Article

Sodium Carbonate Pulping of Wheat Straw—An Alternative Fiber Source for Various Paper Applications

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Abstract: European paper mills are currently facing the question of whether recovered paper, their main raw material, will be available in sufficient quantities and an acceptable quality in the future. An alternative to recovered paper or wood fiber is the use of agricultural residues such as wheat straw. Sodium carbonate-based straw pulping processes have the advantage of not requiring recausticizing for chemical recovery, which reduces investment and operating costs. With the addition of oxygen, delignification can be significantly improved to provide pulps suitable for bleaching. This study compares the pulping of wheat straw using sodium carbonate, sodium carbonate + oxygen, and sodium carbonate + sodium hydroxide + oxygen. Pulping parameters such as temperature, retention time, and chemical charge were varied, and their influence on pulp properties was studied. The use of sodium carbonate alone produced pulps with high yields of up to 72% and comparably high burst and compressive strength. The addition of oxygen and small amounts of sodium hydroxide produced pulps with a high initial brightness of 42% ISO and a low kappa number (18), still at high pulp yields of 62%. These pulps were two-stage bleached to achieve brightness levels of up to 73% ISO.

Keywords: non-wood; alternative fiber sources; wheat straw; pulping; bleaching; papermaking; sodium carbonate pulping; NACO; soda pulping

1. Introduction

The pulp and paper industry is one of the best examples of the biorefinery concept, incorporating the production of materials, chemicals, and energy through established processes. This maximizes the value and utilizes the full potential of lignocellulosic resources. This industry is fully relying on the recyclability and renewability of its most used resources—cellulose fibers. Although in Europe, the recycling rate has reached 70.5% [1], the industry is facing a continuous need for virgin fibers to ensure the required paper quality and to satisfy different market demands. Some of these demands are currently generated by the shift of the packaging industry towards “green” alternatives by replacing plastics with fiber-based materials, which have lower environmental impacts [2]. The rising concern of the migration of mineral oils into packaged food limits the application of recovered paper in the production of paper-based food packaging, thus also leading to an increase in virgin fiber demand [3].

In Germany, advancing digitalization and booming online trade have meanwhile led to an extremely contrasting development in the production of graphic papers and packaging papers. While the production of graphic papers has declined sharply (−35%), an enormously high production growth has been recorded for packaging papers (+20%) [4]. Manufacturers of recycled and packaging papers based on 100% recovered paper are therefore currently facing the question of whether recovered paper, their main raw material, will be available in sufficient quantities, in an acceptable quality, and at affordable prices.
in the future [5]. For certain recovered paper grades, the price has more than doubled in the last two years [6]. These developments are forcing the German pulp and paper industry to look for alternative fiber sources for paper production. An alternative to recovered paper and wood fiber is the use of agricultural residues such as cereal straw. This kind of raw material has several advantages: it is low cost and highly available—there are approximately 11.1 million tons of cereal straw technically available in Germany, of which only 4.3 million tons are currently used (as livestock or for energy). This leaves a biomass potential of 6.8 million tons [7]. Therefore, cereal straw is considered a promising raw material for pulp production due to its abundance and lignocellulosic composition. Worku et al. [8] most recently published a review on agricultural residues as raw materials for pulp and paper production, describing both the potential and the challenges in non-wood pulping. Also, they provide a comprehensive overview of the conventional and alternative pulping processes in this context.

So far, the common pulping process for straw and other non-wood materials has been pulping with sodium hydroxide (NaOH) as the main chemical. NaOH pulping is generally referred to as “soda pulping”. This term might be misleading, since soda is a synonym for sodium carbonate (Na₂CO₃). In NaOH pulping, sodium carbonate is solely used to make up for chemical losses in recovery [9]. For a better demarcation, instead of “soda pulping”, the term NaOH pulping is used in the following. NaOH pulping of non-wood material is a fully developed process, but black liquor recovery still remains a serious problem due to the high silica content of the raw material. Silicates cause severe difficulties in liquor evaporation, burning, and in the lime kiln, which limits the NaOH recovery rate considerably [10]. Promising alternatives to conventional NaOH pulping of non-wood plant fibers are sodium carbonate-based pulping processes. Na₂CO₃ makes it possible to use a simple and low-cost chemical recovery system, which incorporates a combustion unit and a dissolver but without the complication of recausticizing and lime burning units. Pulping of wheat straw using Na₂CO₃ was investigated by Puitel et al. [11,12] and Marin et al. [13]. They found that using Na₂CO₃ as an alkali source for pulping leads to pulps with a higher lignin content. While these pulps might not be suitable for application in bleached paper products, such as office paper, they proposed the potential use of the obtained fibers in the production of packaging papers or for blending with recycled paper to increase the mechanical properties. One drawback of their first study [11] was that they only used one pulping temperature and two levels of chemical charge. All the other pulping parameters, such as the liquor:solid ratio (LSR) and pulping time, remained constant. In the following study, Marin et al. [13] investigated the process factors’ influence on the pulp characteristics, using the response surface methodology. Despite their promising results, the pulping of wheat straw with Na₂CO₃ should be investigated more intensively in this study.

Another alternative is the NACO process, as firstly described by Fiala et al. [14]. The NACO process involves oxygen delignification to a low kappa number in sodium carbonate solution. NaOH can be additionally used as an “activating” and make up chemical. This process was developed to achieve a low lignin content, good unbleached brightness, and reasonable strength properties of the pulp. The oxygen delignification takes place in an alkaline environment with sodium carbonate used as main chemical, recycled through the recovery plant. The Na₂CO₃ losses in the system can be made up by the addition of small amounts of NaOH. This has the aforementioned advantage of using a simple and low-cost chemical recovery system without the complication of recausticizing and lime burning units. To the authors’ knowledge, there was a NACO pilot plant (5 t/d) in Foggia, Italy in the 1980s. The authors have no information regarding whether the plant is still operating. Furthermore, the Italian consulting company IPS engineering offers to act as engineering and contractor for the construction of pulp mills based on the NACO process [15]. Again, there is no information available regarding whether there are currently projects underway for establishing the NACO process.
The present study aims to give a deeper insight into the pulping of wheat straw using sodium carbonate-based pulping processes. Moreover, the pulping equipment and the scale of the experiments should allow for a comparison with the industrial pulp production. First, pulping of wheat straw using $\text{Na}_2\text{CO}_3$ was thoroughly investigated. The LSR, pulping temperature, and chemical charge were varied, and their influence on the pulp and paper properties was examined. Recycled paper pulp from the production of packaging papers and NaOH pulp were used as references. Second, NACO pulping of wheat straw was examined. The pulping temperature and time were varied, and the influence of NaOH addition on pulp properties was investigated. The NACO pulps obtained were bleached in two stages with an acidic or complexing treatment followed by hydrogen peroxide. The bleaching temperature and time were varied. Recycled paper pulp from the production of office paper was used as a reference.

