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ENERGY EFFICIENT TECHNOLOGIES FOR LIGNOCELLULOSIC ETHANOL PRODUCTION

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ABSTRACT: Currently, biofuels are the most significant alternative fuel aiming to provide clean power for transport, in case sustainable production technologies are employed. Due to the increased tendency of turning over the existing agricultural land to biofuel production, lignocellulosic feedstock is gaining increasing support against the use of first generation feedstock such as sugar cane, corn, wheat or sweet potatoes. However, despite the existing pilot plants, energy intensive technological processes like pretreatment and distillation, as well as high cost of enzymes, still prevent market rollout of production facilities, extensive researches being conducted in order to find economically feasible alternatives. New closeto market techniques, withimproved performance in terms of energy and resources, are discussed: the relatively recent SPORL pretreatment, reported as the most effective in size-reduction energy consumption; pretreatment by means of extrusion - a technique in which biomass under goes continuous mixing, heating and shearing, thus suffering physico-chemical disintegration; energy saving pass-through distillation that performs at room temperature, which also offers indirect advantages like the possibility of yeasts and enzymes recovery, and simplified exploitation and maintenance of the distillation equipment. The above mentioned subjects are selectedbased on their reported performances as well as on their market potential and estimated technical and economic feasibility.

Keywords: lignocellulosic ethanol, energy efficiency, energy balance, pass-through distillation, extrusion pretreatment, SPORL

1. INTRODUCTION

The general consensus that the use of fossil fuels has an important share in climate change triggered the adoption of policies and measures aiming to accelerate the implementation of low carbon technologies. In the transport sector, tax incentives, fuel blending rules, purchasing regulations and policies imposing maximum limits for engine emission were seen as solutions towards GHG reduction. Despite these efforts, the 34 billion tons of global CO_2 emissions in 2011 was 3% higher than in 2010, and 2.7% higher than the average annual increase during the last decade [37]. Moreover, transport emissions are expected to rise due to an increase in the number of passenger cars of up to 273 million in Europe by 2050, and 2.5 billion worldwide [40].

In order to overcome these negative effects, several legislative measures were taken by most of the developed and developing countries, and in particular at EU level. In USA, the Energy Independence and Security Act and the U.S. Renewable Fuels Standard are implemented in order to stimulate the use of biofuels for transport [50]. EU has already a tradition in establishing similar measures, the reference one being the Strategic Energy Technology Plan (SET Plan) – an energy technology policy aiming to accelerate the deployment of low carbon technologies, including the use of biofuels in the transport sector [29]. Due to concerns over the sustainability and GHG reduction benefits of some biofuels, on April 2015, the European Parliament approved



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the ILUC¹ Directive, which caps the crop-derived biofuel production and proposes measures to accelerate the shift towards alternative sources. According to the new law, by 2020 the first-generation biofuels should account for a maximum of 7% of energy consumption in transport. The binding target of 10% renewable share in transport fuels by 2020 is still maintained, meaning that the difference should be covered from other resources. In this respect, an indicative 0.5% is established for advanced biofuels, the contribution of which will count double towards the 10% target [11]. This new law, coupled with a former decision on stopping subsidizing the first generation biofuels production after 2020, sends a direct message to industry that the future belongs to advanced, sustainable produced fuels.

The main alternative for petrol engines is bioethanol. Existing spark-ignition engines can use mixtures of gasoline and up to 10% bioethanol without being modified, with a more effective oxidation of hydrocarbon due to the ethanol high content of oxygen, thus diminishing GHG emissions. The flexi-fuel engines can use mixtures with up to 85% ethanol, while specially modified engines can use 100% ethanol [16], [18], [26], [30]. As mentioned earlier, current EU policies support the production of second generation ethanol from lignocellulosic materials, mainly in order to avoid the agricultural land use for biofuels production. However, in order to become economically viable, existing technologies for ethanol production from lignocellulosic biomass² need further improvement in terms of cost reduction, use of natural resources such as water and land, reduced GHG emissions and enhanced energy balance. This review presents three close-to-market techniques, more effective than similar ones, which can be used in the most energy consuming steps of the second generation bioethanol production technology, namely in pretreatment and distillation.

