyrolysis oil. Hydroprocessing of vegetable oils allows easy transformation of fatty acid triglycerides into hydrocarbons. In this study is represented a new process for the production of hydrogenated bio-oils starting with "waste" of petroleum processing (sulfur) to get hydrogen, using concentrated solar energy, for hydrogenation of bio-oils.

Keywords: sulfur-iodine, sulfur, FGD, solar energy, hydrogenation, bio-diesel

1   INTRODUCTION

Sulphur is one of the most common elements in the earth's crust, and occurs widely as an impurity in coal, crude oil and many ores. It is therefore produced on a large scale during such industrial processes as the combustion of coal, oil and oil-derived fuels, oil refining and the production of metals from their ores. Currently, global SO_2 emissions arising from human activity amount to ~140 million tonnes (Mt) per year. SO_2 is one of the principal gaseous pollutants emitted by human activity. It can be a hazard to human health and damages both the natural and built environments. High levels of SO_2 can cause respiratory illness and its presence in the environment causes acid rain that damages both vegetation and buildings. Control and reduction of SO_2 emissions has therefore been recognised as important for safeguarding human health and protecting the environment since the mid-19th century; many countries now set limits on the amount and concentration of sulphur compounds emitted from the stacks of industrial plant. Emissions of SO_2 can be controlled in several ways. It may be possible to switch to a fuel or ore that has a lower sulphur content, or improve the efficiency of the industrial process so that less fuel is required. The sulphur in the fuel or ore can in principle be removed before use; however, in practice, it is uneconomic to remove more than a small percentage of the sulphur. The sulphur can also be removed during use.
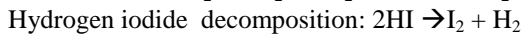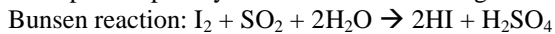
However, in many applications, the most efficient means of controlling SO_2 emissions is to remove the SO_2 from the flue gases before they are released to the atmosphere. Several differing FGD technologies have been developed to this end.

Almost all commercial FGD processes are based on the fact that SO_2 is acidic in nature, and remove the SO_2 from flue gases by reaction with a suitable alkaline substance. The most commonly used alkaline materials are limestone (calcium carbonate), quicklime (calcium oxide, CaO) and hydrated lime (calcium hydroxide). Limestone is an abundant and therefore relatively cheap material and both quicklime and hydrated lime are produced from limestone by heating. Other alkalis sometimes used include sodium carbonate, magnesium carbonate and ammonia. The alkali used reacts with SO_2 in the flue gas to produce a mixture of sulphite and sulphate salts (of calcium, sodium, magnesium or ammonium, depending on the alkali used). The proportions of sulphite and sulphate are determined by the process conditions; in some processes, all the sulphite is converted to sulphate. The reaction between the SO_2 and the alkali can take place either in bulk solution ('wet' FGD processes) or at the wetted surface of the solid alkali ('dry' and 'semi-dry' FGD processes). In wet FGD systems, the alkali (usually as a solution or, more commonly, a slurry) and flue gas are contacted in a spray tower. The SO_2 in the flue gas dissolves in the water to form a dilute solution of acid that then reacts with and is neutralised by the dissolved alkali. The sulphite and sulphate salts produced precipitate out of solution, depending on the relative solubility of the different salts present. Calcium sulphate, for example, is relatively insoluble and readily precipitates out. Sodium and ammonium sulphates are very much more soluble. In dry and semi-dry systems, the solid alkali 'sorbent' is brought into contact with the flue gas, either by injecting or spraying the alkali into the gas stream or by passing the flue gas through a bed of alkali. In either case, the SO_2 reacts

directly with the solid to form the corresponding sulphite and sulphate. For this to be effective, the solid has to be quite porous and/or finely divided. In semi-dry systems, water is added to the flue gas to form a liquid film on the particles in which the SO_2 dissolves, promoting the reaction with the solid.

The sulphur-iodine process for flue gas desulphurization is a new wet scrubbing regenerative FGD process. This process produces two valuable chemicals, sulphuric acid and hydrogen.

The open-loop SI cycle consists of following two reactions:
Bunsen reaction: $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$
Hydrogen iodide decomposition: $2HI \rightarrow I_2 + H_2$
In the Bunsen reaction iodine acts as an oxidizing agent, converting SO_2 into sulphuric acid [1,2].