2. Materials and Methods

2.1. Raw Materials (Collection and Characterization)

Wheat straw (Triticum aestivum L.) was collected from cultivation areas in the north of Germany (harvest 2021). The moisture content of the collected straw was approximately 9%. Debris and impurities were separated, and the cleaned straw was chopped into small pieces (30–40 mm). The chopped straw was stored under standard climate conditions until it was used.

The straw was analyzed as follows: The carbohydrate composition was determined according to a method described by Lorenz et al. [16]. Specifically, a two-stage sulfuric acid hydrolysis method was applied, where the samples were exposed to 72% (w/w) sulfuric acid at 30 °C for exactly 1 h. The hydrolysis continued in the second step with 4% (w/w) sulfuric acid for 40 min at 120 °C in an autoclave. The hydrolysis residues (HR) were washed with deionized water, dried at 105 °C, and the TS content was determined gravimetrically. The HR was then calcined in a muffle furnace at 525 °C for 6 h, cooled in a desiccator, and weighed again. The amount of oven-dry and ash-free HR was considered to be the acid-insoluble lignin content and hereafter is referred to as “lignin”. The quantitative and qualitative carbohydrate compositions in the hydrolysates were analyzed using borate anion exchange chromatography with post-column derivatization and UV detection at 560 nm. The ash and silicate contents were determined according to TAPPI standards T 211 om-02 and T 245 cm-98. The solvent extractives were determined using a Dionex ASE 350 extraction instrument. Therefore, approximately 1 g (oven-dry) of milled sample materials was extracted successively using petrol ether, acetone:water (9:1), and water at 100 bar and 100 °C for 40 min. The total extractive content was determined by adding the single extraction yields.

Recycled paper pulps (RCP) were provided by two different paper mills located in the north of Germany. RCP1 comes from a paper mill that produces corrugated board base paper, and RCP2 comes from a mill that produces office and magazine papers, both based on 100% recovered paper.

2.2. Pulping and Bleaching

The design of the digester is considered to be a key element of the NACO process [14]. One important factor is the intense agitation of the material. This will result in fiber separation, which increases the surface of the raw material. At the same time, the oxygen and the chemicals can be very effectively mixed into the fiber suspension. In this study, a digester was used which was specially designed and built for the pulping of non-wood materials, simulating a horizontal tube digester suitable for a maximum pressure of 10 bar (see Supplementary Materials; Figure S1). Similar to the pulper described by Fiala et al. [14], it is equipped with a replaceable rotor which allows it to work with different rotor designs and different degrees of mechanical action. The operation procedure was follows: The digester was filled with the 2.5 kg of oven-dry straw. The chemicals were dissolved in tap water. The LSR was varied between 2:1 and 6:1. The chemicals were added to the straw
inside the digester. After closing the digester, the rotor was switched on to ensure good mixing of the straw and chemicals. Then, the digester was pressurized with oxygen (in the case of NACO pulping). After reaching the starting pressure of 5 bar, the oxygen valve was closed. No additional gas addition or relief was performed, whereas the temperature was controlled by heating or cooling. The digester was equipped with a jacket for heating, which was filled with steam for heating and water for cooling. The digester was heated to the desired pulping temperature within 25 min. After reaching the desired pulping time, the digester jacket was filled with water and cooled down to room temperature within 30 to 45 min. Then, the excess oxygen pressure was released, the digester was opened, and the pulp was rinsed out using tap water and collected in a 100 L plastic tub. Further water was added to achieve a stock consistency of 4%. The pulp suspension was then transferred to a 12” disc-refiner (Sprout Bauer, Graz, Austria) for further defibration. The refiner gap was maintained at 0.3 mm. A process scheme can be found in the supplementary materials (Figure S3). After defibration, the pulp was thoroughly washed with tap water and dewatered in laboratory centrifuges to a dry content of approximately 30%. Finally, the dewatered pulp was homogenized using a laboratory mixer (GGM Gastro, Hamburg, Germany). The obtained pulps were stored in polyethylene bags at 4 °C until further use.

The selected NACO pulps were bleached in a two-stage sequence. First, the pulps were subjected to acid-washing (A stage) with sulfuric acid. For comparison, the pulps were treated with a chelating agent (Q stage). The pulp consistency was adjusted to 3%. A total of 2.5% sulfuric acid or 0.3% DTPA (based on oven-dry pulp) were charged. The pulps were treated in polyethylene bags submerged in an agitating water bath. Acid washing was conducted at 60 °C for 60 min.

After the and Q stages, the pulps were bleached with hydrogen peroxide (P stage). The pulp consistency was adjusted to 10%. The sodium silicate, sodium hydroxide, and hydrogen peroxide charges were 4%, 2%, and 4%, respectively. The bleaching temperature was varied between 70 and 90 °C. The bleaching time was varied between 120 and 240 min. After each stage, the pulps were thoroughly washed with deionized water, dewatered in a centrifuge, and homogenized in a laboratory mixer.

