Co-storage of wheat straw with acidic wastes can increase methane production

Ali Heidarzadeh Vazifehkhoran*, Maria Cinta Roda-Serrat, Rime El-Houri and Jin Mi Triolo

University of Southern Denmark, Faculty of Engineering, Institute of Chemical Engineering, Biotechnology and Environmental Technology, Campusvej 55, DK-5230 Odense M, Denmark

*Corresponding author. Tel: +4565509084; Email: ahva@kbm.sdu.dk

Abstract

This study investigated the use of acidic wastes as a pretreatment medium combined with particle size reduction to improve anaerobic digestion of Wheat straw (WS). Orange residues from juice factory (DOR) and ultra-filtration retentate of cherry slurry (UFR), which contain weak acids and have a pH of about 3.5, might be efficient for the pretreatment of WS for biogas production. The fresh WS in three different particle size (0.5, 1.5 and 4mm) was co-stored with DOR and UFR separately for two time period of 48 and 72 hr at room temperature. The methane yield of fresh WS (particle size of 0.5, 1.5 and 4 mm) during 60 days of batch anaerobic digestion was 297, 281 and 281 CH_4 NL/kg VS respectively. Pretreatment of WS with DOR and UFR increased methane yield up to 17 and 27% respectively. The results indicate better performance of UFR in comparison to DOR as pretreatment medium.

Keywords: Anaerobic digestion; Hydrolysis; Lignocellulose; Pretreatment;

1. Introduction

Straw is known to be a sustainable second generation bioresource for anaerobic digestion. However, its biogas production potential is low due to its recalcitrant lignocellulosic structure, which reduces the anaerobic transformation rate of straw carbon to less than 50%

in conventional biogas digesters (biodegradability, <50%) [1]. Numerous pretreatment technologies have been developed, but these have proven to be financially unviable, or problems have arisen in upscaling laboratory trials [2]. Accessible surface area for microorganisms and enzymes might be increased by physical pretreatment through size reduction resulting in improvement of enzymatic hydrolysis [3]. High demand of energy for physical pretreatment reduces economic viability of AD [3]. However, it can be combined with chemical pretreatment to make it feasible [4].

Acidic pretreatment is known to be effective in improving hydrolysis by increasing the internal surface area and porosity of a biomass, decreasing the degree of depolymerisation and inducing swelling of the lignocellulosic structure [5,6]. The acid pretreatment can undergo the lignocellulosic matrix in straw, and make the structure of straw easier to be attacked by enzymes and fermentative bacteria [7]. This is an effective pretreatment method for increasing hydrolysis, biodegradability and methane production during the anaerobic digestion of lignocellulosic biomass [8–10]. Using sulfuric acid can substantially improve the biogas production from rice straw by anaerobic digestion, and the highest methane yield was 150 CH_4 NL kg DM^{-1} for 6% acid concentration, which was 99.8% higher than the control group [11]. In the study conducted by Song et.al, four acid reagents (H_2SO_4, HCl, H_2O_2, and CH_3COOH) at concentrations of 1%, 2%, 3%, and 4% were applied to pretreat corn straw and it was found that biogas production from pretreated corn straw with H_2O_2 was higher than corn straw pretreated with H_2SO_4, HCl and CH_3COOH, the ascending order is 3% H_2O_2, 2% H_2SO_4, 2% HCl and 4% CH_3COOH, where the methane yields are 216.7, 175.6, 163.4 and 145.1 CH_4 NL/kg VS respectively [12]. Pretreatment of corn stalk with

H_3PO_4 was assessed in different concentrations (0%, 2%, 4%, 6% and 8%) of H_3PO_4 and the results indicated that the biogas production was 40.75% higher than the control group [13]. Alkaline pretreatment is known to be effective in improving hydrolysis by increasing the internal surface area and porosity of a biomass, decreasing the degree of depolymerisation and inducing swelling of the lignocellulosic structure [14,15]. This is an effective pretreatment method for increasing methane (CH_4) production during the anaerobic digestion of lignocellulosic biomass [16–19]. A review conducted by Zheng *et al.* showed that CH_4 yield can be increased from 3.2% to 230% by alkaline pretreatment [14]. A comparison of the pretreatment of oat straw with lime, acid and steam showed that lime treatment is the most effective at increasing biochemical methane potential (BMP) (lime: 287 CH4 NL/kg VS, acid + steam: 197 CH4 NL/kg VS, steam 201 CH4 NL/kg VS) [20].

