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# Conversion of Cellulose to 5-HMF in the Presence of Silica-Alumina Catalysts Synthesized by Dual Template at Low Temperature

Halit L. HOSGUN *[1], Özlem TOPCU[1] E. Zafer HOSGUN[2], Berrin BOZAN[2]

## Abstract

In this study, which incorporates many principles of green chemistry (use of renewable feedstocks, catalysis, improvement of energy efficiency, and harmless solvents and auxiliaries), the single-phase catalytic conversion of cellulose to 5-HMF in over silica-alumina catalysts was investigated. A series of dual-template silica-alumina catalysts with CTAB as the main template and F127 or triethylamine (TEA) as the co-template were synthesized at a low temperature of 60 °C and characterized by XRD, $N_2$ adsorption-desorption technique, FT-IR and pyridine adsorption FT-IR. The surface area is increased by using the second template in silica-alumina catalyst. In addition, the acidity of the surface was changed by using the second template. The cellulose conversion and yield of 5-HMF increased from 36% to 52% and from 3.13% to 4.24%, respectively, due to the properties gained by using the second template. 52% cellulose conversion and 8.13% selectivity of 5-HMF were obtained in aqueous medium, 220 °C and 6 h reaction time with the catalyst using TEA as co-template. Eco-friendly silica catalysts synthesized at low temperatures with a dual template can be considered as a potential alternative for the conversion of cellulose into value-added biobased products.

**Keywords**: Cellulose, 5-HMF, heterogeneous catalysis, green chemistry

## 1. INTRODUCTION

Despite the increasing demand for energy and chemicals, the supply of fossil resources such as oil, coal, and natural gas is gradually decreasing. In addition to this supply-demand imbalance, considering supply chain security and environmental issues, it is necessary to use alternative sources to fossil fuels for energy and chemical production. As an abundant raw material, lignocellulosic biomass can be used as a substitute for fossil resources [1, 2].

Cellulose, together with hemicellulose and lignin, is the main component of biomass. Many value-added products are derived from glucose by the hydrolysis reaction of cellulose, a polymer composed of multiple D-glucose units linked by β-1,4-glycosidic

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bonds. 5-HMF, one of the high value-added chemicals, is an important building block because it can be converted into many compounds currently derived from petroleum through various reaction pathways [3, 4].

The reaction steps for 5-HMF synthesis from cellulose is carried out in 3 steps [5]:

Step 1: Hydrolysis reaction of cellulose to glucose,

Step 2: Isomerization reaction of glucose to fructose,

Step 3: Dehydration reaction of fructose to 5-HMF.

Lewis acid catalysts are used for the isomerization reaction, while the steps of hydrolysis of cellulose to glucose and dehydration of fructose to 5-HMF take place in the presence of Bronsted acid catalysts [6].

There are numerous studies in the literature on the catalytic conversion of cellulose to 5-HMF using homogeneous catalysts such as metal chlorides [7, 8], mineral acids [9], and ionic liquids [10], as well as solid acid heterogeneous catalysts such as $SnNb_2O_6$-$ZrO_2$ [11], H-ZSM-5 [12], and niobium/carbon composites [13]. Due to the drawbacks of homogeneous catalysts such as corrosion, difficulty in separation from the product mixture, and environmental pollution, many researchers have preferred the use of heterogeneous catalysts in the synthesis of 5-HMF from cellulose [14, 15].

Silica-alumina catalysts with moderate acidity have been used in many industrial applications, e.g., hydrocarbon cracking [16, 17], in deoxygenation/ hydrodeoxygenation reactions [18, 19], in the conversion of methanol to olefins [20], and in bio-oil refining[21, 22]. In their two studies, Pham et al. used Al-incorporated SBA-15 and Al-MCM-41 catalysts to convert cellulose to 5-HMF. Al-incorporated SBA-15 catalysts prepared by the atom implantation method and containing 10% Al, achieved the highest conversion, selectivity, and efficiency values (62.14%, 68.51%, and 42.57%, respectively), while the Si:Al molar ratio was 30. The maximum cellulose conversion (69%) and 5-HMF selectivity (59.04%) were obtained with the MCM-41 catalyst. The authors emphasized that the main factor affecting 5-HMF selectivity and cellulose conversion is the Bronsted/Lewis acid ratio of the catalysts [23, 24].

