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Zhao, Yan; Damgaard, Anders; Christensen, Thomas Højlund

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Bioethanol from corn stover – a review and technical assessment of alternative biotechnologies

Yan Zhao ¹, Anders Damgaard ² and Thomas H. Christensen ^{2,*}

1 School of Environment, Beijing Normal University, Beijing 100875, China

2 Department of Environmental Engineering, Technical University of Denmark,
Kongens Lyngby 2800, Denmark

First author: Yan Zhao, yanzhao@bnu.edu.cn

Corresponding author: Thomas H. Christensen, thho@env.dtu.dk

Running title: Review on bioethanol from corn stover

1 **Abstract**

2 Reviewing the literature from the last decade regarding the bioconversion of corn stover into ethanol, 474
3 references were identified containing 561 datasets. We found 144 datasets which were sufficiently
4 consistent and detailed to address the current state of the art of corn stover conversion to bioethanol, and
5 we were able to categorise 93% of these datasets into eight different technological configurations for the
6 production of bioethanol, based on the pretreatment approaches used. After pretreating, the corn stover is
7 subject to hydrolysis and fermentation, but these two process steps were largely identical in all datasets,
8 albeit a range of operating conditions was reported. The final distillation of the ethanol was very rarely
9 included in the datasets. By parameterising the bioethanol production by 26 parameters, including corn
10 stover compositions, solid loadings, operational conditions, conversion efficiencies and material
11 consumption, we were able to quantify the material flows for each technological configuration and estimate
12 the uncertainty of the flows. The eight technological configurations produced 11-22% ethanol from the dry
13 solid content of the corn stover. Technologies using alkaline-, solvent or ammonia-based pretreatments
14 produced the largest amount of ethanol (19-22%), while fungi-based pretreatment produced much less
15 (11%). All technological configurations resulted in large flows of solid as well as liquid residues, typically
16 containing 60 to 70% of the dry solid corn stover content. Based on the selected datasets, statistical
17 description is provided for all parameters, including mode, median, average and deviation, within each
18 technological configuration. Bivariate correlation analysis across and within all technological
19 configurations indicates that some operational parameters usually considered crucial in laboratory studies,
20 e.g. pretreatment severity, show from a statistical perspective very little correlation with the yields. The
21 review reveals that a great deal of research has addressed the challenge of converting corn stover into
22 bioethanol, but a significant part of these studies is of limited value in terms of scope and documentation
23 when addressing overall material flows and key parameters in a technological context.

24

25 **Keywords**

26 Bioethanol; corn stover; review; technology; pretreatment; material flow analysis

Abbreviations: PT, pretreatment; HL, hydrolysis; FT, fermentation; PS, pretreatment severity; SL, solid loading; TS, total solid.

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1 **1. Introduction**

2 The introduction of biofuels into the transport sector is considered an important and necessary
3 contribution to reducing the dependence of modern society on fossil energy, and bioethanol has already
4 been introduced as an alternative to gasoline in some countries (e.g. USA, Brazil and India) [1-3]. From a
5 sustainability point of view, bioethanol should be produced from secondary biomass deriving mainly from
6 lignocellulosic waste, with the advantages of both utilising the waste through resource recovery and
7 avoiding using biomass that would otherwise be useful as food for human [4]. Significant quantities of
8 lignocellulosic waste are available widely throughout the world; in particular corn stover [2, 5]. Corn is not
9 only the largest agricultural commodity in the world (1.06×10^9 t/y of corn, 7.49×10^8 t/y of wheat and
10 7.41×10^8 t/y of rice) [6], but the by-product part of corn in terms of the stover is also significant. Therefore,
11 bioethanol production from corn stover could be an important technology for producing ethanol as a
12 gasoline substitute.

13 As a typical lignocellulosic feedstock, corn stover contains lignin, cellulose and hemicellulose,
14 collectively constituting a complex polymer structure which restricts reaction media or enzymes to get in
15 close contact with cellulose; thus corn stover is not easily converted into bioethanol [7]. This makes
16 pretreatment which aims toward breaking down the crystalline and polymeric structures an important step
17 prior to the hydrolysis, fermentation and final purification stages. While the latter steps are technologically
18 relatively well known, a lot of research has been carried out recently on the pretreatment of corn stover,
19 including physical, chemical, biological and other processes [8, 9]. Typically, physical pretreatment
20 involves milling, extrusion, and microwave irradiation; physicochemical pretreatment refers to steam
21 explosion, liquid hot water, ammonia fiber explosion and supercritical CO₂ explosion; chemical
22 pretreatment usually applies acid and alkaline substances, and sometimes organic solvent or ionic liquid as
23 reaction media; while biological pretreatment employs microorganisms like different types of fungi [10].
24 Enzymatic hydrolysis is the dominated process for hydrolyzing the carbohydrates, though acid and
25 hydrothermal technologies can also serve as hydrolysis processes. These technologies aim at the same target
26 of maximising ethanol production, but they have essential differences in terms of their approach,
27 operational parameters and yields, and even within the same technology, the operational conditions as well
28 as sugar and ethanol yields vary greatly. Furthermore, full-scale technologies are still in short supply and
29 in the early stages of development [10, 11], and there is no clear picture of which pretreatment processes
30 and overall technological configurations are most efficient in producing bioethanol from corn stover.

