



## Research article

## Integrated thermo-catalytic reforming of residual sugarcane bagasse in a laboratory scale reactor

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## ABSTRACT

The objective of present study was to demonstrate efficient conversion of residual sugarcane bagasse by thermo-catalytic reforming (TCR<sup>®</sup>) into fuels and high-value products in a laboratory scale 2 kg/h unit. None of the toxic or non-toxic chemicals and solvents was employed during the process, thus minimizing negative environmental effects. In addition, a detailed study on the composition of bio-oil using GC-MS, FT-IR and on the properties of biochar using Raman spectroscopy, SEM, SEM-EDS, TEM, TEM-EDX and BET surface analyzer have been reported for the first time for TCR<sup>®</sup> process. At optimum operating parameters, ~57.0 wt% gaseous products, 23.5 wt% biochar, 15.5 wt% aqueous phase and ~4 wt% bio-oil were obtained. The hydrogen content and higher heating value (HHV) of the gaseous product were measured up to 37 vol% and 16.40 MJ/kg, respectively. The bio-oil was naturally separable from liquid phase due to gravity without application of an extracting solvent. Moreover, the bio-oil had very low water (2.6 wt%) and oxygen (10.2 wt%) content as well as HHV of 32.11 MJ/kg. Furthermore, biochar produced from TCR<sup>®</sup> possessed excellent structural and morphological properties, thereby showing potential for several applications in catalysis, soil improvement and for various other purposes. The BET surface area and micropore surface area of biochar were measured 93.144 m<sup>2</sup>/g and 90.654 m<sup>2</sup>/g, respectively whereas, the t-plot micropore volume was measured 0.0487 cm<sup>3</sup>/g.

## 1. Introduction

Fossil fuel based conventional oil reserves remained primary source to meet energy and chemicals demands of mankind in the last century. On the contrary, 21st century is witnessing an exponential growth in research trend directed towards the production of green and sustainable energy from bio-renewable resources. Indeed, bio-renewable feedstocks have potential to meet forthcoming energy crisis and abridge greenhouse gases emission [1–3]. Consequently, application of biomass-derived fuel and chemicals is made mandatory in several countries [4,5]. Particularly, several building block chemicals have been identified by US department of energy, which has potential to serve as feedstock for various applications in petroleum, petrochemical and chemical industries [6]. In addition, several other “drop-in” biofuel and additives from furanic platform chemicals have been extensively reported [7].

Interestingly, biomass as feedstock is considered significantly economical, especially in developing countries, as compared to the delivered cost of crude oil [8].

Thus, attempts have been made to produce biofuel, bio-oil, biodiesel, combustible gases and value-added chemicals from different sources of biomass via various conversion technologies [9–12]. Certainly, conversion of biomass into fuel and value-added chemicals can be helpful in reducing environmental load. Moreover, development of efficient and sustainable technologies will lead to reduced dependency on crude oil import by non-oil producing countries. Eventually, it will help to boost their economy and capacity to tackle agricultural waste. In this regard, agricultural and industrial biomass waste such as wheat straw, rice husk, rice straw, corncob, palm shell and sugarcane bagasse have been reported to be conceivable alternate energy resource for the agrarian economy [13]. Moreover, sugarcane bagasse is produced in

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115 countries including both developed and developing nations such as India, Brazil, USA, China, Australia etc., making it readily available feedstock worldwide [14].

Interestingly, the majority of technologies for efficient utilization of biomass resources have focused either on individual components conversion or involved addition catalysts and solvents. However, limitation to handle raw biomass and complexity in products separation from these processes necessitates the development of alternative methods for direct conversion of biomass into fuel and value-added chemicals. However, high activation barriers for lignocellulosic biomass conversion such as RSB essentially require processing of feedstock to elevated temperatures [15]. In this regard, several research groups have employed pyrolysis process for direct conversion of RSB into fuel and other value-added products [16,17]. Nevertheless, a very high oxygen (~38 wt%) and water (13.8 wt%) content in the produced bio-oil may limit its application in turbines [18].

Thus, Fraunhofer UMSICHT has employed an integrated approach for direct thermo-catalytic reforming of RSB in an auger type reactor to produce biochar, bio-oil and combustible gases at laboratory and pilot scale. The primary objective of present study was to utilize residual sugarcane bagasse to produce fuel and chemicals. Subsequently, a secondary objective was to maximize total yield of the combustible gases that can be directly used for power generation. Yet another objective was to get low oxygen-containing bio-oil as well as biochar with improved properties as byproducts of the process for direct application in various purposes. In this approach, an indigenously built auger reactor for intermediate pyrolysis followed by a catalytic reformer was employed. The TCR<sup>®</sup> process uses agricultural waste as renewable feedstock to produce fuel and value-added products beyond energetic needs. Moreover, the TCR<sup>®</sup> process does not use any chemical, catalysts or solvents and operates at ambient pressure, thereby leading to a safer chemistry for accident prevention. In addition, nearly 100% recovery of products and energy makes it an energy efficient design which theoretically emits nothing to the environment. In this paper, we have discussed the design and operation of 2 kg/h bench scale TCR<sup>®</sup> along with a discussion of the effect of temperature and moisture content of feedstock on products properties and composition.