This study explored the use of acid-containing wastes as a pretreatment medium that could replace industrial chemicals, to enhance methane production from WS in combination with mechanical pretreatment and particle size reduction. As well as, due to the high content of easily degradable compounds in DOR and UFR they might help to boost energy production in biogas plant.

2. Materials and methods

2.1. Substrates and inoculum used

The fresh WS used in this study was provided by the agricultural consulting company, Centrovice in Denmark. DOR was collected from a local juice industry in Denmark called Rynkeby Foods A/S. UFR was a side stream from the processing of sour cherry biowaste. Pressing residue from sour cherry wine production was kindly provided by Frederiksdal Kirsebærvin (Harpelunde, Denmark). The residue was extracted using a citrate-phosphate aqueous buffer (0.25 M, pH 3) for 60 min at 50°C and a solid:liquid ratio of 1:2 (w/w). The cherry stones were removed by coarse filtration, and the resulting slurry was ultra-filtered using a ceramic monotubular inopor® ultra membrane (γ-Al_2O_3, 10 nm) to produce a particle-free extract (permeate). The stream rejected by the ultrafiltration membrane (UFR) was used as a pretreatment medium in this study.

The dry matter (DM) and volatile solids (VS) in DOR was 65 (±1) g/kg and 62 (±0.7) g/kg respectively, where these values for UFR were 62 (±1.1) g/kg and 56 (±0.7) g/kg respectively (Table 1) and both of these had a pH of 3.5. The inoculum used for the batch test was obtained from the Fangel Biogas Plant in Denmark by processing a mixture of animal manure and industrial organic waste under mesophilic conditions (37°C). The inoculum was degassed at 37°C for two weeks in an incubator before the batch assay was performed.

2.2. Wheat straw pretreatment

The pretreatment of WS was performed at three different particle sizes and two different time spans. The sample size was reduced to 0.5, 1.5 and 4mm. Fresh WS was stored with DOR and UFR at a ratio of 1:9 (w/w) and room temperature (20°C) for 48 h and 72 hr in closed containers of 500ml. There were 17 samples in all: WS (3 samples), DOR, UFR, pretreated WS with DOR (6 samples) and pretreated WS with UFR (6 samples). A schematic diagram of pretreatment process is shown in Figure 1.

2.3. Experimental procedure

Biogas and methane production were determined in batch mode at a 2.5:1 inoculum-to-substrate ratio on a VS basis in 500mL batch digesters with 30% headspace. The batch digesters were flushed with nitrogen gas to provide complete anaerobic conditions. Anaerobic digestion was conducted under mesophilic conditions (37°C) for 60 days. Raw biogas is released and read off using syringe in batch mode until the pressure in headspace reaches ambient pressure. The methane concentration in the gas collected from the digesters was measured on a gas chromatograph (7890A; Agilent Technology, USA) supplied with a thermal conductivity detector and a 30m×0.320mm column (J&W 113-4332; Agilent Technology, USA). The measured methane was corrected for standard conditions (273K and 101.325kPa). DM and VS were measured according to the standard procedure by drying and igniting samples at 105°C and 550°C, respectively [21]. Ethanol, glycerol and sugars including maltotriose, maltose, lactose, glucose and fructose were determined using high-performance liquid chromatography (HPLC, Agilent 1100, Agilent Technologies Deutschland GmbH & Co. KG, Waldbronn, Germany). Volatile fatty acid (VFA) concentrations from C_2–C_5 were analyzed by a gas chromatograph (Hewlett Packard 6890, Ontario, ON, Canada) with a flame ionisation detector and 30m×0.25mm×0.25 μ m column (HP-INNOWax, Agilent Technologies, Santa Clara, CA, USA). Prior to injection into the GC and HPLC, the samples were diluted with deionised water and filtered through a 0.2μ m nylon membrane filter. In the case of VFA determination, the pH value was adjusted to about 2 using phosphoric acid. For the VFA calibration curve, nine standard solutions containing six VFAs were used in triplicate, with concentrations ranging from 0.25 to 100mM.