1 To address the current state of the art of different approaches for corn stover conversion to bioethanol,
2 a literature review was conducted on bioconversion processes, focusing on a technological perspective from
3 nearly 500 papers published over the last 10 years. This was achieved by using material flow analysis and
4 statistically assessing all of the relevant parameters identified in the study. From each dataset we extracted
5 data and generated statistical distributions on key parameters for operational conditions and component
6 yields within all the technological configurations including pretreatment, hydrolysis and fermentation.
7 These also form the basis for the mass flow analysis for each technological configuration. The results from
8 material flow and statistical analysis can provide comprehensive and undiscovered information across the
9 individual studies and the technologies. This can serve for potential improvement of bioethanol production
10 from corn stover regarding the choice of relevant technologies and operational parameters. The review also
11 identified the most promising technological approach to produce bioethanol from corn stover and identified
12 where further research and development are needed.

14 **2. Approach and methods**

15 **2.1 Data sources**

16 Given the scarce information of industrial practices, only academic publications were included in this
17 review for consistent, transparent and scientific purposes. Web of ScienceTM was searched for the last 10
18 years (2007-2016) for research directly or indirectly related to ethanol produced from corn stover (or corn
19 stalks), with particular focus on conversion processes, without involving review articles. We identified 474
20 papers, as shown in Section A1.1 of Supporting Information.

21 The 474 papers contained 561 datasets, which we evaluated on the basis of their completeness and
22 consistency, as described in Section A1.2 of Supporting Information. The focus and quality of data in the
23 papers varied significantly, but 144 datasets from 120 papers (see references of [13-132]) with relatively
24 high completeness and/or consistency were selected and subjected to further analysis. In addition, the basic
25 information for all 561 datasets is listed in Section A1.3 of Supporting Information, including author and
26 publication information, process classification and scale information and the basic values of glucan, glucose
27 and ethanol yields, where available.

28 **2.2 Technological configurations**

29 For the data analysis, we grouped 141 out of the 144 datasets into eight technological configurations
30 according to pretreatment characteristics [12]. This is because the pretreatment process is a significant and

1 the most studied step in the bioconversion of corn stover to ethanol. The pretreatment strongly affects the
2 availability of substrates for the enzymatic hydrolysis and the quantity and composition of what is input
3 into the fermentation process. In most of the reported studies, the fermentation step and the final distillation
4 (if included in the dataset) were almost identical. A technological configuration is a combination of
5 processes that addresses all steps required in pretreating and converting corn stover to ethanol, namely
6 pretreatment, hydrolysis, fermentation and distillation. Within each technological configuration, variations
7 appear, for example in retention time, temperature and the usage of chemicals and enzyme, and thus also
8 in conversion efficiencies. The eight technological configurations are described below. The remaining three
9 datasets out of the 144 applied emerging solvent-based pretreatment and chemical hydrolysis [13-15],
10 which were not included in this study for statistical reasons, although they did show high completeness
11 and/or consistency (see Table A11, Section A1.3 in Supporting Information). We also identified research
12 using radiation and electrochemistry in the pretreatment process as well as hydrothermal and
13 bioelectrochemical hydrolysis, but these datasets were few in number and uncertain and/or did not provide
14 the consistency needed for identification as a full process configuration (see Table A12, Section A1.3 in
15 Supporting Information). A detailed description of these technological configurations is available in Section
16 A2.1 of Supporting Information.

17 The eight technological configurations are defined briefly as follows, while the reference numbers
18 involved in each configuration can be found in Section A1.3 of Supporting Information.

19 • S1-Acid (27 datasets from references [16-40]): Primarily dilute sulphuric acid pretreatment,
20 occasionally hydrochloric acid and organic acid pretreatment. Pretreated corn stover is subjected to
21 enzymatic hydrolysis and then fermentation after washing with water.

22 • S2-Alkaline (19 datasets from references [30, 38, 41-56]): Primarily sodium hydroxide
23 pretreatment, occasionally calcium hydroxide and calcium carbonate pretreatment. Pretreated corn stover
24 is subjected to enzymatic hydrolysis and then fermentation after washing with water.

25 • S3-Solvent-based (14 datasets from references [17, 21, 22, 24, 29, 57-65]): Ionic liquid (IL)
26 and/or organic solvent (OS) pretreatment. Pretreated corn stover is subjected to enzymatic hydrolysis and
27 then fermentation after solvent separation and washing with water, or sometimes without washing.

28 • S4-Steam explosion (17 datasets from references [66-82]): Primarily steam explosion without a
29 catalyst, and in one case acid is used as a catalyst. Pretreated corn stover is subjected to enzymatic
30 hydrolysis and then fermentation after washing with water.