2.3. Pulp Characterization

The pulp yield was determined gravimetrically. The kappa number was measured according to TAPPI standard T 236 om-99. The pulp brightness was measured according to TAPPI standard T 452 om-02. The consumption of hydrogen peroxide was determined titrimetrically. Therefore, 50 mL of undiluted bleaching filtrate was added to a 300 mL Erlenmeyer flask, in which 15 mL of sulfuric acid (2 mol/L) and 15 mL of potassium iodide solution (1 mol/L) were added. Then, titration with sodium thiosulphate (0.1 mol/L) was conducted until the transition point. The equivalence between 1 mL of titrated sodium thiosulfate solution and 0.0017 g hydrogen peroxide was established. With this, the concentration of hydrogen peroxide in the bleaching filtrate and subsequently the consumption of hydrogen peroxide can be calculated.

2.4. Pulp Beating, Handsheet Preparation, and Paper Testing

Laboratory pulp beating was performed using a Jokro mill (FRANK-PTI, Birkenau, Germany) according to the German standard Zellcheming V/5/60. The beating degree was determined according to the German standard Zellcheming V/7/61 using a Schopper Riegler Freeness tester (FRANK-PTI, Birkenau, Germany). Handsheets were made using a Rapid-Koethen sheet former (FRANK-PTI, Birkenau, Germany). The handsheet grammage was set to 75 g/m². The following methods were used for paper testing: tensile, tear, and burst strength, Zellcheming V/12/57; strength index calculation according to TAPPI standard T 220 sp-01; and compression index according to TAPPI standard T 826 om-04.
3. Results
3.1. Raw Material Characterization

The wheat straw used in this study was analyzed for its carbohydrate (cellulose and hemicelluloses), lignin, and ash contents, as well as the amount of extractives. Zhang et al. [17] most recently published a comparison of the lignin distribution, structure, and morphology in wheat straw and wood, referring to six other studies where wheat straw was used as the raw material. Table 1 shows a comparison of the composition of the wheat straw used in this study and values from other studies as well as the composition of spruce wood (Picea abies L.) as a reference.

Table 1. Composition of wheat straw (present and other studies) and spruce wood. Values in %, based on oven-dry materials. Standard deviations are shown in brackets.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Present Study</th>
<th>Other Studies [17]</th>
<th>Spruce Wood [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>36.4 (0.2)</td>
<td>32–45</td>
<td>41.6</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>23.1 (0.4)</td>
<td>20–45</td>
<td>25.2</td>
</tr>
<tr>
<td>Lignin</td>
<td>20.5 (0.2)</td>
<td>11–26</td>
<td>29.5</td>
</tr>
<tr>
<td>Extractives</td>
<td>10.5 (0.1)</td>
<td>ND</td>
<td>3.6</td>
</tr>
<tr>
<td>Ash</td>
<td>10.5 (0.2)</td>
<td>0–2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

1 Lignin: Ash-free residue after 2-step acid hydrolysis with 72% H₂SO₄; analogous to the acid-insoluble lignin content. 2 ND: Not determined.

As can be seen from Table 1, the cellulose content of the wheat straw used in this study was 36%, which is within a similar range to that reported in other studies. However, compared to spruce wood, the cellulose content in the straw was lower. This is partly due to the higher content of hemicelluloses, which can be up to 45% [17]. Furthermore, wheat straw contains high amounts of inorganic components (mainly silicates), as depicted by its ash content of 10.5%. Compared to spruce wood, wheat straw has a lower lignin content. In this study, the lignin content of the straw was 20.5%. In other studies, lignin contents as low as 11% were reported [17]. Low lignin contents of the raw material can generally be translated to lower pulping effort, e.g., lower pulping temperature and less chemicals. This, and the open structure of straw, is often regarded as one of the main advantages of straw over wood as a raw material for pulping [8]. One major drawback, however, is the presence of inorganic components, such as silicates. In alkaline pulping, silicates are dissolved and remain in the black liquor, causing severe problems in evaporation and combustion [19]. A possible solution to this can be the use of pulping chemicals with a lower alkalinity. In NaOH pulping, NaOH is used as the main chemical. As a strong base, NaOH can easily dissolve the inorganic components from wheat straw. Na₂CO₃, on the other hand, is a weaker base compared to NaOH. As reported by Marin et al. [13], pulping of wheat straw with Na₂CO₃ led to pulps with higher lignin content. Therefore, it can be assumed that in the pulping of straw, components without Na₂CO₃ are dissolved, including silicates. In theory, silicates should mostly remain in the pulp, thus relieving the chemical recovery system. In the following, the ash content of selected pulps from NaOH pulping and pulping with Na₂CO₃ will be compared and discussed.

3.2. Na₂CO₃ Pulping
3.2.1. Influence of Liquor:Solid Ratio (LSR)

Pulping with sodium carbonate—hereinafter referred to as Na₂CO₃ pulping—was initially tested at different liquor:solid ratios (LSR) between 2:1 and 5:1. The amount of Na₂CO₃ used was 20%, based on oven-dry straw. The pulping temperature and time were kept at 150 °C and 30 min, respectively. Figure 1 shows the results of the Na₂CO₃ pulping at different liquor:solid ratios.
It was observed that the degree of delignification varied when looking at the material after pulping. At an LSR of 2:1, the straw hardly differed visually from the starting material. The higher the LSR, the greater the apparent difference between the starting material and the end product. The digested straw was always found to be more in clumps than in individual stalks, which indicated a higher degree of pulping (see Supplementary Materials; Figure S2).

As can be seen from Figure 1, the highest pulp yield of 72% was achieved at a 2:1 LSR. Increasing the LSR to 5:1 led to a decrease in the pulp yield by 5%. Similarly, the kappa number also decreased by 20 units. The pulp brightness increased only slightly from 12 to 15 %ISO at the 5:1 LSR. With the 2:1 LSR, almost all pulping liquor was absorbed by the straw, so that there was almost no free liquid left. If larger quantities of liquid are added, the straw can therefore be impregnated more effectively. In addition, this improves diffusion and dissolution of lignin into the black liquor. However, a high LSR of 5:1 has the disadvantage of the pulping reactor being charged with more liquid that has to be heated up to the desired temperature, thus requiring more energy input. For this reason, further experiments were conducted at an LSR of 3:1.