There are various methods for the preparation of ordered metal oxides and zeolites. The use of various templates is one of these methods. In some cases, the use of two templates is preferred. In the literature, there are studies on zeolites (ZSM-5 [25, 26], HZSM-5 [27], AlPO-18 [28], SAPO-CLO [29]), alumina [30] and silica [31–33] synthesized using dual templates. Emdadi et al. synthesized nanolayer coupled ZSM-5 zeolites using Gemini-type surfactants and TPAOH as binary templates. The hydrophobic alkyl chains of the Gemini-type surfactant used in this study effectively limited the growth of ZSM-5 nanolayers. On the other hand, TPAOH played a simple role in the formation of a self-column of zeolite precursors to strengthen the interlamellar structure [34]. In their study, synthesizing a hierarchically layered titanosilicate-1, Wang et al. used the bolaform surfactant as the primary template and the co-template TPAOH. It was reported that the bolaform surfactant enabled the formation of ultrathin nanolayers of TS-1 crystals, while TPAOH induced and regulated nucleation [35]. Shi et al. reported surface area of 96 $m^2/g$ and 102 $m^2/g$, respectively, in their alumina synthesis using SDS and CTAB single template, while the surface area of alumina using SDS and CTAB dual template was 140 $m^2/g$ [36].

In this study, silica-alumina catalysts were synthesized by dual templating with CTAB as the main template and F127 or triethylamine (TEA) as co-templates. A series of samples were prepared by changing the molar ratio of CTAB to F127 or TEA (1:4, 1:8, 1:16). The textural properties and crystal structures of the prepared samples were characterized and their catalytic activities in the conversion of cellulose to 5-HMF were evaluated. Water is used as a solvent in the conversion of cellulose into value-added chemicals. This study also covers many principles of green chemistry such as the use of cellulose as a feedstock (use of renewable feedstock), the preference of heterogeneous catalysts instead of homogeneous catalysts (catalysis), low-temperature synthesis (increase of energy efficiency) and the use of water as a solvent (benign solvents and auxiliaries).

## 2. EXPERIMENTAL

### 2.1. Materials

Aluminum nitrate nonahydrate ($Al(NO_3)_3$ $9H_2O$) from Fluka was used as the Al source. Sodium silicate solution as Si source, ($(Na_2O(SiO_2)_x$ $xH_2O)$, d=1.39 g/cm$^3$), Pluronic F127, and cellulose (CAS Number:9004-34-6, product code C6288) were supplied by Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB), sulfuric acid (d=1.83 g/cm$^3$, in >95% purity), and triethylamine (TEA, d=0.728 g/cm$^3$, in 99% purity) were purchased from Aldrich, Fischer Scientific, and Acros Organics, respectively. All chemicals were used as received.

### 2.2. Synthesis Procedure of Catalyst

Solution A and solution B are obtained by dissolving surfactant (CTAB and varying amounts of TEA or F127) and aluminum nitrate nonahydrate in water. Solution A, solution B and 2.5 mL of $H_2SO_4$ were added to the sodium silicate solution and stored in an oven at 60 °C for 7 days. The samples were then washed until the pH = 10 and filtered. The samples were then dried overnight and calcined in an oven (12 h at 550 °C, under heating conditions of 1 °C/min). The CT was coded for the samples synthesized with CTAB/TEA, whereas the CF was coded for the samples synthesized with CTAB/F127. The numbers at the end of the codes represent the molar ratio of CTAB:TEA or CTAB:F127 used. C stands for the sample prepared with CTAB.

### 2.3. Characterization Studies

X-ray diffraction analysis was performed to determine the crystal structure. XRD of Rigaku Ultima III brand operated with a voltage of 40 kV and 15 mA, scanning speed of 4 °C/min. The surface and pore properties of the catalysts were determined with nitrogen adsorption-desorption isotherms using the Micromeritics TriStar 3020 model. Prior to measurement, all samples were degassed under these conditions: first at 90 °C for 1 hour and then at 300 °C for 24 hours under vacuum. Surface area, pore volume, and pore diameter were calculated using BET (Brunauer-Emmet-Teller) theory using these isotherms. FTIR analyzes were performed using Perkin Elmer Spectrum Two spectrophotometer systems to identify characteristic peaks and functional groups. Spectra were recorded over the spectral range of 4000-400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The DRIFT analyses with pyridine-adsorbed patterns were performed on the same FT-IR instrument in the 400- 4000 cm$^{-1}$ range.