1 • S5-Liquid hot water (11 datasets from references [35, 58, 83-91]): Compressed hot water or
2 hydrothermal pretreatment without a catalyst. Pretreated corn stover is subjected to enzymatic hydrolysis
3 and then fermentation after washing with water.

4 • S6-Ammonia-based (27 datasets from references [22, 24, 29, 38, 39, 64, 92-109]): Primarily
5 ammonia fibre expansion (AFEX), occasionally low moisture anhydrous ammonia (LMAA) and ammonia
6 recycle percolation (ARP) pretreatment. Pretreated corn stover is subjected to enzymatic hydrolysis and
7 then fermentation after ammonia removal, or sometimes washing with water.

8 • S7-Fungi (11 datasets from references [53, 110-119]): Various fungi species are used for
9 pretreatment. Pretreated corn stover is subjected to enzymatic hydrolysis and then fermentation directly
10 with two cases of washing with water.

11 • S8-Combi (15 datasets from references [97, 98, 120-132]): Various combinations of physical,
12 chemical and thermochemical pretreatment. Pretreated corn stover is subjected to enzymatic hydrolysis and
13 then fermentation after washing with water.

14 **2.3 Process parameters**

15 The selected datasets were not complete seen from a technological point of view, probably due to their
16 different purposes and the research focus, and so this made any direct comparison of the results impossible.
17 Therefore, we defined parameters able to describe all processes in the technological configurations, thereby
18 making it possible to obtain systematic quantitative information from the datasets both across and within
19 technological configurations. The material flows, carbon flows and ethanol yields were calculated based on
20 the parameters identified in Table 1. Data on corn stover composition, solid loading, operational conditions,
21 conversion efficiencies (yields in each process), material consumption, and generated ethanol are reported
22 data or calculated from reported data, following which they are treated as independent parameters, except
23 for pretreatment severity (PS) and some of the raw materials data (e.g. OPP_RM), which were derived from
24 other basic data and are thus dependent.

25 **2.4 Material flows**

26 Based on the parameters in Table 1, compiled for each of the 141 datasets considered consistent,
27 material flows as dry solids and as carbon were estimated for each of the eight technological configurations
28 with the EASETECH (version 2.5.3) material flow and LCA model [133] and presented by using the
29 statistical substance flow model STAN (version 2.6.8) [134]. The many datasets available for each
30 technological configuration allowed for quantifying any uncertainty in material flows while maintaining

1 the overall mass balance, including the flows of components, carbon, ethanol, fermentation gas, solid
2 residue and liquid residue. Some datasets did not contain enough information to obtain all relevant
3 parameters for material flows, and so these datasets were supplemented with median values from existing
4 data on the same parameter and in the same technological configuration.

5 **2.5 Statistical analysis**

6 For the selected 141 datasets, statistical analysis was performed to investigate parameter distribution
7 and correlation. The statistical description, including the average, deviation, mode and distribution of each
8 parameter in each process configuration, was calculated with the statistical software MiniTab 17.1. The
9 correlation analysis of key parameters was performed with the statistical software IBM SPSS 20.0.
10 Specifically, the bivariate correlation analysis applied a Spearman correlation coefficient with a two-tailed
11 test of significance in the confidence levels of 95% and 99%.

13 **3. Results and discussion**

14 **3.1 General information mined from the literature**

15 The time-wise distribution of the 474 papers (2007-2016), on the bioconversion of corn stover to
16 ethanol, showed an increase from 2007 to 2011 followed by a levelling off at around 60 annual publications
17 (Figure 1).

18 The pretreatment covered 11 different approaches, but four of them covered about two-thirds of all
19 datasets in the publications: acid pretreatment (S1, 143 datasets), steam explosion pretreatment (S4, 92
20 datasets), ammonia-based pretreatment (S6, 75 datasets) and alkaline pretreatment (S2, 62 datasets). Figure
21 2 shows that pretreatment with acid and with steam explosion dominated 10 years ago, but have dropped
22 in recent years. In contrast, solvent-based and combi pretreatments receive increasing attention.

23 Hydrolysis was for more than 95% of the publications enhanced by the use of enzymes. Cellulase
24 (such as Cellic™ Ctec2 or Ctec3 from Novozyme) was used in all the studies as a single enzyme or in an
25 enzyme cocktail, sometimes with glucosidase or xylanase as supplements.

26 Fermentation to ethanol, which was included in approximately half of the studies, was rather
27 conventional, using mainly yeast (92%) and sometimes bacteria (8%), and needs no further description in
28 this context. Purification was often not described in the research, but it would typically involve distillation,
29 which is a well-known technology with relatively stable and high effectiveness.

30 The 474 publications contained in total 561 sets of data, with 98% from laboratory-scale studies and

1 only 11 datasets from pilot-scale experiments. Only one study addressed a techno-economic assessment for
2 a full-scale technology [57], which suggests that experimental data on corn stover conversion to bioethanol
3 are still in the early stage. The majority of the datasets focused on the pretreatment technology, and fewer
4 than 20% reported on the full combination of pretreatment, hydrolysis and fermentation. Very few datasets
5 included the final distillation of the bioethanol.

