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Pilot technology of ethanol production from oat hulls for subsequent conversion to ethylene

E.A. Skiba [a,*], O.V. Baibakova [a], V.V. Budaeva [a], I.N. Pavlov [a], M.S. Vasilishin [a], E.I. Makarova [a], G.V. Sakovich [a], E.V. Ovchinnikova [b,*], S.P. Banzaraktsaeva [b], N.V. Vernikovskaya [b], V.A. Chumachenko [b]

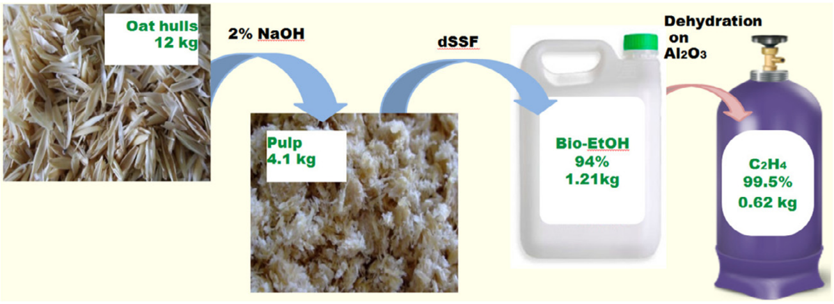
[a] *Institute for Problems of Chemical and Energetic Technologies, Siberian Branch of the Russian Academy of Sciences (IPCET SB RAS), Socialisticheskaya Str., 1, 659322 Biysk, Altai Krai, Russia*

[b] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences (BIC SB RAS), Pr. Akad. Lavrentieva, 5, 630090 Novosibirsk, Russia*

HIGHLIGHTS

- Complete cycle of ethanol processing from oat hulls was tested at the pilot setup.
- Oat hulls were alkali-pretreated in a setup with a rotary-pulsating apparatus.
- Total sugar yield at 33.3 g/L solid loading was 97.9% of the overall hydrolyzables.
- dSSF of oat hull at 60 g/L solid loading gives 95 g ethanol/kg oat hulls.
- The overall ethylene production index was no less than 38–51 g/kg oat hulls.

GRAPHICAL ABSTRACT



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ABSTRACT

Complete cycle of ethylene production from oat hulls as widespread agricultural waste was studied on a pilot scale. The cycle involved mechano-chemical, biotechnological and catalytic units. The oat hulls were pretreated with a 2%(w/w) sodium hydroxide solution in a setup consisting of a rotary-pulsating apparatus and a 100-L vessel to produce a pulp containing 90.3% of hydrolyzables. Simultaneous saccharification and fermentation of oat hull pulp with delayed inoculation (dSSF) into ethanol using commercial enzymes CelloLux-A and BrewZyme-BGX and non-GMO yeast *Saccharomyces cerevisiae* was carried out in 63-L reactor. At a solid loading of 33.3 g/L, the yield of reducing sugars was 97.9% on overall hydrolyzables basis. The ethanol yield during dSSF at a solid loading of 60 g/L was as high as 95 g ethanol/kg oat hulls. The produced raw-ethanol sample contained low impurities of methanol, propanol and alkali metals. The rectified ethanol samples were used for dehydration to ethylene with the overall production index as high as 38–51 g ethylene/kg oats hulls. A negative impact of the propanol and alkali metals impurities in the rectified ethanol on conversion and selectivity to ethylene were observed. Being purified from organic impurities, ethanol was dehydrated with higher conversion and selectivity to ethylene. When the ethanol samples that contain less than 0.02 g/L organic and no sodium impurities were used in ethanol dehydration process, the yield of ethylene was as high as 56 g ethylene/kg oats hulls. In this work, 12 kg of oat hulls was converted to 1.21 kg 94%(w/w) ethanol, which was then converted to 0.62 kg 99.5% ethylene; this is the first experimental study devoted to the production of ethylene from oat hulls on a pilot scale.

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* Corresponding authors at: pr. Akademika Lavrentieva, 5, Novosibirsk 630090, Russia (E.V. Ovchinnikova).
E-mail addresses: eas08988@mail.ru (E.A. Skiba), evo@catalysis.ru, ava@sibnet.ru (E.V. Ovchinnikova).

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1. Introduction

Nowadays the second-generation ethanol production from lignocellulosic feedstocks having no food value is one of the economically promising and ethically attractive renewable resource-based technologies [1-12]. Advances in biotechnologies have helped to commercialize many polymers that conventionally are obtained from petroleum feedstocks [1,4]. In recent years the green ethylene from ethanol process has expanded as the technology based on renewable resource [1,13,14]. Many factors, such as independence from the sources of petrochemical raw materials, the possibility to create low-capacity plants [14], the high quality of the ethylene produced, the simplicity of the technology, and the economic and environmental issues make green ethylene production technologies rather promising especially for the low-tonnage production of chemicals with high added value [14-16]. The alumina ethanol dehydration catalysts protrude to be the most suitable for commercial use due to the stability under undiluted feed and sufficient activity at 400–420 °C [13-21].

Ethanol production process is difficult to scale up for all major stages of the technology either during pretreatment step [22-24], enzymatic hydrolysis [24,25], alcoholic fermentation [25] or during product rectification [26,27]. When scaling-up the process, a decrease in the ethanol yield with respect to lab-scale level is often observed. For the effective commercialization of the process, every technological stage must be thoroughly investigated, followed by the complete cycle of bioethanol production on a pilot scale studies. To simplify the process and to reduce the production cost, it seems quite reasonable to integrate two or more processing steps.