2. PRETREATMENT

The first step of the lignocellulosic ethanol production technology is pretreatment, followed by enzymatic hydrolysis, fermentation, distillation and dehydration. Pretreatment consists of physical, chemical, physico-chemical and/or biological methods that are used to perform structural disconnection of the biomass structure at molecular level, in order to allow enzymes from the subsequent enzymatic hydrolysis step to break down cellulose and hemicellulose into sugars for fermentation. The main components of lignocellulosic biomass are cellulose (35-50%), hemicellulose (20-35%), lignin (15-20%), extractives and ashes (15-20%) [35].

Cellulose molecules are made up of chains of β -glucose monomers, gathered into microfibrils. It has a strong, crystalline structure, interrupted from place to place by amorphous regions. Hemicelluloses are formed of a variety of C5 and C6 monosugars (xylose, glucose, arabinose, rhamnose, mannose, galactose), have an amorphous structure and are linked to the cellulose fibrils by hydrogen bonds [1]. Lignin – a biopolymer with a highly disordered structure - confers mechanical strength to the cell wall. There are also hydrogen bonds between cellulose and lignin molecules, while chemical bonding is present between hemicelluloses and lignin [4]. Both lignin and hemicelluloses protect cellulose fibrils by forming a matrix around them.

Therefore, the efficiency of the enzymatic hydrolysis process is determined by a pretreatment step that (1) disrupts this matrix and exposes cellulose and hemicellulose to enzymes, (2) reduces the cellulose crystallinity and (3) increases the material's pores size and surface area, thus offering enzymes maximum access to carbohydrates [30]. Other important key factors to be considered for an optimum pretreatment method are energy and water consumption, minimum formation of fermentation inhibitors, low environmental and technological risks, feedstock versatility, potential for by-products, and economic feasibility.

A first usual pretreatment operation is mechanical grinding, which destroys the binding layer of lignin, hemicellulose, and cellulose, decreases the crystallinity of cellulose [5], and also increases the biomass specific area, thus exposing cellulose as much as possible to enzymatic attack. A subsequent thermo-chemical stage will promote hydrolysis and further degrade the feedstock structure at molecular level. The most common thermal and/or chemical methods are steam explosion, acid pretreatment, LHW (liquid hot water), AFEX (ammonia fiber explosion), wet oxidation, CO₂ explosion, ozonolysis, and more. They have achieved varying levels of success, but they still have technical and economic barriers to overcome before commercialization like

¹Indirect Land Use Change

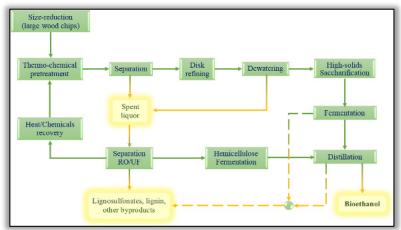
²Different species of wood, cereal straw, corn stover, sunflower stalks, cellulose wastes, herbaceous biomass etc.

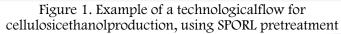
equipment corrosion, high pressure or temperature requirement, high energy consumption, the necessity of hydrolyzate neutralization, low rate of cellulose conversion, expensive routes for chemicals recovery, high capital cost, etc. [14], [34], [35], [38], [45], [49]. These inefficiencies make them inappropriate for commercial application.

3. SPORL PRETREATMENT

In case of biomass with high lignin content, most of the existing pretreatment methods are not efficient; however, SPORL³ and Organsolv can achieve more than 90% conversion of cellulose. Both of them are effective against hardwood and softwood but, when compared with SPORL, Organosolv has some major drawbacks: low concentration of hemicellulosic sugar, use of organic solvents that are hazardous to environment and health, complexity and cost of the recycling process of organic solvents that can inhibit enzymatic hydrolysis and fermentation, and high capital investment [7], [25], [39].