## 2. Materials and methods

RSB in pelletized form was received from Brazil and stored in an airtight closed container to prevent moisture absorption. On an average, RSB pellets density was measured to be 1.4 kg/m<sup>3</sup> whereas average moisture content was found to be < 8.5 wt%. Similarly, the average size of the RSB pellets was measured to be 10 mm in diameter and 10–35 mm in length (Fig. S-1). In general, RSB pellets were used without any further treatment or modification. However, a known amount of distilled water was sprayed on RSB pellets to study high moisture content effects on conversion and composition of gaseous products. Similarly, a known amount of RSB sample was dried for 24 h in an electrically heated oven to perform experiments with reduced moisture content. Silica wool and candle filters (NSF standard) were procured from Silica Service- und Vertriebsgesellschaft für Dämmstoffe mbH and Top Filter, respectively. Washing liquid was produced from the laboratory plant unit by thermo-catalytic reforming of woody biomass [19]. For information on analytical methods, please refer Supplementary information.

### 2.1. Experimental setup

Thermo-catalytic reforming (TCR<sup>®</sup>) reactor is an electrically heated auger type reactor (Fig. 1, Fig. S-2 for actual image) developed and built by Fraunhofer UMSICHT, Sulzbach Rosenberg, Germany. The TCR<sup>®</sup> reactor setup consists of a 7-liter feed vessel with manual agitator (1), electrically heated horizontal auger reactor (2) of 100 mm diameter and 1000 mm length followed by a vertical reforming unit (3) of 100 mm

diameter × 910 mm height Post this, a shell and tube type heat exchanger (4) is provided to condense vapors coming from the reforming unit. An external chilling unit (5) is provided to maintain the temperature at −5 °C in the condenser. The condensation unit (4) is followed by a gravity settler (6) to collect the liquid products from the vapors. Provisions have been made to collect condensed liquid products from the vapors condensation unit and separation unit via a common condensate collection system (7). The gravity settler unit is followed by an ice-cooled second heat exchanger (8) and a gas washing unit (9) for further purification of incondensable gases. Moreover, three additional filters namely activated carbon filter (10), candle filter (11) and silica wool filter (12) are provided. In addition, a volumetric gas flow meter (13), an online gas analyzer (14) and a gas calorimeter (15) are attached to TCR<sup>®</sup> reactor setup. Moreover, the TCR<sup>®</sup> reactor system is completely insulated and well equipped with necessary instruments and accessories. Furthermore, system operation was carried out with the help of Siemens SIMATIC Win CC system.

### 2.2. Experimental procedure

In a typical thermo-catalytic reforming procedure; the TCR<sup>®</sup> reactor was first disassembled and cleaned prior to each trial. Then the reforming unit was filled with 500 g of woody char in order to prevent entrance of dust and fine particles into the outlet of the reformer. Thereafter, the inlet of the reforming unit was connected to the outlet of the horizontal auger reactor. Similarly, a gas washing bottle was filled with 700 g aqueous phase obtained from TCR<sup>®</sup> of woody biomass. In addition, a candle filter and a silica wool filter were weighed and connected to the system. Thenceforth, the complete TCR<sup>®</sup> system was closed and purged with nitrogen at 70 mbar to ensure no leakage from the system. Subsequently, the online gas analyzer was started and 30–35 mbar nitrogen gas was purged to remove oxygen from the TCR<sup>®</sup> setup. The Nitrogen purging was stopped when the oxygen concentration reached 0.1%. It is well known that a temperature above 500 °C–600 °C is required for efficient conversion of lignin and lignocellulosic biomass [20]. Thus, the temperature set points, 200 °C in the first zone, 400 °C in the second zone and 500 °C in the third zone of the horizontal auger reactor were fixed. Moreover, temperatures in both stages of reforming unit were kept between 500 °C–700 °C. Thereafter, heating was started at the rate of 90 °C/min to reach the given temperature set points. Furthermore, rotation of all screws inside the reactor was started simultaneously.

When desired setpoint temperatures in the horizontal reactor and vertical reformer were reached, the first screw conveyor in the reactor was stopped. Accordingly, the TCR<sup>®</sup> reactor setup was purged with nitrogen to remove traces of oxygen. Thenceforth, the feed vessel was opened and 3 kg of RSB was charged into the system. After closing the feed vessel, the TCR<sup>®</sup> system was purged again with nitrogen until the oxygen content in the system reached 0.1%. Subsequently, the nitrogen purging was stopped and the pressure of the system was reduced to 5 mbar. Thereon, the initial reading of the gas flow meter was noted and the first screw of the horizontal reactor was switched on to start the feed into the reactor. In addition, the RSB in the feed vessel was agitated after every 15 min with the help of a mechanical agitator.

Due to rotation of first the screw of the reactor, the feed material moved into the first heating zone maintained at 200 °C to vaporize light volatile components and raise its temperature. Eventually, the second screw conveyor moved the heated feed to the second zone maintained at 400 °C. Majority of volatile compounds and oxygenates of the RSB were removed in the second zone in the form of vapors leaving behind biochar. Thereon, biochar and vapors moved through the third heating zone (at 500 °C) by the third screw conveyor to ensure recovery of remaining volatile components from the newly formed biochar. Ultimately, vapors and biochar from the third zone of the horizontal reactor moved into a vertical reforming unit maintained at a temperature range of 500 °C–700 °C. The reforming unit employed herein

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