The DRIFT analyses were used to determine the content of Brønsted and Lewis acid sites on the catalyst by infrared spectra of pyridine (Py-IR) adsorbed on the catalysts as in the literature [37].

### 2.4. Study on the Catalytic Conversion of Cellulose to 5-HMF Performance of Catalysts

Temperature had the greatest effect on cellulose degradation, as the temperature increases up to 220 °C when the concentration of ionic products increases in the subcritical water range [38]. The reaction temperature and time were selected from previous work for comparison of results[14, 38]. The reactions were carried out in a Teflon-lined autoclave at 220 °C for 6 h. The ratio of cellulose to catalyst was 4:1 (w/w) and the reaction was carried out in an aqueous medium. After filtration through a 0.45 µm filter, the collected clear liquids were analyzed by High Performance Liquid Chromatography (HPLC, Agilent 1100, USA). The HPLC system was equipped with a refractive index detector (Agilent) and a Bio-Rad column (300 mm × 7.8 mm, Aminex HPX-87H) at 60 °C. The mobile phase was 0.005 M $H_2SO_4$ at a flow rate of 0.6 mL $min^{-1}$. Cellulose conversion (X), 5-HMF yield (Y), and selectivity (S) were calculated using the following equations:

$$X_{\text{Cellulose}}\ (\%)=\frac{\text{Amount of cellulose reacted (g)}}{\text{Initial amount of cellulose (g)}}\times 100 \quad (1)$$

$$Y_{\text{5-HMF}}(\%)=\frac{\text{Produced 5-HMF (mole)}}{\text{Glucose content of cellulose (mole)}}\times 100 \quad (2)$$

$$S_{\text{5-HMF}}\ (\%)=\frac{\text{Produced 5-HMF (mole)}}{\text{Cellulose reacted (mole)}}\times 100 \quad (3)$$

The glucose content of cellulose was determined using moles of glucose units in cellulose.

## 3. RESULTS

### 3.1. Characterization of the Catalysts

The $N_2$ adsorption-desorption isotherms and the pore size distribution curves of catalysts prepared with CTAB/F127 and CTAB/TEA dual templates are shown in Figure 1 and Figure 2, respectively. As can be seen in Figure 1 and Figure 2, the catalysts prepared with dual templates exhibit a type IV isotherm with a pronounced H3 hysteresis loop according to the IUPAC classification. The BET, external and microporous surface areas, and pore volumes of all catalysts are listed in Table 1. The silica-alumina catalyst synthesized with CTAB has a relatively low surface area (41.8 $m^2/g$). Using F127 or TEA with CTAB as a template significantly increases the surface area of the catalysts. Increasing the molar ratio of TEA and F127 increased the surface area and pore volume of the catalysts. However, further increasing the molar ratio of F127 from 8 to 16 decreased surface areas. The results also showed that the catalysts with TEA had smaller micropore surface area. According to the BJH pore size distribution results, it was found that TEA resulted in smaller mesoporous silica particles, while F127 increased the particle diameter. This is compatible with the literature [39].

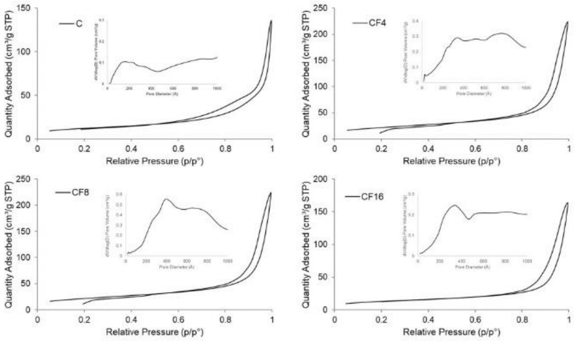

Figure 1 $N_2$ adsorption-desorption isotherms and BJH pore size distribution plots (insets) of the catalysts prepared with CTAB/F127