SPORL is reported to be the most energy efficient pretreatment method in terms of sugar production per unit of consumed energy. The first step consists of chipping woody biomass in large pieces of up to 38 mm length/width and a thickness of about 6 mm. Wood chips are then reacted for 10-30 minutes and at 160-190°C, with a solution of 1-8% bisulfate and 0.5-2.2% sulfuric acid (on oven dry wood), depending on wood type [14], [44], [53]. The substrate is created by means of a disk-refiner that separates the pretreated softened chips at a fiber interface level. In most of the pretreatment methods, the lower the particle size after the preliminary biomass mechanical grinding, the higher the enzymatic hydrolysis yields. However, mechanical size reduction usually accounts for 50-60% of the total pretreatment cost, mostly due to its high energy requirements [5]. The SPORL approach of making the size-reduction process in two stages, namely before and after thermochemical treatment, led to important energy savings. Typical energy consumption in the process of mechanical disk-milling of wood is 200-600 Wh/od kg wood, which represents 10-30% of the ethanol energy obtained at a usual rate of 300 L/t wood [42], [53]. Using SPORL, a specific energy of less than 50 Wh/kg od wood was reported for size reduction when lodgepole pine was treated for 30 minutes at 180°C, with 2.21% sulfuric acid charge. Keeping the substrate for 48 h at a cellulase loading of 15 FPU/od g resulted in more than





links between enzymes and lignin, the process of cellulose saccharification is improved, which results in increased fermentation yields. Lignosulfonate is a byproduct of the thermo-chemical treatment with potential economic value that can be used as raw material by other industries like the production of dispersants, emulsifiers and adhesives. Most of the equipment and technology used for pulp making, disk milling, chemical recovery, and wastewater treatment is on the market for decades, being used in the pulp and paper industry. Current disk-refining technology can handle throughputs of up to 1,000 t/day. These last aspects lower the initial capital costs and increase the process scalability, allowing SPORL implementation on an industrial scale, in particular by integration into pulping mills [33], [53]. Figure 1 shows an example of cellulosic ethanol production technology using SPORL.

90% enzymatic cellulose saccharification efficiency, with glucose yields of 370 g/kg od wood [53].

Besides energy efficiency and excellent results for cellulose recovery, there are several other features that make SPORL a potential solution for commercial implementation. The process parameters can be set up to generate negligible amounts of fermentation inhibitors like furfural and hydroxymethylfurfural (HMF). By weakening the hydrophobic

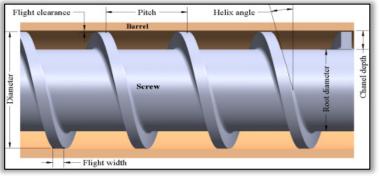
³Sulfite Pretreatment to Overcome Recalcitrance of Lignocelluloses

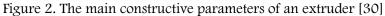
4. PRETREATMENT BY EXTRUSION

Continuous pretreatment by means of extrusion is a new biomass deconstruction process in the area of cellulosic ethanol production, in which biomass undergoes chemical and physical changes through continuous crushing, mixing, heating and shearing [22], [35], [51]. Results consist of biomass defibrillation, fibrillation and shortening of the fibers, increased surface area, reduction of cellulose crystallinity, and cellulose swelling, providing good accessibility of carbohydrates to enzymatic activity [2], [27], [46], [48]. This process can be developed in a very large range of temperatures, with or without acid or base addition [30].

The main industrial applications of extrusion are the manufacture of polymeric products and certain areas of food industry. The two main types of extrusion equipment are single-screw and twin-screw extruders. Single-screw extruders have the advantage of simplicity, lower cost and ease of use in the production process. Moreover, they can be designed to take higher torsional loads during processing. Twin-screw extruders allow high-quality mixing and better defined biomass processing times. Currently, the twin-screw technology has achieved the capacity to

handle considerably increased torque loads that makes them appropriate for high-capacity applications. The twin-screw extrusion technology can further be divided into non-intermeshing and fully intermeshing technologies, both with co-rotating or counterrotating screws. Taking as reference the polymer industry, the current output levels of extruders can exceed 4,000 kg/h [36]. A typical





screw design consists of a single-screw flight with three sections (feed, transition, and metering zone), that rotates inside a barrel (Figure 2). Better performances are obtained using variable pitch, a design that requires CNC manufacturing.

Modern screw and barrel components are both modular, particularly in case of twin screws. Barrel length can be adjusted by adding or removing barrel sections. Each screw can be composed of a number of individual elements combined strategically for better performances and in accordance with the functional parameters of the process (Figure 3). The constructive features of each element type (length, pitch, helix angle) correspond to a specific role within the process [6], [30]:

- » Forward or reverse blocks of elements are designed to transport bulk material, without significant mixing or shearing effect; reverse screws can be used to convey the material backwards for improved shearing and mixing effects [41];
- » Kneading elements intensify shear and mixing in order to achieve a higher degree of pulverization of the material, but have lower transport effect; they are in forward, reverse or neutral orientations;
- » Compression blocks;

(a)

Combing blocks for granulation, if necessary.