2 PROCESS DESCRIPTION

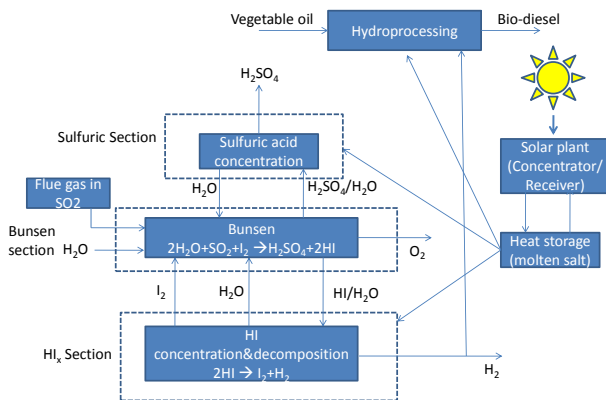The simplified scheme of the process is illustrated in fig.1.

Fig. 1. General scheme for the process

2.1 Bunsen and HIx section

The flowsheets previously developed by General Atomics [3] for both the Bunsen and HIx sections have been assumed.

Accordingly, the exothermic Bunsen reaction takes place mostly in a heat exchanger reactor operating at 7 bars and 105–120 °C. An excess of water and iodine characterizes the feed from the HIx and sulfuric sections in order to allow acceptable reaction rates and easy separation of products (H_2SO_4 and HI) into two liquid phases [4]: an upper phase essentially constituted by diluted H_2SO_4 and a heavier phase containing HI, water, and excess I_2. The gas phase composed of oxygen and residual SO_2 is separated from the two liquid phases in a downstream vessel. H_2SO_4 and HI are further produced in a secondary (boost) reactor and in scrubber towers used for oxygen separation. As far as the HIx section is concerned, Roth and Knoche [5] developed a

flowsheet later investigated by General Atomics. It consists of a reactive distillation column, operating at 22 bars, fed by the $HI/H_2O/I_2$ stream coming from the Bunsen section, which is pressurized and preheated up to 262 °C. The product from the bottom, essentially I_2 at 310 °C, and a $HI/H_2O/I_2$ side stream (at 251 °C) are cooled down and recycled to the Bunsen section. Whilst I_2 is concentrated in the bottom section of the column, HI dissociation takes place in the upper part so that the top stream is a gas mixture mostly consisting of hydrogen. HI traces can be quantitatively removed at room temperature in a downstream water scrubber. The resulting hydrogen yield is extremely low if compared with the column hold up (1 mol of H_2 is produced for about 126 mol of feed): this is the major drawback of this process configuration, owing to the large excess of water and iodine required in the Bunsen section [6,7] that at least determines high operating and capital costs for the HIx section.

2.2 Sulfuric section

The lower density phase contains all the H_2SO_4 acid at a concentration of about 50% by weight with traces of I_2 and SO_2. The concentration of H_2SO_4 is increased to be about 57% by weight by reacting the H_2SO_4 phase with molten iodine and SO_2. Then sulfuric acid is concentrated in a series of flash evaporators and separators. The final concentration is 95-98% by weight [5].

2.3 Solar plant facility

The solar concentrator plant, designed by the ENEA, is based on a technologically adapted version of the linear parabolic geometry of SEGS (Solar Electric Generating System), successfully operated at Kramer Junction, California, for about 20 years. The innovations introduced by the ENEA mainly concern the use of a non-flammable heat transfer fluid with low environmental impact together with the utilization of a thermal storage device designed to provide thermal power at a constant rate, regardless of variations in solar power availability due to solar irradiation fluctuations and night/day cycles. See fig. 2.

Regarding the heat transfer fluid, a molten salts mixture consisting of 60% sodium nitrate and 40% potassium nitrate has been chosen as energy carrier operating in the 290–550 °C temperature range. The linear parabolic mirrors concentrate the direct sunlight radiation on a receiver pipe absorbing radiant energy and converting it to high temperature sensible heat of the molten salts, which are collected and sent to a hot tank for heat storage. On demand, the hot salts are delivered to the chemical process and cooled down to lower temperature levels. After cooling, molten salts are sent to the cold tank and successively pumped to the parabolic troughs for restarting the heat collection loop. The relevant temperature drop (about 260 °C) between the hot and cold tanks provides a significant storage capacity in terms of thermal energy (about 1kWh