6 Mass balances are crucial for quantifying material flows and for assessing the overall technology, but
7 only 68 out of 561 datasets included mass balances to a different extent. We noted in the literature survey
8 that those publications with mass balances in general garnered more citations than those without mass
9 balances, details of which can be found in Section A3.2 of Supporting Information.

10 **3.2 Material flows in eight technological configurations**

11 Figure 3 presents the material flows for the technological configurations S1-S8, which represent 100
12 units of dry matter in mass and account for five material fractions: glucan (representing cellulose), xylan
13 (representing hemicellulose), lignin, ash and “others”. In cases where information about the composition
14 was incomplete, “others” was introduced to account for different approaches used in characterisation and
15 in order to balance consistently the flows to 100 units. Table 2 summarises the major outputs of the material
16 flow analysis, and more details about the material flows can be found in Section A4.1 of Supporting
17 Information. Outputs can exceed 100% of corn stover solids, due to the uptake of water during hydrolysis.

18 Focusing on the production of ethanol, Table 2 shows clearly that ethanol output varies among
19 technologies as well as within technologies. Ethanol production was between 11-22 % of total solids in
20 corn stover. In broad terms, the relative standard deviation of ethanol output was around 20-25% within a
21 technology, with those using alkaline, solvents and ammonia in pretreatment (S2, S3 and S6) showing the
22 highest output of ethanol (19-22%), while pretreatment with fungi (S7) resulted in the lowest ethanol output
23 (11%).

24 All technologies generated an amount of gas (mass unit) from fermentation nearly as large as the
25 ethanol output (around 96% of ethanol output based on dry matter), except for the technology using fungi
26 in the pretreatment stage (S7), where off-gases also formed due to the direct biological degradation of part
27 of the lignocellulose.

28 All technologies generated large flows of residues, typically of the order 60 to 70% of the input mass.
29 Acid pretreatment (S1) seemed to generate slightly higher amounts of residue, while pretreatment with
30 ammonia (S6) or fungi (S7) generated slightly fewer residues. The distribution between solid and liquid

1 residues varied between technologies, but typically, the liquid residue, which consisted of dissolved
2 components, generated in and washed out after pretreatment, constituted the majority. The fungi-based
3 technology (S7) was an exception, with nearly twice as much solid as liquid residue.

4 In terms of the carbon content of the corn stover, the overall picture is that approximately 15-25% of
5 the carbon becomes ethanol and 8-12% becomes CO₂, released as off-gases from ethanol fermentation. A
6 significant proportion of C was found remaining in the residues, with typically 16-36% in the solid and 20-
7 50% in the liquid residue (details and diagrams of carbon flows can be found in Section A4.2 of Supporting
8 Information).

9 **3.3 Corn stover composition and ethanol yields**

10 The composition of the corn stover used in the research and reported in 133 datasets showed a number
11 of variations – averages and standard deviations were: 36.2%±3.2% of cellulose (as glucan), 22.7%±4.2%
12 of hemicellulose (as xylan), 18.5%±3.7% of lignin, 5.0%±2.7% of ash and 18.3%±7.9% of others. Figure
13 3 shows that the average corn stover composition was not exactly the same between the technological
14 configurations, but statistical tests based on the glucan content suggest on a 95% confidence level that only
15 the corn stover used in alkaline pretreatment (S2) had an average glucan content slightly higher than the
16 average of all 133 datasets reporting on the glucan content: 2% more glucan on a dry basis or, relatively,
17 5.5% more glucan than the average corn stover. This may contribute potentially to the observed high
18 (second highest) bioethanol yield of this technological configuration, but it will not change the fact that it
19 is one of the top technologies from the view of ethanol production. Comparisons between any two specific
20 technological configurations, however, showed that glucan content was not identical in the combinations
21 S2 versus S6, S4 versus S7 and S6 versus S7 (see Section A5.1 in Supporting Information).

22 Theoretically, the average composition of corn stover in terms of glucan (36.2%) and xylan (22.7%)
23 could yield, if all processes of pretreatment, hydrolysis and fermentation were 100% efficient, ethanol
24 corresponding to 20.6% and 13.1%, respectively, i.e. a maximum ethanol yield by mass of 33.9% of the
25 dry solids in the corn stover.

26 Overall, ethanol yield from the raw glucan content of the corn stover typically varied in the range 35-
27 85%, as illustrated in Figure 4a. The ammonium-based technological configuration (S6) showed values in
28 the interval of 75-90%, while the fungi-based technological configuration (S7) showed values in the interval
29 of 35-50%. The other technological configurations also varied in their ethanol yields relative to glucan
30 content, but they were all located around the value of 70% – as also reported by the USA National

1 Renewable Energy Laboratory [28]. Relating ethanol yield to the sum of glucan and xylan in the corn stover
2 did not change the picture (Figure 4b), except that the average yields decreased significantly (note that only
3 a few datasets allow for including both glucan and xylan).