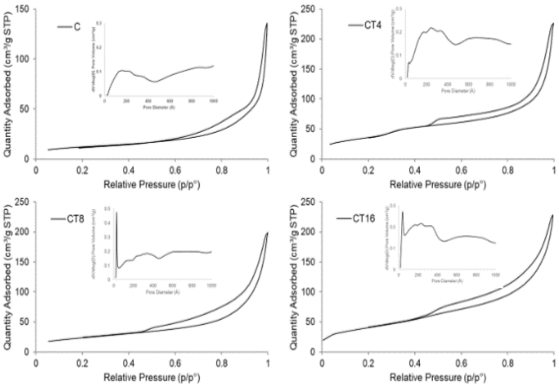

Figure 2 $N_2$ adsorption-desorption isotherms and BJH pore size distribution plots (insets) of catalysts prepared with CTAB/TEA

Table 1 Texture parameters of the catalysts.

| Sample | $S_{BET}$ ($m^2/g$) | $S_{ext}$ ($m^2/g$)[a] | $S_{micro}$ ($m^2/g$)[b] | $V_{pore}$ ($cm^3/g$) |
|---|---|---|---|---|
| C | 41.8 | 33.9 | 7.9 | 0.183 |
| CT4 | 85.0 | 76.6 | 8.4 | 0.293 |
| CT8 | 136.6 | 135.9 | 0.7 | 0.348 |
| CT16 | 145.8 | 142.9 | 2.9 | 0.357 |
| CF4 | 76.18 | 63.74 | 12.44 | 0.334 |
| CF8 | 80.23 | 66.54 | 13.69 | 0.452 |
| CF16 | 45.10 | 36.85 | 8.25 | 0.246 |

a: BJH adsorption branch
b t-Plot method

The XRD patterns of the synthesized catalysts are shown in Figure 3. A peak centered approximately at $2\theta = 23°$ in the XRD pattern indicates that the catalysts are amorphous. This result is consistent with the literature [40, 41]. There are no alumina diffraction lines in the XRD patterns of the samples. This can be explained by the fact that almost all Al is contained in $SiO_2$ [42].

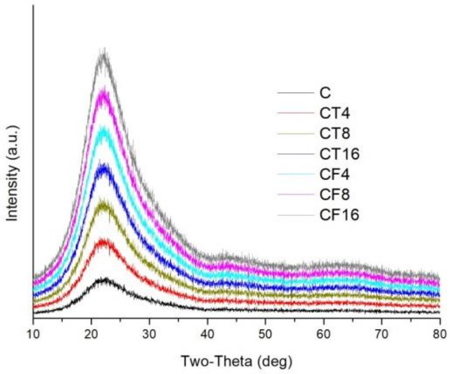

Figure 3 XRD patterns of catalysts

The FTIR spectra of the catalysts are shown in Figure. 4. Absorption bands around 1100 $cm^{-1}$, 820 $cm^{-1}$ and at 470 $cm^{-1}$ were identified. The band at 470 $cm^{-1}$ can be attributed to the bending vibrations of Si-O-Si. The other two bands at 820 $cm^{-1}$ and 1100 $cm^{-1}$ are due to the Al-O-Al stretching and the asymmetric stress vibrations of Si-O (Si), respectively [43, 44].

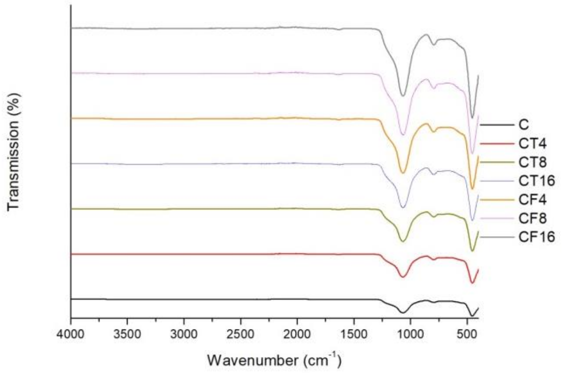

Figure 4 FTIR spectra of the samples

Pyridine was adsorbed on the synthesized catalysts and the acidic properties were investigated using the FT-IR spectra (see in Figure 5). The peaks around 1540 $cm^{-1}$ and 1450 $cm^{-1}$ correspond to Brønsted acids and Lewis acids, respectively. The band at 1490 $cm^{-1}$ is attributed to the presence of both Brønsted and Lewis acid sites [45, 46]. While CTAB itself does not exhibit Brønsted or Lewis acid peaks, use of the co-template resulted in Brønsted and Lewis acids.