for 5 l of molten salts). Research finalized to further improvements of SEGS technology is currently in progress with the development of new parabolic troughs, with the general aim of cost reduction and material improvement. The receiver pipe, located on the focal line of the mirrors, is composed of two concentric cylinders separated by a vacuum gap for thermal insulation: the external glass cylinder represents a protective casing, while the internal steel cylinder absorbs solar energy by means of the heat transfer fluid. A spectrally selective coating compound for receiver tube, developed and specifically designed by the ENEA to maximize the efficiency at higher temperatures (550 °C), covers the steel pipe and guarantees maximum absorption of solar radiation and reduction of infra-red emissions from hot tubes. Such a solar collection system is easily adaptable to the features of a large number of potential sites in high-level solar radiation areas and theoretically permits to provide thermal energy continuously except for protracted cloudy periods (>2–3 days).

The design of the solar plant involves the evaluation of the active surface of the mirrors (A) and the thermal storage capacity (T), which are functions of the solar radiation level of the site, the process heat requirements, the solar energy collection efficiency, and the chemical process operative conditions. Regarding the latter point, there are two main alternative routes:

• to collect all the solar radiation available over the year and, as a consequence of solar irregularities and seasonal fluctuations, to produce hydrogen at a variable rate;

• to keep constant the energy delivered to the process varying the contribution of an additional fossil source o biomass and cutting-off solar radiation peaks in the summer.

The second solution has been chosen in order to guarantee a constant hydrogen output and to ease the process control and operation, as the chemical plant does not tolerate large deviations of the process parameters from the designed working conditions.

Furthermore, during winter periods, when solar radiation is low, solar plant is shutdown for maintenance operations. This strategy permits to reduce thermal storage capacity and fossil source utilization [8].
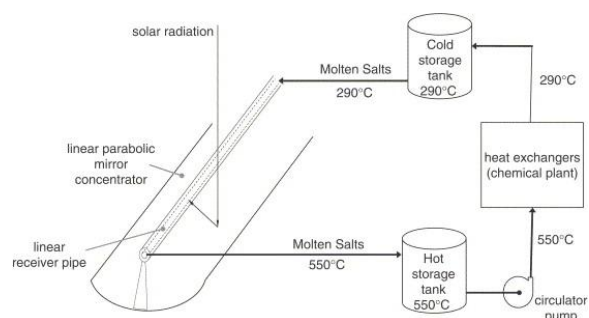

Fig. 2. Schematic of the solar parabolic trough concentrator with thermal storage and molten salts loop.

3 BIOMASS

Biomass can be converted into fuels and chemicals indirectly, by gasification followed by Fischer–Tropsch conversion to liquid fuels, or by direct thermochemical conversion processes, including pyrolysis, high-pressure liquefaction, and solvolysis. However, the oils obtained from direct conversion processes cannot be used as transportation fuels without prior upgrading due to their high oxygen content (35–40 wt% dry basis) and water content (15–25 wt%). The oxygenated compounds present in raw biooils impart a number of unwanted characteristics such as thermal instability (reflected in increasing viscosity upon storage), corrosiveness and low heating value. This instability is associated with the presence of reactive chemical species, notably aldehydes, ketones, carboxylic acids, alkenes and guaiacol-type molecules. Upon prolonged storage, condensation reactions involving these functional groups result in the formation of heavier compounds. Polymerization reactions involving polyhydroxyphenols or methoxyphenols can result in the formation of a solid coke-like product during crude bio-oil distillation. The quality of bio-oils can be improved by the partial or total elimination of the oxygenated functionalities present. To date, two main deoxygenation methods have been studied for this purpose. The first comprises bio-oil cracking over solid acid catalysts at atmospheric pressure, resulting in simultaneous dehydrationdecarboxylation. The other utilizes typical hydrotreating conditions, i.e., high hydrogen pressures in combination with conventional hydrodesulfurization catalysts for the hydrogenation of unsaturated groups (with elimination of oxygen aswater) and hydrogenation- hydrocracking of large molecules.

3.1   Hydroprocessed vegetable oil

Pavel Šimacˇek et al. have studied some fuel properties of hydroprocessed rapeseed oil obtained at various reaction conditions using commercial Ni–Mo catalyst. Hydroprocessing of rapeseed oil was performed in a bench scale flow reactor equipped with a salt bath heating system. Organic liquid product (OLP) obtained by hydroprocessing of rapeseed oil at 360 °C and 7 MPa was chosen for preparation of blends with mineral diesel fuel [9].

ACKNOWLEDGMENTS

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