### 3.2.2. Influence of Pulping Temperature

In a second series, Na$_2$CO$_3$ pulping was conducted under different pulping temperatures between 140 and 160 °C (Figure 2). The LSR was kept at 3:1. The amount of Na$_2$CO$_3$ used was 20%, based on oven-dry straw. The pulping time was kept at 30 min.

As can be seen from Figure 2, the influence of the pulping temperature on the pulp yield, kappa number, and pulp brightness is rather insignificant. Increasing the pulping temperature from 140 to 160 °C led to a decrease in the pulp yield of 4%, whereas the kappa number only changed by 3 units. The pulp brightness remained at the same level of 13–14 %ISO. Possibly, at a higher pulping temperature of 160 °C, chromophore formation occurs, resulting in a lower pulp brightness. Furthermore, under alkaline conditions, the phenol structures of lignin are favored to be oxidized to quinone structures, which are a contributor to the yellowish color of pulp [20]. In NaOH pulping of wheat straw, the temperature has a higher impact on delignification, as observed by Sheoran et al. [21]. In their study, increasing the temperature from 135 to 148 °C led to a kappa reduction of almost 20 points. It can be concluded that Na$_2$CO$_3$ pulping of wheat straw is limited in terms of pulping intensity. A considerable increase in pulping temperature had almost no effect on pulp yield and delignification. This is most likely due to the use of Na$_2$CO$_3$, which
is a weak base and might be limited regarding the cleavage of the ether bonds in lignin. Even if this can be seen as a clear disadvantage of Na$_2$CO$_3$ pulping, it also means that the pulping process itself is much more stable and less susceptible to temperature fluctuations, for example.

![Figure 2. Influence of pulping temperature on Na$_2$CO$_3$ pulping of wheat straw (LSR: 3:1; chemical charge: 20% Na$_2$CO$_3$; time: 30 min).](image)

3.2.3. Influence of Chemical Charge

Finally, Na$_2$CO$_3$ pulping of wheat straw was conducted at four different Na$_2$CO$_3$ charging levels between 12 and 24%, based on oven-dry straw. The LSR was kept at 3:1. The pulping temperature and time were set at 150 °C and 30 min, respectively (Figure 3).

![Figure 3. Influence of chemical charge on Na$_2$CO$_3$ pulping of wheat straw (LSR: 3:1; temperature: 150 °C; time: 30 min).](image)

It was observed that increasing the charge of Na$_2$CO$_3$ from 12 to 24% (+100%) led to a decrease in the pulp yield of only 2%. The kappa number decreased from 75 to 71. The pulp brightness remained rather constant at 13–14 %ISO. In NaOH pulping of wheat
straw, a similar change in the chemical charge has a much higher impact on the pulp yield and delignification. In previous experiments on NaOH pulping of wheat straw, the NaOH charge was changed from 18 to 24%, while all the other pulping parameters remained constant. In these experiments, the pulp yield decreased by 6%, and the kappa number changed from 16 to 9 [22]. Again, this clarifies that Na2CO3 pulping of wheat straw is limited regarding lignin degradation. Analogous to the limited temperature effect, this can be seen as a disadvantage of Na2CO3 pulping, but it also means that the pulping process itself is quite stable and low chemical dosages can be used.

In Section 3.1, the hypothesis was put forward that, in Na2CO3 pulping, silicates mostly remain in the pulp, while in NaOH pulping, silicates are almost completely dissolved in the black liquor. This is because NaOH is a stronger base compared to Na2CO3. Therefore, the ash and silicate content from selected pulps were analyzed and compared (Table 2).

Table 2. Ash and silicate content of wheat straw and selected Na2CO3 and NaOH pulps. Values in %, based on oven-dry starting material (wheat straw). Standard deviations are shown in brackets.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Wheat Straw</th>
<th>Na2CO3 Pulp ¹</th>
<th>NaOH Pulp ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>10.5 (0.2)</td>
<td>7.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Silicates</td>
<td>9.7 (0.3)</td>
<td>7.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

¹ Pulping conditions: LSR: 3:1; chemical charge: 12% Na2CO3; temperature: 150 °C; time: 30 min. ² Pulping conditions: LSR: 3:1; chemical charge: 12% NaOH; temperature: 150 °C; time: 30 min.

It was observed that silicates are dissolved in Na2CO3 pulping, but to a much lower extent compared to NaOH pulping. While approximately 80% of the silicates from wheat straw remained in the Na2CO3 pulp, almost 70% of the silicates where actually dissolved in NaOH pulping. Decreasing the silicate load in black liquor after pulping can have a significant benefit for the recovery system, since silicates cause severe problems in evaporation and combustion of black liquor.

In summary, Na2CO3 pulping of wheat straw delivered pulps in yields of up to 72%, with a high kappa number of up to 81 and with generally low brightness levels of approximately 14 %ISO. Considering that the used wheat straw contains 21% ash components and extractives, which most likely are dissolved in pulping, the maximum recovery of fibers is 79%. Hence, a pulp yield of 72% is equivalent to a fiber recovery rate of 91%, which clearly shows the potentiality of the Na2CO3 pulping process. Working at a higher LSR of 5:1 improved Na2CO3 pulping, reflected in lower pulp yields, a lower kappa number, and slightly increased pulp brightness. Considering the required additional energy (for heating) at an LSR of 5:1, it was suggested to instead conduct pulping at an LSR of 3:1. Neither the pulping temperature nor the chemical charge had any tangible effect on pulp yield or delignification. This means that Na2CO3 pulping of wheat straw can be conducted under very mild conditions, saving energy and chemicals. As a reference, NaOH pulping with 12% NaOH based on oven-dry straw under otherwise identical pulping conditions delivered a pulp yield of 59%. The pulp brightness was higher, with 21 %ISO, and the kappa number of the NaOH pulp was significantly lower at 26. This clearly shows that NaOH pulping is more intense due to the use of a stronger base.