Figure 3. Example of screw elements: a) transport element;

b) kneading module, showing the five elements and the rotation with 45° of each element Channel depth directly influences the work applied to the biomass along the screw. It has the largest value in the feed area, and then progressively decreases along the compression zone. The ratio between the channel depth in the feed zone and the discharge zone defines the compression ratio – a parameter that affects both material flow and shear development inside the barrel [23].

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Extruded material experiences a range of residence times and rates of shear development based on the type of twin-screw extruder, screw design and speed, and ratio between the length L and diameter D of the extruder (known as L/D ratio). Moisture content has similar effects as it influences the friction coefficient developed between the material and the surfaces of screw and barrel. Moisture degree also changes when feed ports, which can be added in any location along the barrel, are used for the addition of chemicals in liquid phase. Similar ports can be used downstream to remove liquor, vent gases, or extract samples of material. Cast heaters are used to adjust barrel temperature in order to meet the pretreatment requirements. Due to its influence on the degree of feed melting/softening, it indirectly affects the flow pattern and residence time. Both the diversity of extruder profiles that can be obtained by using different types of screw and barrel elements, and the possibility to easily set up process conditions (residence time, temperature, moisture, etc.), give the extrusion system high flexibility in searching for optimum pretreatment performance [30], [36], [46]. Extrusion equipment can be used with or without chemical catalyst. Table 1 exemplifies some experimental results in terms of sugar yield, obtained with no catalyst, and with alkali or acid catalysts.

Biomass	Type of extruder	Pretreatment	Screw speed/ Barrel temperature	Glucose yield	Other data	References
Corn cobs	Single~ screw	Physical; no catalyst	75 rpm/125°C	75%	49% xylose recovery	[21]
Switchgrass	Single- screw	Physical + NaOH (0.02g/g)	118 rpm/180°C	90.5 %	81.5% xylose recovery; 88% combined sugar recovery	[19]
Soybean hulls	Twin~ screw	Physical; no catalyst	350 rpm/80°C	95%	Moisture: 40%	[26]
Wheat straw	Extrusio n type mixer	Physical + NaOH	35 rpm/98°C	92%	43% pentosans recovered; 72% removed lignin	[3]
Rice straw	Twin~ screw	Physical + H_2SO_4 (3 wt%)	40 rpm/120°C	no data	Xylose yield: 83.7%	[6]

Table 1. Examples of experimental results performed with various types of extruders,

Information regarding energy consumption during the extrusion process is extremely scarce. A report on the extrusion of rice straw with a twin-screw extruder to prepare high monomeric xylose hydrolysate showed that best performances were achieved at 30 rpm and 120°C, with a specific mechanical energy consumption of 191.8 Wh/kg wood [6]. This value should not be compared with results from other mechanical size-reduction processes due to the fact that the biomass delivered by the extruder is disrupted at a level that cannot be achieved by other mechanical methods; resulting material is ready for enzymatic hydrolysis and this performance requires higher energy levels. In addition, very promising results were obtained at temperatures around 100°C (table 1), with residence periods of the order of minutes, which results in lower specific consumption of thermal energy than in case of other pretreatment methods. Research on micro/nanofibrillation of woody biomass through extrusion revealed that power consumption linearly decreases on a logarithmic scale when the discharge capacity of the extruder increases, demonstrating additional energy savings for industrial scale applications [27].

This novel technology has numerous advantages that make it a very promising alternative to existing pretreatment methods: continuous operation, availability of commercial systems of various capacities, simplicity in operation and maintenance, adaptability to various feedstocks, short processing times, effective mixing and destructuration of biomass, low-to-moderate optimal process temperatures (50-130°C) [2], rapid transfer of heat, little or no washing of pretreated material leading to lower inputs in terms of water and energy, easy to scale-up in industrial application, no solid loss or effluent disposal. Due to its advantages this technique can also be integrated in small-scale applications.