4 **3.4 Glucan and xylan fate**

5 Glucose and xylose are considered the main substrates for the fermentative production of ethanol. The
6 ability of the technological configuration to convert solid glucan and xylan to glucose and xylose,
7 respectively, and to route these dissolved compounds to the fermentation step, is the key factor in obtaining
8 high yields of ethanol. In most published research, the focus has fallen on glucan, which is the major
9 substrate component, and routing the derived glucose to fermentation, where yeast converts glucose to
10 ethanol. In many cases, little attention has been paid to xylan and xylose, which chemically in terms of
11 composition and in terms of conversion differ significantly from glucan and glucose. The hydrolysis of
12 xylan to xylose, and the fermentation of xylose to ethanol, is typically done by different enzymes (xylanase
13 such as Cellic™ Htec2 and Htec3 from Novozyme) and different organisms (such as ethanolic *E. coli*) [41,
14 135-137] than the cellulase/glucanase used in converting glucan to glucose and the yeast employed to
15 convert glucose to ethanol.

16 Figure 5 illustrates the fate of glucan and xylan in the technological configurations, all the way through
17 to ethanol. Where data were not provided directly by the references, we calculated the fate from reported
18 data on component concentrations and balanced these against the ethanol data, where possible. We
19 neglected microbial growth in these calculations. Data in pretreatment and hydrolysis are available in
20 70%~90% of the 141 datasets. However, fermentation possesses only 61 and 28 available data for ethanol
21 yields from glucose and xylose, respectively, and the missing data were not included in the statistical data.

22 The pretreatment step opens and partly dissolves the fibre structure of corn stover, and in most cases
23 a liquid reject is removed and the remaining solids are transferred to the hydrolysis step. Acid pretreatment
24 (S1) seems often to lose both glucan and xylan to the liquid residue, and steam-explosions (S4) as well as
25 liquid hot water (S5) lose a significant part of the xylan. Alkaline (S2) and ammonia-based (S6)
26 pretreatments lose the least amount of xylan in this regard. It should be noted that the variation is large
27 within each technological configuration, thereby suggesting that most of the glucan and xylan, if proper
28 attention is paid, can be kept in the solid fraction transferred to hydrolysis.

29 The hydrolysis step converts glucan and xylan into dissolved glucose and xylose, respectively, and the
30 liquid fraction is transferred to fermentation. Figure 5 shows that in general all technological configurations

1 are better at transferring glucose than xylose to the liquid flow routed to fermentation. Conversion of glucan
2 to glucose is particularly high for the solvent-based pretreatment (S3), while acid-based pretreatment (S1)
3 often shows lower glucan as well as xylan conversion efficiencies. In addition, in the hydrolysis step, we
4 observe large variations within each technological configuration.

5 The data on fermentation are less substantial. Nearly all reported experiments observed between an
6 80-100% conversion of glucose to ethanol, and the type of microorganism (yeast or bacteria) had no
7 statistically significant influence on the ethanol yield. In contrast, large variations were observed for the
8 conversion of xylose, also within a single technological configuration. However, it should be noted that
9 several references reported the high conversion of xylose to ethanol. In contrast, in S7, only a few datasets
10 included fermentation and showed low values, resulting in low average ethanol yields, which potentially
11 contributes to the relatively lower ethanol production and high amounts of residues discussed in Sections
12 3.2 and 3.3.

13 Figure 5 illustrates that the actual performance of a technological configuration varied significantly in
14 relation to its ability to convert solid glucan and xylan to ethanol, which suggests that a great deal can be
15 obtained by optimising each individual process in the technological configurations. However, it also
16 suggests that some approaches in the pretreatment and hydrolysis stages tend to perform better and may
17 potentially be easier to optimise, as shown by the glucose yields after pretreatment and hydrolysis in Figure
18 A4, Section A5.2 in Supporting Information.

19 **3.5 Process parameters**

20 The differences in ethanol production between technological configurations, as well as variations
21 within a technological configuration, may be caused to some extent by differences in operational parameters
22 such as temperature, retention time, solid loading, etc. Figure 6 presents the distribution of nine key
23 operational parameters according to technological configurations. The distribution of additional operational
24 parameters in each technological configuration is included in Figure A3, Section A5.2 in Supporting
25 Information. Due to the focus of the published research, most data are available for pretreatment and the
26 hydrolysis but much less so for fermentation.

27 Solid loading (%TS) in the pretreatment varied highly between technological configurations, ranking
28 from very dilute systems with only less than 5% TS to close to dry systems, with the latter mainly applied
29 in technological configurations with solvent (S3) and steam explosion (S4) pretreatments, but as shown in
30 Figure 6, large variations were also found within the single technological configuration. Fewer differences

1 and variations were apparent in hydrolysis and fermentation.

2 Pretreatment retention time varied typically between a few minutes to a few hours, with fungi
3 pretreatment having a much longer retention time of the order of one to several weeks. The retention times
4 for hydrolysis and fermentation were typically a day to a week, with 48 to 72h as the most frequent values
5 (details in Table 3).