3.2.4. Paper Properties and Comparisons with Reference Pulps

The pulp yield, kappa number, and pulp brightness are characteristic values for the classification of pulps and the benchmarking of processes. From a papermaking view, the optical, surface, and especially strength properties are also of major importance. Hence, a Na2CO3 pulp was selected for handsheet preparation and paper testing. As reference, a NaOH pulp as well as a recycled paper pulp (RCP1) were chosen. The Na2CO3 and the NaOH pulp, which were also produced in this study, are characterized as follows:

- Na2CO3 pulp: 3:1 LSR, 12% Na2CO3, 150 °C, 30 min; 72% yield, kappa 75;
- NaOH pulp: 3:1 LSR, 12% NaOH, 150 °C, 30 min; 59% yield, kappa 26.
The RCP1 was sampled from a paper mill that produces corrugated board base paper based on 100% recovered paper. The RCP1 was not beaten, while the Na$_2$CO$_3$ and the NaOH pulp were beaten for 2 and 4 min in a laboratory Jokro mill. Figure 4a shows the beating degree of the selected pulps at 0, 2, and 4 min beating times. The unbeaten RCP1 showed a beating degree of 37 °SR, while the Na$_2$CO$_3$ and NaOH pulps were at a lower level of approximately 28 °SR. After a comparably short beating time of 4 min, the beating degree of the Na$_2$CO$_3$ and NaOH pulps increased to 53 and 50 °SR, respectively.

![Figure 4](image.png)

**Figure 4.** Pulp and paper properties of the selected Na$_2$CO$_3$ pulp, reference NaOH, and recycled paper pulps: (a) beating degree vs. beating time; (b) tensile index vs. beating degree; (c) burst index vs. beating degree; (d) compression index vs. beating degree.

Compared to softwood and hardwood pulps, straw pulps require much less energy in beating or refining to develop the desired paper properties. This is mainly due to the morphological structure of straw. Straw pulp fibers are shorter, approximately 0.6 mm, than wood pulp fibers, which are 0.8 mm (hardwood) and 2.0 mm (softwood). Furthermore, they tend to collapse easier/faster in pulping and beating [23]. While requiring less refining energy is a clear advantage of straw pulps, high beating degrees and poor dewaterability can cause severe problems, e.g., for the paper machine. Straw pulps contain higher amounts of fiber fines compared to wood pulps. Gao et al. [24] found that in chemo–mechanical pulping of wheat straw, hemicelluloses were dissolved and re-adsorbed to the fiber surface, in beating or refining to develop the desired paper properties. This is mainly due to the

morphological structure of straw. Straw pulp fibers are shorter, approximately 0.6 mm,

than wood pulp fibers, which are 0.8 mm (hardwood) and 2.0 mm (softwood). Further-

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increasing the pulp hydration and resulting in poor water filtration during paper formation.

For understanding and comparing the paper properties, the tensile, burst, and compression strength of Na$_2$CO$_3$ and NaOH pulps as well as of the RCP1 are presented as strength indexes in Figure 4b–d.

The NaOH pulp developed a higher tensile index after beating with up to 77 Nm/g compared to the Na$_2$CO$_3$ pulp after beating with up to 56 Nm/g. Analogously, the burst index of the NaOH pulp was approximately two units higher than the Na$_2$CO$_3$ pulp. Both the tensile and burst strength of paper are primarily dependent on fiber fibrillation and inter-fiber bonding. With increasing pulping intensity and delignification, the fiber matrix becomes more opened. Hence, in subsequent beating of the pulp, the fibers are more fibrillated, and inter-fiber bonding is improved. The tear index of the Na$_2$CO$_3$ and the
NaOH pulp started on a level of approximately 5 mN·m²/g and decreased over beating to 4.2 and 4.5 mN·m²/g. Regarding the compression index, the advantage of the NaOH pulp decreases. As described before, compression strength is also related to the degree of pulping and delignification. Simultaneously, fiber stiffness contributes to the development of compression strength. In this case, a lower degree of delignification can be advantageous because the lignin acts like a supporting membrane, keeping the fiber structure intact and stiff [25]. With much higher lignin contents, Na₂CO₃ pulps can develop a high compression strength, making them suitable for the production of packaging papers, e.g., corrugated board. Compared to a reference recycled paper pulp (RCP1), both the NaOH and Na₂CO₃ pulps showed superior strength values. At the same beating degree, the tensile and burst index of the Na₂CO₃ pulp was 100% higher, and the compression index was approximately 77% higher compared to the recycled paper pulp. This clearly demonstrates the potential of straw pulps in general. With deteriorating recovered paper quality, primary fibers from wheat straw can be used to upgrade recovered paper-based paper products, especially in the still booming packaging paper sector. One promising application can be its use as a reinforcement pulp. Here, relatively small amounts (10–30%) of straw pulp are added to a recycled paper pulp to improve the paper strength. Salehi et al. [26] investigated the potential of high-yield straw pulps for enhancing the strength properties of recycled paper. By adding up to 20% of straw pulp to a recycled paper pulp, they could improve the tensile index by 22%, the burst index by 43%, and the SCT index by 26%.

3.3. NACO Pulping

Na₂CO₃ pulping of wheat straw delivered pulps with a high yield, high kappa number, and low brightness of 14 %ISO on average. While these pulps are suitable for application in packaging papers (“brown grades”), they are not eligible for bleached paper products (“white grades”), e.g., graphic and tissue paper. Fiala et al. [14] developed the NACO process to achieve a low lignin content, good unbleached brightness, and at the same time, reasonable strength properties of the pulp. The addition of oxygen in the pulping process is intended to compensate for the low alkalinity of Na₂CO₃ and to increase delignification. Based on their results, the NACO process should be further investigated in this study. The goal was to obtain pulps that are suitable for bleaching and application in bleached paper products. The kappa number of the pulp should be below 20, and the pulp brightness should reach a level of at least 40 %ISO. If these values are reached, the pulp might be bleached using a simple bleaching sequence.

3.3.1. Influence of Pulping Temperature and Pulping Time

At first, the pulping temperature and the pulping time in NACO pulping of wheat straw was investigated. Three temperature levels (120, 140, and 160 °C) and three time levels (60, 90, and 120 min) were defined (Figure 5). The LSR was set at 6:1, and the amount of Na₂CO₃ used was 20% based on oven-dry straw. The oxygen pressure was 5 bar.