2.4. Data analysis

A first-order kinetic model was fitted to the cumulated methane production.

$$B_t = B_0 \cdot [1 - e^{(-k_h \cdot t)}] \quad (1).$$

B_t (CH4 NL/kg VS) is the cumulative methane yield at time t, B_0 (CH4 NL/kg VS) is the ultimate methane yield, k_h (1/day) is the first-order hydrolysis constant, and t is the anaerobic digestion time (days). The effect of the pretreatment was assessed by comparing the hydrolysis constant (k_h, 1/day).

Analysis of variance (ANOVA) and Tukey's method were applied to assess the data, as a multi-comparison test at a significance level of $\alpha = 0.05$, using SAS 9.2. The paired *t*-test was applied to evaluate the significance of the differences between the data.

3. Results and discussion

The characteristics of the samples are reflected in Table 1. Among sugars, lactose was the one was not detected in the samples. It is interesting that mechanical pretreatment and particle size reduction increased the fructose content significantly by 6.61, 10.57 and 17.56 g/kg for 4, 1.5 and 0.5mm respectively. Regarding glucose, it was only present in the WS with particle size of 0.5mm. Mechanical pretreatment leads to the depolymerisation of macromolecules in cell walls where it can transform the macromolecules of WS cell wall into water-soluble substances [22]. The only VFA detected in DOR, UFR and the pretreated samples was acetic acid. DOR and UFR have a pH of 3.5 and they contain different organic acids which can act as a pretreatment agent for WS.

There are not many studies to assess the effect of particle size on methane yield. Most studies reported that methane yield increases in inverse proportion to the particle size, but also some results showed negligible effect on the methane production [23]. Kivaisi and Eliapenda showed that by particle size reduction of bagasse and coconut fibres from 5mm to less than 0.85 mm, methane yield increased by an average of 30% [24]. In our study, decreasing the particle size from 4 to 1.5mm did not have significant impact on methane production. However, reduction of particle size to 0.5mm led to 5% increase in methane yield in comparison to particle size of 1.5 and 4mm. The cumulative methane yield of WS with particle size of 0.5, 1.5 and 4mm after 60 days of digestion was 297, 281 and 281CH4 NL/kg VS. This tiny effect can be due to release of some sugars from lignocellulosic structure of WS during milling.

It was indicated by Song et.al that by utilization of hydrogen peroxide, sulfuric acid, hydrochloric acid and acetic acid for pretreatment of corn straw, the methane yield enhanced by 115, 75, 62 and 45%, respectively [12]. Pretreatment of bagasse and coconut fibers with hydrochloric acid increased methane production by 32 and 76 respectively [24]. A pretreatment of newsprints with mixture of acetic acid and nitric acid led to the production of biogas by three times from 97 CH4 NL/kg VS for the untreated newsprints to 364 CH4 NL/kg VS for the pretreated ones. Nitric acid might be replaced by another strong acid like hydrochloric acid [25]. Application of DOR and UFR had significant impact for pretreatment of WS in all the particle sizes tested, with the improvement ranging from 7 to 27% (Figure 2). Generally, the performance of UFR was much better than DOR. DOR increased the methane yield between 7-17% while enhance of methane yield of WS using UFR was between 19-27%. Due to the presence of weak acids and lack of strong acids in DOR and UFR, the improvement in methane yield in our study was not as good as other studies using strong acids for pretreatment.

The effect of mechanical pretreatment, DOR and UFR on hydrolysis constant is reflected in Figure 3. Mechanical pretreatment (Particle size reduction) had a small impact on the hydrolysis constant, where it increased from 0.06 (1/day) for particle size of 4mm, to 0.07 (1/day) for 1.5mm, and to 0.08 (1/day) for 0.5mm. Despite BMP, DOR had a little bit better impact on hydrolysis constant in comparison to UFR. However, both DOR and UFR doubled the hydrolysis constant of pretreated WS compared to fresh ones ($p<0.01$). This is of great importance, because a high rate of hydrolysis will reduce the retention time in anaerobic digestion in biogas plants and thus the cost of biogas production.