6 The pretreatment temperature usually increased to reach 120-180°C in the different technological
7 configurations, except for the fungi pretreatment, and in some cases of pretreatment with steam explosion
8 and liquid hot water the temperature reached 200°C or even higher (Figure 6). In specific cases, a higher
9 temperature was used, but this was often linked to shorter retention times, thereby suggesting that
10 pretreatment severity did not deviate very much (see Section A5.2 of Supporting Information). This
11 phenomenon is explained further in Section 3.6 from a statistical perspective. The hydrolysis step is often
12 at a moderate temperature (50°C) and fermentation at a mesophilic temperature (37°C).

13 Pretreatment with hot water (S5) or fungi (S7) demanded no use of chemicals, while the dosage of
14 chemicals in the other pretreatments varied dramatically, often between 5-20% of the TS in the corn stover.
15 An exception was the solvent-based pretreatment (S3), where dosages could exceed 5 kg solvent per kg of
16 TS. It was expected that a significant fraction (>95%) of ammonia as well as solvents used in the
17 pretreatment could be recovered and reused in the technological configurations of S6 and S3, respectively,
18 although this aspect often was not addressed in laboratory studies. The dosage of enzymes in the hydrolysis
19 step also varied significantly, typically between 10 to 100 g per kg of TS fed into the hydrolysis stage.
20 Details on enzyme dosage calculation are available in Section A2.2 in Supporting Information.

21 Datasets representing pilot-scale studies were not significantly different from those covering
22 laboratory-scale studies, except with respect to the use of chemicals. Data from three pilot-scale studies [28,
23 44, 93] used two to five times fewer chemicals per kg TS than averages for corresponding technological
24 configurations reported in the laboratory scale (S1-Acid, S2-Alkaline and S6-Ammonia-based,
25 respectively).

26 **3.6 Statistical parameter assessment**

27 On the basis of all available data in each technological configuration, statistical descriptions of the
28 parameter distributions, including mode, median, average and deviation, for all operational parameters are
29 presented in Table 3. This information reveals the most commonly used conditions in every process within
30 each technological configuration, so that we can better understand the difference introduced by the intrinsic

1 property and parameter variation of the configurations. The statistical information for all the yields can be
2 found in Section A5.3 in Supporting Information.

3 **3.6.1 Best-practice within a technological configuration**

4 Based on the parameter statistics, we can define a probable “best-practice” using the top 15% of the
5 yields in each individual process, and we can also estimate the expected ethanol production of the
6 technological configuration as described in Section A6.1 of Supporting Information. The results are shown
7 in Table 4 in terms of “best” efficiencies of each process step as well as the ethanol yields from glucan and
8 xylan. The technological configuration with ammonia-based pretreatment (S6) shows a potential ethanol
9 production of 30.6% of the total solid in corn stover, followed by S2 (27.0%), S8 (26.5%), and S3 (26.3%)
10 (see Table 4). The conversion of glucan to ethanol is “best-practice” in the range 88% to 93% of the
11 maximum potential except for the technological configuration using fungi in pretreatment. Table 4 also
12 shows that the bioconversion of xylan to ethanol varies much more (25-85%) in the “best-practice”
13 technologies, suggesting that high xylan conversion efficiency is crucial to overall ethanol production.

14 Compared with the ethanol production obtained from material flow analysis (Figure 3), the “best-
15 practice” is supposed to produce approximately 30%~50% more ethanol within each technological
16 configuration. This indicates that most of the studies did not succeed in optimizing the entire configuration
17 for bioethanol production, given their focuses on specific processes. Therefore, technological optimization
18 must be considered from a systematic perspective in the future, to maximize the ethanol production capacity
19 from corn stover.

20 **3.6.2 Pretreatment and hydrolysis across technological configurations**

21 In addition to the observation that the fate of glucan and xylan in pretreatment and hydrolysis is crucial
22 to overall ethanol production, some experimental studies [37, 138-143] have also considered as important
23 parameters such as lignin content, pretreatment severity and solid loading to overall ethanol production. To
24 assess the general validity of these observations, we conducted bivariate correlation analyses on all 141
25 datasets across all technological configurations with respect to compositions and yields of glucan/glucose,
26 xylan/xylose and lignin in pretreatment and hydrolysis. The results are shown in Table 5.

27 We observed a strong correlation between the yield of glucan/glucose and xylan/xylose in both
28 pretreatment and hydrolysis, in that when one was high, the other was likely to be high as well. Lignin
29 content in the raw corn stover was negatively correlated with the yields of both glucose and xylose in
30 hydrolysis at a 99% confidence level, suggesting that a high content of lignin in corn stover does indeed

1 make it more difficult for enzymatic hydrolysis to make the sugars available for fermentation into ethanol.
2 In contrast, no significant correlation was observed between xylan content in raw materials and any yield
3 in pretreatment or hydrolysis. Furthermore, the yields of xylan and lignin in pretreatment did not show a
4 strong correlation with the yields of glucose and xylose in the subsequent hydrolysis. From this point of
5 view, the existence of lignin is very likely adverse to sugar yields in hydrolysis, but xylan routed to
6 hydrolysis does not necessarily affect the success of hydrolysis, as observed otherwise in some laboratory
7 studies.