As can be seen from Figure 5a, in NACO pulping, the temperature has a significant impact on the pulp yield and kappa number. At 160 °C, the pulp yield decreased by 15%, and the kappa number decreased by 22 units. Although the delignification was clearly improved at higher temperatures, the pulp brightness was not positively affected. In fact, the brightness even decreased from 23 %ISO to 18 %ISO at 160 °C. A possible explanation for this might be that, at higher temperatures, the formation of chromophores is higher than the removal of the native chromophores of lignin [20]. For further experiments, the pulping temperature was kept at 140 °C.

Increasing the pulping time from 60 to 120 min (Figure 5b) resulted in a further drop of the kappa number to 45. However, the pulp yield remained rather unchanged and decreased by only 2% at 120 min. The pulp brightness was also not improved at longer pulping times. From these results it was concluded that a pulping time of 90 min gives the best results in terms of delignification. Therefore, the pulping time was kept at 90 min for further experiments.
for this might be that, at higher temperatures, in alkaline pulping, the formation of chromophores is higher than the removal of the native chromophores of lignin [20]. For further experiments, the pulping temperature was kept at 140 °C.

3.3.2. Influence of NaOH Addition and Pulping Time

Fiala et al. [9] proposed the use of small amounts of NaOH in NACO pulping as an “activating” and make up chemical. It can be assumed that NaOH improves delignification and elevates the pulp brightness. Therefore, in a second set of experiments, the influence of NaOH addition in NACO pulping of wheat straw was investigated (Figure 6).

As can be seen from Figure 6, the addition of small amounts of NaOH significantly improves the delignification in NACO pulping. The kappa number decreased from 47 to 26 when adding 2% NaOH, and was further reduced to 18 at 5% NaOH. Simultaneously, the pulp brightness increased from 25 %ISO to 42 %ISO. Astonishingly, the pulp yield was almost not affected by the addition of NaOH. At 5% NaOH, the pulp yield only decreased by 2%. It can be stated that with the addition of NaOH, the target kappa number of less than 20 and the target brightness of at least 40 %ISO can be achieved.
To see if an extension of the pulping time could further improve delignification, two additional experiments were conducted where the pulping time was increased to 180 and 240 min (Figure 7).

![Figure 7. Influence of pulping time on NACO pulping of wheat straw (LSR: 6:1; oxygen pressure: 5 bar; 5% NaOH; temperature: 140 °C).](image)

### 3.4. Bleaching of NACO Pulps

Kalyoncu et al. [27] most recently investigated the bleaching of wheat straw alkaline pulps, with a focus on the evaluation of suitable chelating agents for the Q stage. Chelating agents, like EDTA or DTPA, prevent the contact of hydrogen peroxide with transition metals (particularly iron, copper, or manganese), reducing the catalytic degradation of peroxide and preventing the resulting cellulose degradation. Transition metal ions can reduce the viscosity of pulp and accelerate the darkening of the final product. While Kalyoncu et al. [27] postulate the successful use of chelating agents for the removal of transition metals, they do not present any data on the effect in subsequent peroxide bleaching (P stage), e.g., peroxide consumption. Kordsachia [28] compared the use of chelating agents in a Q stage with acid washing (A stage) of wheat straw NaOH pulps. In this study, acid washing of the pulp was more effective than the treatment with chelating agents (Q stage). In particular, calcium, magnesium, and manganese ions could be removed to a much greater extent when performing acid washing with sulfuric acid. It was also found that in subsequent peroxide bleaching, much less of the peroxide was consumed. After the Q stage, 99% of the peroxide was consumed, while after acid washing, only 60% of the peroxide was consumed. Additionally, the final pulp brightness was higher when conducting acid washing of the pulp. Considering these results, a comparison of the A and Q stage in bleaching of NACO pulps was made.

#### 3.4.1. Comparison of Acid Washing (A Stage) and Q Stage and their Influence on the Subsequent P Stage

The acid washing of a selected NACO pulp was conducted using sulfuric acid (H$_2$SO$_4$) at a target pH of approximately 2.0. The Q stage was conducted using DTPA at a target pH of 4.5. The consistency, temperature, and time were the same for both treatments (see Section 2.2). The results of the A and Q stages of a selected NACO pulp are presented in Table 3.
Table 3. Acid washing (A stage) and Q stage of NACO pulp (pulping conditions: LSR: 6:1; chemical charge: 20% Na₂CO₃, 5% NaOH; oxygen pressure: 5 bar; temperature: 140 °C; pulping time: 90 min; initial brightness: 42.1 %ISO; kappa number: 18.4).

<table>
<thead>
<tr>
<th>Pulp Characteristics</th>
<th>A Stage</th>
<th>Q Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp brightness, %ISO</td>
<td>42.4</td>
<td>42.3</td>
</tr>
<tr>
<td>Kappa number</td>
<td>18.3</td>
<td>18.4</td>
</tr>
<tr>
<td>Total pulp yield</td>
<td>58.0</td>
<td>57.4</td>
</tr>
</tbody>
</table>

1 based on raw material.

Similar to the results from Kordsachia [28], neither the A nor Q stage had any distinguishable effect on the pulp brightness or kappa number. The effectiveness of these treatments can therefore only be verified in the subsequent peroxide bleaching stage (P stage). Both pulps from the A and Q stages were subjected to peroxide bleaching at a consistency of 10%, using 4% sodium silicate, 2% NaOH, and 4% H₂O₂ (values are based on oven-dry pulp). The bleaching temperature and time were set at 80 °C and 120 min, respectively. Table 4 shows the results of the peroxide bleaching of selected NACO pulps after the A and Q stages.

Table 4. P stage of selected NACO pulps (bleaching conditions: 4% sodium silicate, 2% NaOH, and 4% H₂O₂, 80 °C, 120 min).