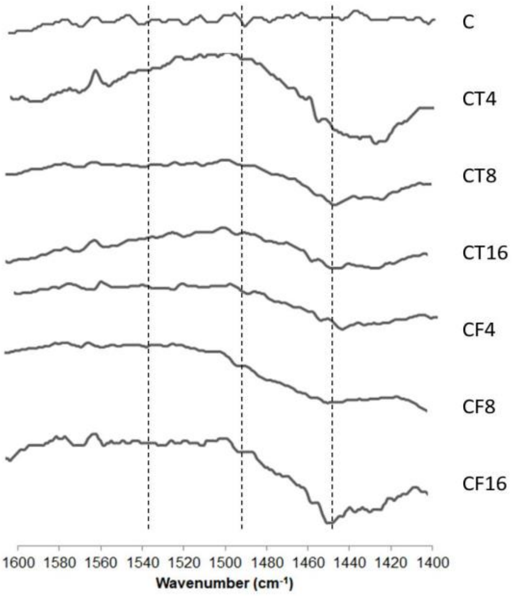

Figure 5 The infrared spectra of the catalysts adsorbed with pyridine

## 3.2. Results of the Catalytic Activity Studies

The results of the experiments on the synthesis of 5-HMF from cellulose in the presence of catalysts synthesized with the dual template using CTAB as the main template and F127 or triethylamine (TEA) as the co-template are shown in Table 2. The conversion of cellulose was 36%, and the yield and selectivity of 5-HMF were 3.13% and 9.64%, respectively, with the catalyst when only CTAB was used as the template, at 220 °C and 6h, respectively. This result could be due to the absence of Brønsted and Lewis acid sites of the catalyst. The combination of CTAB and TEA has a positive effect on the conversion of cellulose to 5-HMF. At a molar ratio of CTAB:TEA of 1:4, the conversion of cellulose was increased by 45%, while the yield of 5-HMF increased slightly. Further increasing the molar ratio of CTAB:TEA resulted in lower conversion of cellulose but higher yield of 5-HMF. Catalysts synthesized with CTAB and F127 as dual templates were not as effective as CTAB/TEA in the conversion of cellulose. CTAB/F127 catalysts showed a slight increase in both the conversion of cellulose and the yield of 5-HMF at all molar ratios. Only a 1:8 CTAB/F127 has a high selectivity of 11.02%.

Table 2 Values for conversion, yield and selectivity values obtained from experiments carried out with different catalysts.

| Sample | $X_{Cellulose}$ (%) | $Y_{5\text{-}HMF}$ (%) | $S_{5\text{-}HMF}$ (%) |
|---|---|---|---|
| C | 36 | 3.13 | 9.64 |
| CT4 | 52 | 3.84 | 8.13 |
| CT8 | 39 | 4.04 | 11.63 |
| CT16 | 42 | 4.24 | 11.09 |
| CF4 | 38 | 3.67 | 10.6 |
| CF8 | 39 | 3.86 | 11.02 |
| CF16 | 41 | 3.35 | 8.96 |

The results obtained in this study were compared with studies from the literature on the conversion of cellulose to 5-HMF carried out in a single phase (Table 3). Although high cellulose conversion or 5-HMF efficiency was obtained in a short time with the homogeneous catalysts $FeCl_3$ and $CrCl_3$, there are difficulties in the separation of the product mixture. As for the reaction conditions, ionic liquids were often used, which are expensive and practically unsuitable for large-scale applications. Considering the surfaces of the catalysts and the water used as reaction medium in this study, we can assume that the obtained results are consistent with those reported in the literature. A catalytic conversion of cellulose using only water as a solvent, as in this study, was performed by Nandiwala et al. In the study by Nandiwala et al. in the presence of a bimodal-HZ-5 catalyst with a Si/Al ratio of 30 at a cellulose/catalyst ratio of 1:2 (the cellulose/catalyst ratio in this study was 4:1), 67% cellulose conversion and 46% 5-HMF yield were achieved [12].