5. PASS-THROUGH DISTILLATION

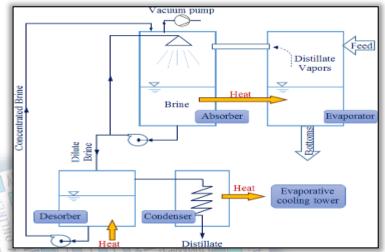
In chemical industry, distillation is used for around 95% of all fluid separation, this process being considered as responsible for 3% of the world energy consumption [7]. In bioethanol plants, fouling of thin stillage evaporators and reboilers is a common problem at temperatures above

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80°C. This issue translates in maintenance and redundant equipment. The plant cooling water temperature limits the condensing temperature at about 45...50°C during summer, and consequently the minimum boiling temperature at minimum 70°C. These temperatures destroy both the expensive enzymes that are denaturated above 60°C, and yeasts that start to die at more than 30°C. One solution to address this limitation, moving the temperature down to a safe 30°C, would be the use of refrigerated condensers. However, due to high capital costs and costs related to the refrigeration process, this solution is appropriate for small production volumes with high selling price, but not for large scale production of price competitive biofuels. Cost and energy problems are also experienced if vacuum pumps are intended to be used to reduce the pressure and initiate evaporation at low temperature, at the same time extracting the ethanol vapors from the evaporator. In industrial applications the vacuum pumps should be very large and would come with infeasible energy costs. The use of expensive ethanol-selective membrane based separation methods poses the same problem of fouling, which restricts the permeation rate and is difficult or impossible to remove.

Pass-through is a very new concept developed by Drystill – a Canadian technology provider company - that performs distillation at room temperature with half of the energy requirements when compared to current conventional distillation methods available on the market. It is based on a combination of existing, mature processes that have now being put together. A pilot plant based on this method was built by the chemical recycler Fielding Chemical Technologies Inc. in order to process complex hazardous high-solids aqueous waste streams without the use of self-sustaining combustion [12].

Pass-through distillation uses gas absorption technology, which makes use of a recirculating absorbent fluid in order to perform distillation at room temperature. An absorption step and a desorption one are introduced in order to perform evaporation and condensation at different pressures (Figure 4). The evaporator and the absorber operate at low pressure and temperature that, in an application for water distillation, were 30 torr and 30°C. In the absorber, a lithium bromide brine is sprayed to absorb the vapors, while the vacuum pump removes only the relatively small amounts of air and non-condensable gases that were captured within the feed, thus maintaining the low operating pressure. During the absorption, the latent heat of evaporation achieved within the evaporator and the heat of mixing are released by the absorbing vapors, adding mass and energy to the brine. As a result, the brine becomes diluted and its temperature raises.



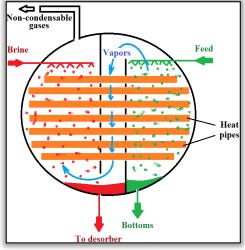
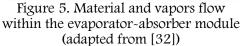


Figure 4. Simplified diagram of a pass-through distillation system (adapted from [32])



In order to maintain the operating temperature, a heat-pipes based heat exchanger is used to move heat from the absorber to the evaporator, providing the latter the necessary thermal energy to drive the evaporation process (Figure 5). This circular flow of heat between the absorber and evaporator, where the heat of evaporation is re-used for evaporation, defines a passive system that can perform at no additional external thermal energy. This is the first step of the equipment in achieving energy savings. In order to maximize the absorption process, vapors travel counter-current to the absorbent brine.

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Heat pipes technology involves liquid-vapor phase change, offering high thermal conductivities (5,000...200,000 W/mK), low cost, as well as simple and reliable operation. Each heat pipe is vacuumed, filled with a working fluid and sealed. A metallic wick structure saturated with the working fluid is distributed over the entire inner surface of the pipe. The side of the pipe placed in the higher temperature area acts as an evaporator, while the other side is the condenser. The working fluid in the evaporator area takes up latent heat and evaporates. In the condenser the vapors transfer their heat and change into the liquid phase. Due to the capillary action of the wick, the working fluid is then returning from the condenser to the evaporator.