<table>
<thead>
<tr>
<th>Pulp Characteristics</th>
<th>A–P</th>
<th>Q–P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp brightness, %ISO</td>
<td>67.9</td>
<td>64.5</td>
</tr>
<tr>
<td>Kappa number</td>
<td>10.3</td>
<td>11.6</td>
</tr>
<tr>
<td>H₂O₂ consumption, %</td>
<td>48.7</td>
<td>51.0</td>
</tr>
<tr>
<td>Total pulp yield, %</td>
<td>55.7</td>
<td>55.7</td>
</tr>
</tbody>
</table>

1 based on raw material.

Peroxide bleaching of selected NACO pulps resulted in a significant increase in pulp brightness. Compared to the unbleached pulp, the brightness increased by up to 26 points (A–P). There was also a remarkable decrease in the kappa number, down to 10.3 (A–P). The acid-washed pulp showed a slightly higher brightness level and lower kappa number after the P stage compared to the pulp after the Q stage. Furthermore, the consumption of peroxide over the P stage was lower when the pulp was subjected to acid washing. This generally shows that transition metal-induced peroxide degradation could be effectively limited or even prevented. This result, that acid washing leads to better bleaching results in the subsequent P stage compared to a Q stage, does not correspond to the general opinion that the Q stage has advantages over the A stage. It is generally assumed that in a Q stage, heavy metals are effectively incorporated into complexes and subsequently washed out, while more alkaline earth metals, which have a stabilizing effect on hydrogen peroxide, remain in the pulp due to the higher pH of approximately 4–5. A possible explanation for the better results after acid washing could be seen in a very high content of calcium ions in the wheat straw pulps, which impair the effectiveness of the complexing agent and presumably also reduce the bleaching effect of the P stage. The better bleaching result after acidic washing could therefore be primarily due to the further dissolution of calcium ions [28]. Although the peroxide bleaching could be stabilized through prior to the A or Q stage and a significant brightness improvement was achieved, the final brightness of 68 %ISO was still under the desired level of at least 70 %ISO, which was defined as a prerequisite for use in bleached paper products, such as office paper. Therefore, further bleaching experiments were conducted, with a focus on brightness improvement through either higher bleaching temperatures or longer bleaching times.
3.4.2. Influence of Bleaching Temperature and Bleaching Time

At first, the retention time in peroxide bleaching was extended from 120 to 240 min while reducing the bleaching temperature from 80 to 70 °C. This experiment should be regarded as having “milder” bleaching conditions. Again, a comparison between the A and Q stage prior to the P stage was made.

Figure 8a shows the results of the P stage at 70 °C and 240 min. Compared to bleaching at 80 °C and 120 min, the brightness could not be improved. The kappa number could only be reduced to 9 and 10. Again, the pulp from prior acid washing delivered better results in terms of pulp brightness and kappa number. Also, the peroxide consumption was lower, at 48%. In general, the “milder” bleaching conditions did not achieve the desired brightness level of 70 %ISO. Kordsachia [28] investigated the conditions in peroxide bleaching of NaOH wheat straw pulps. It was found that at 90 °C, the pulp brightness was significantly higher, with up to 75 %ISO compared to 80 °C with 69 %ISO. Therefore, “harsh” bleaching conditions were investigated by elevating the bleaching temperature to 90 °C.

As can be seen from Figure 8b, bleaching at 90 °C resulted in significant improvements in the pulp brightness and kappa number. Compared to 80 °C, the pulp brightness increased to 73 %ISO, and the kappa number could be reduced to 5 (A–P). It was also found that at a higher temperature, the peroxide consumption increased to up to 78%. This indicates an increased peroxide degradation at 90 °C. Still, there were sufficient amounts of residual peroxide left to prevent accelerated darkening and brightness decrease of the pulp.

To conclude, it was feasible to achieve the desired brightness level of at least 70 %ISO in a two-stage bleaching process, with the A or Q stages followed by hydrogen peroxide bleaching. A comparison of the unbleached and bleached NACO pulp is shown in Figure S4 (Supplementary Materials). Acid washing, against all presumptions, was found to be the better option, specifically for the stabilization of peroxide in the subsequent P stage. Finally, this bleached pulp was used for handsheet preparation and paper testing.

3.4.3. Paper Properties and Comparison with Reference Pulp

To depict the influence of pulp bleaching on the paper properties, the unbleached NACO pulp was also selected for handsheet preparation and paper testing. Furthermore, a recycled paper pulp (RCP2) was chosen as a reference. RCP2 was sampled from a paper mill that produces office and magazine paper based on 100% recovered paper. The RCP2 was not beaten, while the NACO pulps were beaten for 5 and 10 min in a laboratory Jokro mill. Figure 9a shows the beating degree of the selected pulps at 0, 5, and 10 min beating times.

Figure 8. Influence of bleaching time and temperature in peroxide bleaching of selected NACO pulps (comparison of A and Q stage): (a) 70 °C, 240 min; (b) 90 °C, 120 min. The pulp brightness and kappa number of unbleached NACO pulp are provided as a reference.
The unbeaten RCP2 showed a beating degree of 50 °SR, while the unbleached and bleached NACO pulps were at lower levels of approximately 23 and 31 °SR, respectively. After a comparably short beating time of 5 min, the beating degree of the NACO pulps increased to 43 and 66 °SR, respectively. After 10 min of beating, the beating degree of the NACO pulps increased to 55 and 77 °SR for the bleached NACO pulp. As described before (Section 3.2.4), straw pulps respond very intensively to beating and refining. On the one hand, this can be beneficial because less refining energy is required to develop the desired paper quality, e.g., paper strength. On the other hand, such high beating degree levels of above 70 °SR most likely cause problems in dewatering of the paper machine.

For understanding and comparing the paper properties, the tensile, tear, and burst strength of the unbleached and bleached NACO pulps, as well as of the RCP2, are presented as strength indexes in Figure 9b–d.