Table 3 Some studies on the synthesis of 5-HMF from cellulose in a single phase in the literature.

| Catalyst | Solvent | co-solvent / co-catalyst | Cellulose/Catalyst (g/g) | Reaction Time | Reaction Temperature (°C) | $X_{Cell}$ (%) | $Y_{5\text{-}HMF}$ (%) | Reference |
|---|---|---|---|---|---|---|---|---|
| $FeCl_3$ | Water | 1-ethyl-3-methylimidazolium chloride | 0.1/0.06 | 10 min | 140 | 72.4 | 23.6 | Abou-Yousef et.al.[7] |
| $CrCl_3$ | Water | 1-ethyl-3-methylimidazolium chloride | 0.1/0.06 | 10 min | 140 | 35.6 | 84.9 | Abou-Yousef et.al.[7] |
| Bimodal-HZ-5 | Water | - | 0.25/0.5 | 4 hr | 190 | 67 | 46 | Nandiwale et.al.[12] |
| Phosphotungstic acid (PHA) | THF | Water | 0.5/0.5 | 6 hr | 190 | na | 8.50 | Fan et. al.[14] |
| Amberlyst-15 | THF | - | 0.5/0.2 | 6 hr | 190 | na | 9.30 | Fan et. al.[14] |
| Al-MCM-41 | Water | 1-butyl 3-imidazium chloride | 2/0.2 | 2 hr | 170 | 69 | 40.56 | Pham et.al.[24] |
| Sulfuric acid modified Active Carbon | Water | 1-Butyl-3-methylimidazolium chloride | 0.1/0.05 | 1 hr | 120 | na | 36.33 | Tyagi et.al.[47] |
| Cr doped Sulfuric acid modified Active Carbon | Water | 1-Butyl-3-methylimidazolium chloride | 0.1/0.05 | 1 | 120 | na | 49.02 | Tyagi et.al.[47] |
| $ChnH5\text{-}nCeW_{12}O_{40}$ | Water | - | 0.5/0.2 | 5 hr | 160 | 74 | 13.6 | Lai et. al.[48] |
| $Cr[(DS)H_2PW_{12}O_{40}]_3$ | Water | - | 0.2 g/0.06 mmol | 2 hr | 150 | 77.1 | 52.7 | Zhao et.al.[49] |
| CT-4 | Water | - | 1/0.25 | 6 hr | 220 | 52 | 3.84 | This study |

na: not available

## 4. CONCLUSION

This study was carried out considering many rules of green chemistry, namely synthesis at low-temperature, use of water as an environmentally friendly solvent, reaction in the presence of a heterogeneous catalyst and use of renewable raw materials. In summary, dual templated silica-alumina catalysts were synthesized at low temperature, and their catalytic activity was tested for the conversion of cellulose to 5-HMF in water as solvent. The use of co-templates in the synthesis of the catalysts resulted in an increase in surface area from 41.8 $m^2/g$ to 145.8 $m^2/g$. In addition to the increase in the surface area of the catalyst synthesized using single CTAB as a template, it was observed that the acidity of the surface area of the catalysts synthesized using the dual template also changed. Catalysts synthesized using TEA as co-template showed better cellulose conversion and 5-HMF yield after 6 h reaction time in water at 220 °C compared to catalysts synthesized using F127 as co-template. When cellulose was converted in the presence of CT16 catalyst, the highest 5-HMF yield of up to 4.24% was obtained at 42% cellulose conversion. This is the first report describing the synthesis of 5-HMF from cellulose using a silica-alumina catalyst synthesized at low temperature as a dual template. The results obtained in this study for cellulose conversion and 5-HMF yield, carried out according to green chemistry rules, are compatible with other studies on 5-HMF synthesis from cellulose in the literature.

***Authors' Contribution***

HLH: Supervision, Investigation, Analysis and interpretation of the data.
ÖT: performed the experiments and collected data, interpretation of the data.
EZH: Investigation, HPLC analysis, interpretation of the data.
BB: Supervision, interpretation of the data, revised and editing the manuscript.

***The Declaration of Conflict of Interest/ Common Interest***

No conflict of interest or common interest has been declared by the authors.

***The Declaration of Ethics Committee Approval***

This study does not require ethics committee permission or any special permission.

***The Declaration of Research and Publication Ethics***

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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