Due to the diversity of biomass in the form of wood, grass, agricultural and forestry residues, etc., and varieties in their chemical compositions and properties, a method of pretreatment of lignocellulosic raw materials is the key factor for efficient commercialization of bio-ethanol synthesis [8-12,28,29]. A proper pretreatment is to increase the yield of fermentable sugars in enzymatic hydrolysis step, to decrease the formation of by-products inhibitory to microorganism growth, and to reduce capital and operating costs [30]. To a large extent, the cost of bioethanol will be determined by the pretreatment's efficiency [29]. Current methods of pretreatment are rather diversified [31–37].

Chemical pretreatment of biomass can considerably modify physical and chemical characteristics of the feedstock by destruction the lignocellulosic matrix, partial hydrolysis of hemicelluloses, partial abatement of cellulose crystallinity, and degradation of lignin structure, thereby improving the biomass reactivity to enzymatic hydrolysis [28,32,33].

Alkaline pretreatment (AP) of lignocelluloses by sodium hydroxide [31-35] is one of the most efficient methods to enhance the ethanol production. By this method lignin is removed from the composite plant matrix, and hemicelluloses are hydrolyzed. The reaction mechanism involves saponification of intermolecular ester bonds by which hemicelluloses and lignin are cross-linked [32,34]. The saponification eventually cleaves those bonds, and cellulose microfibrils are exposed to alkali action. The cellulose degree of polymerization declines, cellulose simultaneously swells, whereby the cellulose internal surface is increased to make cellulose more accessible to enzymes [32,33]. However, some alkali are converted to salts or are incorporated as salts into lignocellulosics during the pretreatment process so that the treatment of a large amount of salts becomes a challenging issue in alkaline pretreatments [34,35]; this is a limitation of alkaline pretreatment. Another limitation is the high capital cost for recycling alkali [32]. Despite this, the AP has certain operational advantages, including lower reaction temperature and pressure, no need for complicated reactors, and the ability to reuse the residual alkali [34]. It is reported that the amount of furfural or HMF in the hydrolyzates obtained by AP is much lower than that resulting from dilute-acid pretreatments [32].

To intensify the pretreatment, relevant mechanical and chemical actions and equipment are applied [36,37]. Before using biomass in the process, a finely dispersed mixture of suspensions must be obtained. High-speed turbulent flows, pressure pulsation, cavitation effects and other hydrodynamic actions are applied to enhance mass-transfer rate, in addition to mechanical action to comminute the feedstock. These kinds of action may be useful in terms of simplification the chemical conditioning of biomass. From this point of view, a rotary-pulsating apparatus [37] can be successfully applied.

Simultaneous saccharification and fermentation with delayed inoculation (dSSF) of the pretreated lignocellulosic feedstock is considered as an ideally integrated process for ethanol production [2,38]. This process has clear advantages over conventional separate hydrolysis and fermentation (SHF) in the production of ethanol from lignocellulosic feedstock, as follows. The ethanol yield is improved due to eliminating end-product inhibition of cellulose hydrolysis. The microorganism can utilize the sugars for growth and ethanol production as soon as they are formed. Moreover, dSSF does not require separate reactors for enzymatic saccharification and fermentation of generated sugars to ethanol [25]. The temperature optima of saccharification and fermentation are considerably distinct, but this can be successfully overcome by delayed inoculation [39,40].

In order to implement enzymatic hydrolysis under manufacturing conditions, effective, commercially available cellulolytic enzymes capable to transform various plant polysaccharides into simple sugars are needed. Previously the commercial enzymes CelloLux-A (Sibbiopharm Ltd, Russia) and BrewZyme BGX (Tarchomin Pharmaceutical WorksPolfa S.A., Poland) were shown to be active biocatalysts for this purpose [41].

This paper is focused on the pilot technology of the ethanol production that uses the oat hulls as a feedstock; the impact of impurities in bioethanol on the process of ethylene production is discussed. The oat hulls is a unique kind of annually reproducible and widely spread biomass [6,7,41,42]. Oat hulls are ~28% of the grain weight and are accumulated at an industrial scale at the grain-processing facilities. This is a morphologically homogeneous raw material that is naturally calibrated by size and thickness and requires no milling when processed. Studies on ethanol production from oat hulls are carrying out in Canada [6], Brazil [7] and Russia [41,42], but no references to the articles on ethylene production from oat hulls was found. The complete ethanol production cycle at a pilot scale, including AP of oat hulls, dSSF, and distillation was investigated in the paper. Alkaline pretreatment of oat hulls feedstock and rotary-pulsating apparatus were employed, virgin and pretreated oat hulls were analyzed. An enzyme cocktail of commercial cellulase preparations was used for saccharification. Non-GMO yeast of the Russian National Collection of Industrial Microorganisms was utilized for fermentation and distillation. Raw ethanol was rectified to 94% (w/w) and then used to produce ethylene on alumina catalyst [21]. With the intensive current development of biotechnologies, accompanied by an increase in the types of bioresources used, as well as with the expansion of the fields of application of the resulting bioproducts, the emerging issues of the influence of impurities become topical. Effect of impurities in bioresources on subsequent output of the target products was discussed in [43-47] with reference to bioethanol reforming [45,47], but was not considered to date for the bioethanol dehydration to ethylene. The analysis of the impact of typical impurities in the product of biotechnology on the processes of its downstream treatment is necessary in view of optimal development of new biotechnologies.