8 Pretreatment severity calculated as a combination of temperature and retention time (see Section A2.2
9 in Supporting Information) has commonly been used in the literature for explaining varying sugar yields
10 [66, 86, 142, 144]. According to the correlations observed in Table 5, across all datasets pretreatment
11 severity has little correlation with yields in general, except for the xylan yield in pretreatment. This suggests
12 that the more severe the pretreatment, the more xylan/xylose is lost to the liquid reject flow removed at the
13 end of pretreatment by washing. Since xylose fermentation into ethanol is an important part of the overall
14 ethanol production process, as shown in Table 4, each technological configuration should balance
15 pretreatment severity against the undesirable loss of xylan/xylose. Table 5 also reveals a weak but
16 statistically positive correlation between pretreatment severity and the proportion of lignin remaining after
17 pretreatment in the solid flow being routed to hydrolysis. We do not consider this an observation of general
18 validity, though, because it originates from the fact that the technological configurations S4 (steam
19 explosion pretreatment) and S5 (liquid hot water pretreatment) are specifically efficient in keeping lignin
20 in the solid fraction, although the severity of the pretreatment is high. These two technological
21 configurations use only water and steam in pretreatment, and thus they require higher temperatures and/or
22 longer retention times (Figures A3e and A3f, Section A5.2 in Supporting Information).

23 **3.6.3 Pretreatment and hydrolysis within each technological configuration**

24 Bivariate correlation analysis was also performed within each of the seven technological
25 configurations for the fate of glucan and xylan against operational parameters, including solid loading,
26 temperature, retention time, dosage of chemicals and enzymes as well as pretreatment severity. Supporting
27 Information (Section A6.2) contains correlation coefficients and their level of significance for the bivariate
28 analysis.

29 The overall outcome of the correlation analysis is that a single, dominant parameter, or a few dominant
30 operational parameters, cannot be identified within the single technological configuration. Significant

1 statistical correlations with high correlation coefficients (≥ 0.4) were identified in some cases (16 out of
2 169), but although a likely explanation could be hypothesised for one correlation, we could not find
3 consistent explanations across all correlations identified within a technological configuration. More
4 specifically, seven out of the 16 significant correlations related to solid loading (five from pretreatment and
5 two from hydrolysis), and four out of the 16 related to chemical dosage and four to reaction time (three
6 from pretreatment and one from hydrolysis). No significant correlation was observed between pretreatment
7 severity and any yield of glucan/glucose and xylan/xylose, thereby suggesting that pretreatment severity
8 does not necessarily correlate to the yields as expected.

9 In general, the statistical results might suggest that the effect of combined pretreatment and hydrolysis,
10 which determines how much glucose and xylose are routed to the ethanol fermentation reactor, is influenced
11 by many factors and, perhaps, interacting factors. However, after pretreatment, glucan/glucose and
12 xylan/xylose should stay in the solid flow routed to hydrolysis, while after hydrolysis, glucose and xylose
13 should be fully dissolved and transferred to the liquid flow routed to the ethanol fermentation reactor. Hence,
14 future studies should pay more attention to the control of the solid-to-liquid ratio and the amount of washing
15 water, as well as the separation processes applied. Information about these issues was very scant in existing
16 laboratory studies.

17

18 **4. Conclusions and prospects**

19 Over the last decade, the bioconversion of corn stover into ethanol – intended for the substitution of
20 gasoline – has been subject to intensive research. We found 474 references directly or indirectly addressing
21 the issue, thereby presenting a total of 561 datasets. The vast majority of the reported research was at the
22 laboratory scale (98%), and none was from actual full-scale plants. Not all datasets were complete, and
23 some were too rudimentary to provide consistent information about bioethanol production from a
24 technological point of view, i.e. how much ethanol can we obtain from corn stover with different
25 technologies, and what are the key operational parameters in each process? We found that 144 datasets were
26 consistent and contained enough detail to contribute to an evaluation of the current state of the art of corn
27 stover conversion to bioethanol. A large range of technological approaches was researched, but we could
28 categorise 93% of the datasets into eight different technological configurations for ethanol production. The
29 main differences between the technological configurations were found in the pretreatment phase. The
30 ensuing processes of hydrolysis and fermentation into ethanol were largely identical in the eight

1 technological configurations, although a range of operating conditions was reported. The final distillation
2 was rarely included in the datasets. The priority of the research, to focus on pretreatment and hydrolysis,
3 clearly reflects the notion that the challenge in converting corn stover into bioethanol lies in making as large
4 as possible a fraction of the cellulose and hemicellulose-rich materials available as sugars that are easy to
5 ferment into bioethanol.