The last step takes place in the desorber and consists of separating the distillate from the diluted brine, thus restoring the brine concentration. The clean, thermally stable diluted brine, makes possible the use of multiple effect distillation (MED) through externally supplied heat (Figure 6). In MED, each evaporator vessel reuses the energy from the previous one. To

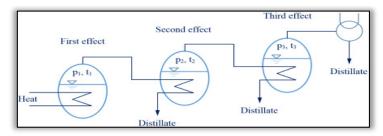


Figure 6. The operating principle of multiple-effect distillation (adapted from [31])

make this process possible, distillation is performed at progressively lower temperatures and pressures. A typical reduction in energy consumption is 50% when compared to conventional distillation [10], performance ratio being proportional with the number of effects [9].

The pass-through distillation system has a very good chance to become a new standard among separation technologies due to the following main advantages [9], [24], [33]:

- » Depending on system configuration, this technology can perform with up to 60% of the energy required by conventional distillation;
- » Room-temperature operation in the evaporator-absorber module offers a solution towards the recovery of biocatalysts and enzymes;
- » Water lost through evaporation in cooling tower is proportional to the energy that it should remove from the system. In pass-through distillation, up to 80% reduction in water consumption can be achieved due to the less energy used and also because of the replacement of energy-inefficient equipment (distillation columns, evaporators, rectifier columns, etc.);
- » Possibility to work with high solids fermentable broth;
- » Overall reduction in energy consumption proportionally translates into GHG reduction;
- » Lower maintenance and capital expenditure.

6. DISCUSSION AND CONCLUSIONS

Although there are few LCA studies on second generation bioethanol, the existing data show that the energy ratio is higher than one [28], [43], [44]. This means that second generation bioethanol provides more renewable energy in the form of ethanol than the fossil energy used for producing, transporting and processing the biomass [8], [15]. However, even if basic conversion technologies of lignocellulosic biomass into bioethanol are not new, market uptake is still burdened due to various factors, one of the most important being the operational and investment costs. In spite of these costs, some technologies are currently tested worldwide in pilot plants, but in the meantime new improved approaches and methods are developed for each intermediate technological step. Usually, these new breakthroughs are investigated individually or tested on an already existing, not yet mature, technological flow. As presented before, the new solutions provided in this paper are reported to be cost-effective, resource efficient, economically viable, and they address the efficiency of most energy-expensive technological steps: pretreatment and distillation. The experimental findings that support these conclusions lead to the idea that, if combined in the same technological flow and properly adjusted, these processes would significantly improve energy balance and, consequently, GHG emission levels, as follows:

» Usually pretreatment is preceded by biomass size-reduction. SPORL method achieves a reduction in energy consumption by up to 80% [38], [53] due to the very coarse chopping before thermo-chemical pretreatment followed by a fiberization of pretreated, softened material, as well as because lower energy levels are necessary for mixing chemicals and pulp during pretreatment. Thermal energy recovery from thermo-chemical process should also be considered. According to current practices from the paper industry, where pulping process is

similar to that of the lignocellulosic ethanol production using SPORL, 50% of thermal energy can be recovered [52].

- » In case of extrusion pretreatment, energy economies could be achieved directly or indirectly due to rapid heat transfer, short residence time, moderate temperature, no formation of fermentation inhibitors (which eliminates energy consumption for detoxification and water decontamination), no need for effluent disposal and no solid loss (in case of simple physical extrusion that works without liquid fraction) [20]. Using the recovered residual lignin for fueling the conversion process will further improve the overall energy balance.
- » On the separation step, up to 60% energy economies can be achieved by replacing conventional distillation with multiple effect, pass-through distillation. This solution also triggers other indirect energy savings due to both lower water consumption and replacement of existing energy-inefficient equipment, as well as because ethanol can now be extracted from high-solids fermentable broth without the fouling related issues.

In the context of an increased worldwide trend towards new developments in cellulosic ethanol industry, the main key to make biorefineries economically viable and sustainable is the optimization of a technology made up of high efficiency, close-to-market individual processes. **Note**

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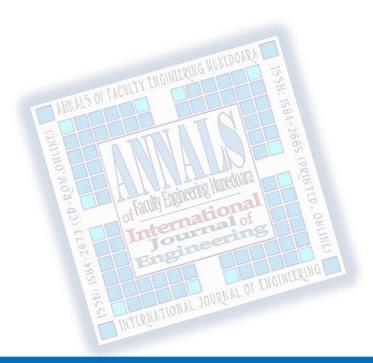
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