The bleached NACO pulp developed a slightly higher tensile index after beating with up to 66 Nm/g compared to the unbleached NACO pulp after beating with up to 63 Nm/g. However, when comparing the tensile strength at identical beating degrees, the unbleached NACO pulp showed a better performance. Figure 9c depicts a general decrease in tear strength through beating for both unbleached and bleached NACO pulps, down to 2.3 mN*m²/g. The tear strength of paper is primarily dependent on the fiber length and the individual fiber strength. Wheat straw pulps have shorter fibers compared to especially softwood pulp fibers, as described in Section 3.2.4. Through bleaching and further delignification, the fiber matrix becomes more opened. Hence, in subsequent beating of bleached pulp, the fibers are not only more fibrillated, but they are also shortened more extensively. While the NACO pulps showed higher values for their tensile and burst index, the tear index was much lower compared to the RCP2, with 4.7 mN*m²/g. Most likely, the RCP2 contained bleached softwood fibers, which are longer and have a higher individual fiber strength than wheat straw pulp fibers.
4. Discussion

Na$_2$CO$_3$ pulping of wheat straw delivered pulps in high yields of up to 72%, high kappa numbers of up to 81, and a low brightness of approximately 14 %ISO. At a higher liquor:solid ratio (LSR) of 5:1, Na$_2$CO$_3$ pulping was intensified, resulting in lower pulp yields and a lower kappa number. However, it was suggested to use a lower LSR of 3:1 to save energy during the heating process. Neither the pulping temperature nor the chemical charge had any significant influence on the pulp yield, kappa number, or pulp brightness. Hence, Na$_2$CO$_3$ pulping can be conducted under rather moderate conditions, saving energy and chemical costs. This is particularly worth mentioning because the price of NaOH (“caustic soda”) is usually higher than that of Na$_2$CO$_3$ (“soda ash”). In Europe, the most recent price for caustic soda was quoted as 372 USD/t while the price for soda ash was 266 USD/t [29,30]. Regarding pulping intensity and delignification, the NaOH pulping process is superior to Na$_2$CO$_3$-based pulping processes due to the usage of a stronger alkali. With the identical chemical charge of 12%, the NaOH pulp showed a significantly lower pulp yield of 59% compared to the Na$_2$CO$_3$ pulp yield of 72%. Furthermore, the kappa number of the NaOH pulp was almost 50 units lower than the kappa number of the Na$_2$CO$_3$ pulp. This clearly proves that the pulping intensity and delignification were much higher in NaOH pulping. The Na$_2$CO$_3$ pulps showed inferior paper strength compared to the NaOH pulps. However, they still had much higher strength values than a reference recycled paper pulp. This makes Na$_2$CO$_3$ pulps suitable for applications in packaging paper products, e.g., as a reinforcement pulp, upgrading the quality of recycled paper products and meeting the demand for alternative fiber materials.

NACO pulping of wheat straw delivered pulps with a high initial brightness of up to 42 %ISO and a low kappa number of 18, still at relatively high pulp yields of above 60%. Increasing the pulping temperature and time intensified the delignification in NACO pulping but had a reverse effect on the pulp brightness. The addition of small amounts of NaOH (2–5%) significantly improved the delignification and resulted in a high unbleached brightness.

Through a combination of acid washing and peroxide bleaching (A–P), a final pulp brightness of 73 %ISO could be achieved. Two-stage bleached NACO pulps are suitable for applications in graphic papers, such as office and magazine paper, supplying the paper cycle with fresh fibers and strengthening the declining graphic paper sector.

5. Conclusions

Sodium carbonate-based pulping of wheat straw was studied in this work, and the main conclusions obtained are as follows:

Based on the results obtained in this study, sodium carbonate-based pulping processes are perfectly suited for non-wood raw materials such as wheat straw. A broad range of pulp qualities can be produced, from unbleached pulp for applications in packaging papers to bleached pulps for applications in graphic papers.

Further work will focus on the use of Na$_2$CO$_3$ pulps as reinforcement fibers in packaging paper products. It is planned to make mixtures of wheat straw Na$_2$CO$_3$ pulps with recycled paper pulps in ratios of 10%/90% to 30%/70%. These mixtures should then be used for the production of corrugated board. For the NACO pulps, further investigations should focus on the optimization of the pulping conditions, with a focus on reducing the NaOH charge. The bleaching process, especially the P stage, should also be further optimized. Here, the possibility of recycling and reusing the NaOH from the P stage in pulping should be investigated. Acid-washed NACO pulps should be analyzed for the content of transition metal ions to provide further data to understand the effectiveness and benefits of acid washing compared to a Q stage. Bleaching can be optimized and extended by adding P stage experiments at 70 °C and 120 min and 90 °C and 240 min. Peroxide bleaching can be further optimized by using the kappa number as an extra parameter to estimate the effective amount of hydrogen peroxide consumed in the bleaching reactions [31]. After optimization of the bleaching sequence, larger amounts of bleached
NACO pulp should be sampled and tested. A mixture of NACO pulps with recycled paper pulps can also be considered here. For both processes of Na$_2$CO$_3$ and NACO pulping, further improvements can be considered through the valorization of the ash components and extractives that are removed from the feedstock. This would allow for the development of a biorefinery concept.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14010162/s1, Figure S1: Horizontal batch digester in operating mode (left), rotor design (middle), and loading the digester with straw (right); Figure S2: Wheat straw after Na$_2$CO$_3$ pulping at different liquor:solid ratios (LSR): 2:1 (left) and 5:1 (right); Figure S3: Process scheme of Na$_2$CO$_3$ and NACO pulping; Figure S4: Brightness sheets of NACO pulps before (left) and after bleaching (right).

Author Contributions: Conceptualization, F.S., T.K. and B.S.; methodology, F.S., T.H. and M.P.E.; writing—original draft preparation, F.S. and T.K.; writing—review and editing, B.S.; visualization, F.S. and Y.C.; supervision, B.S.; project administration, B.S. and T.K.; funding acquisition, F.S., T.K. and B.S. All authors have read and agreed to the published version of the manuscript.

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References
5. Tofani, G.; Cornet, I.; Tavernier, S. Multiple linear regression to predict the brightness of waste fibres mixtures before bleaching. Chem. Pap. 2022, 76, 4351–4365. [CrossRef]


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