6 Very few datasets provided data on the material flows, but by parameterising them, we were able to
7 quantify the material flows for each technological configuration, including estimates of flow uncertainty.
8 Of the dry solid content of corn stover, the eight technological configurations produced 11-22% ethanol.
9 Technologies using alkaline, solvent-based or ammonia-based pretreatments saw the highest ethanol
10 production (19-22%), while the fungi-based pretreatment produced much less ethanol (~11%). All
11 technological configurations resulted in large flows of solid as well as liquid residues. Of the carbon in the
12 corn stover, 15-25% was converted to bioethanol, while the remaining carbon was found in off-gasses and
13 residues. The utilisation of carbon in residues, which is extremely important for the overall energy balance,
14 was barely reported in laboratory studies. The review reveals not only that a lot of research has addressed
15 the challenge of converting corn stover into bioethanol, but also that a significant part of the research is of
16 limited value when addressing overall material flows and indicating how well the employed technology
17 can ensure that sugars in the flow enters the bioethanol fermentation process.

18 Based on all of the extracted parameters and the statistical distributions established for key operational
19 parameters, we showed that the optimisation of all steps could make all technological configurations
20 produce high amounts of bioethanol. Technologies using fungi for pretreatment will always produce
21 significantly less bioethanol and seem less attractive from a technological point of view. Bivariate
22 correlation analysis across and within all technological configurations revealed that some operational
23 parameters, which often are claimed to control the processes, for example pretreatment severity, generally
24 showed little correlation with yields and bioethanol production. This indicates that a single dominating
25 parameter, or a few dominating operational parameters, can hardly be identified within the technological
26 configurations.

27 We conclude on the basis on the literature review that bioethanol production from corn stover is still
28 in its early stages and more research is needed; focus should be on:

29 • Glucan/glucose as well as xylan/xylose: Glucan/glucose is the main component in corn stover for
30 producing bioethanol and most previous research focus on this aspect, but xylan/xylose can also contribute

1 significantly if not lost in the pretreatment and if efficiently converted in the fermentation process. It is
2 important to respect that according to the statistics derived from the literature review, glucan/glucose and
3 xylan/xylose do not behave the same in the pretreatment and washing process and that some fermentation
4 process, but certainly not all are able to utilize the xylose. The literature does not provide a clear message
5 here but suggests an issue to be addressed in future research.

- 6 • Technology: The statistical analysis of the large amount of research data on bioethanol production
7 suggests that there is a large potential for optimizing each technological approach to obtain high ethanol
8 efficiencies, maybe 19-22% of the corn stover on a dry mass basis. Many technological configurations are
9 feasible, but three technologies so far look most promising (alkaline, solvent- or ammonia-based
10 pretreatment), while one technology (fungi-based pretreatment) seems of less potential, probably because
11 part of the easily degradable sugars are being degraded already in the pretreatment step and not utilized for
12 ethanol in the later fermentation.

- 13 • Mas flows: Aiming at developing efficient technologies, it is crucial to document all mass flows
14 (total solids, glucan/glucose, xylan/xylose, carbon) from the corn stover to the bioethanol product,
15 including all the side and residue flows. This will document the efficiency in the bioethanol technology and
16 point to importance of also managing the significant side flows and residues.

17

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25

26 **Appendix A. Supporting information**

27 Supporting information associated with this article can be found in the online version.

28

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- 45

1 **Captions of figures and tables**

2 Figure 1 Number of annual datasets and publications on corn stover conversion into bioethanol, in total and
3 according to technological configurations

4 Figure 2 Distribution of datasets per year (2007-2016) according to technological configuration for
5 converting corn stover to bioethanol

6 Figure 3 Material flows (average with standard deviation) for eight technological configurations of corn
7 stover conversion into ethanol, based on 100 mass units of input dry matter (numbers “x/y” in
8 parentheses stand for x available data from y datasets for C6 (glucan/glucose) or C5 (xylan/xylose)
9 in the process)

10 Figure 4 Ethanol yield in eight technological configurations (S1-S8) for producing ethanol from corn stover
11 relative to the content of a) raw glucan and b) the sum of raw glucan and xylan, respectively (solid
12 circle: median; hollow triangle: average; box: first to third quartile; line: minimum and maximum;
13 asterisk: outlier; dashed line: reference value from USA National Renewable Energy Laboratory
14 [28])

15 Figure 5 Distribution of the fate of glucan and xylan according to the process step (pretreatment, hydrolysis,
16 fermentation) and technological configuration (S1-S8) (data for S8 not shown, because S8 contains
17 different process step combinations not directly referable to the above graphical presentations)

18 Figure 6 Distribution of key process parameters according to technological configuration (data for S8 not
19 shown, because S8 contains different process step combinations not directly referable to the above
20 graphical presentations)

21

22 Table 1 Parameters identified in the process configurations for bioconversion of corn stover into ethanol

23 Table 2 Summary of output flows (%) (average with standard deviation) for eight technological
24 configurations of corn stover bioconversion into ethanol, based on 100 mass units of dry matter in
25 the input

26 Table 3 Statistical description of the operational parameters in each technological configuration (M: mode;
27 MD: median; A: average; SD: deviation)

28 Table 4 Performance estimation of probable best technologies, with a top 15% of yields (%)

29 Table 5 Correlation coefficients between key parameters in the pretreatment and hydrolysis processes
30 within all available data (141 datasets)