4. Conclusions

Individual utilization of mechanical pretreatment for WS has negligible impact on methane yield of WS. However, combination of mechanical pretreatment with application of DOR and UFR had substantial effect on methane yield and hydrolysis constant of WS ($p<0.01$). The present study demonstrated that faster methane production from pretreated WS by DOR and UFR will shorten the retention time of anaerobic digestion and it could reduce the operational cost of biogas plants. Therefore, utilization of DOR and UFR for pretreatment of WS could be promising.

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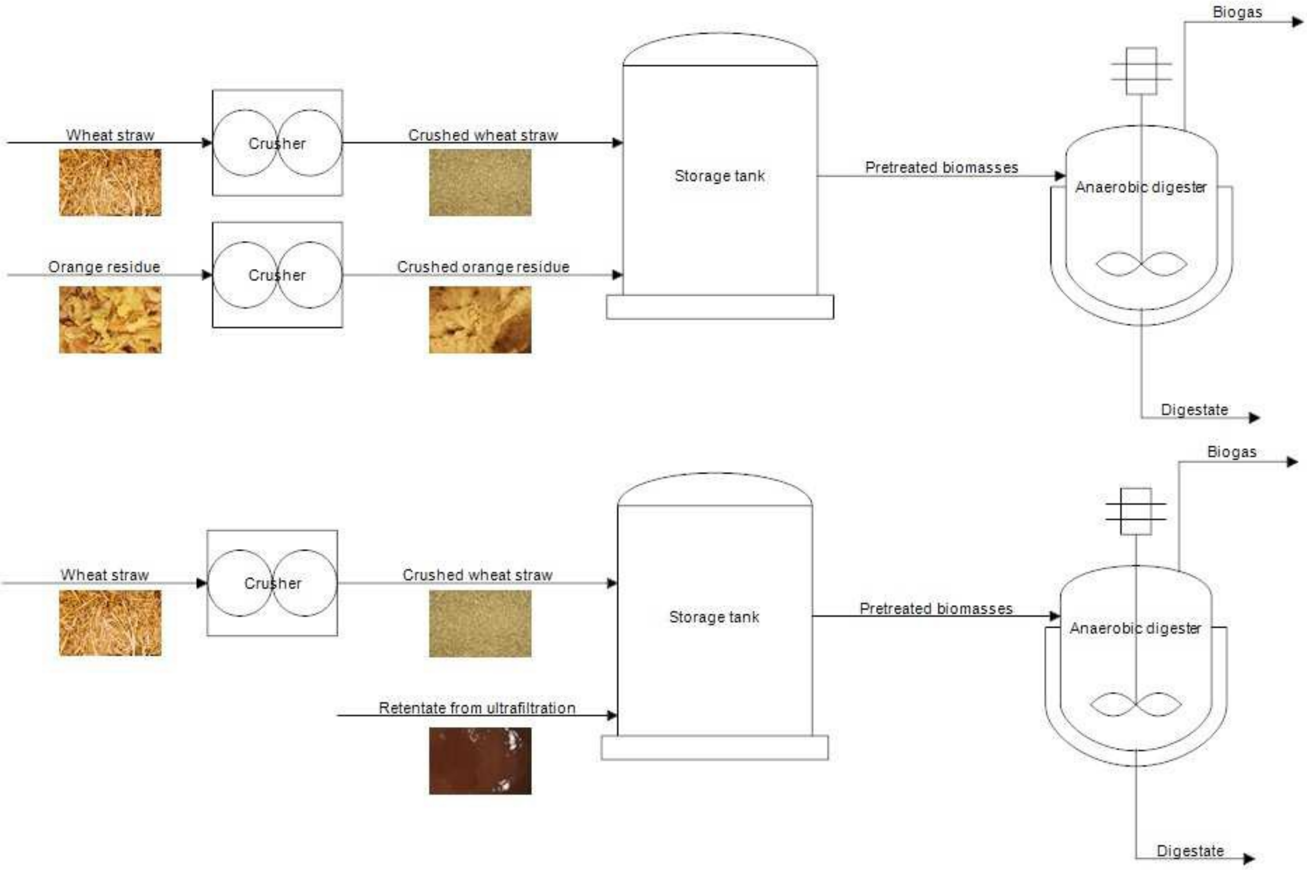

Figure 1- The pretreatment process of WS by UFR and DOR

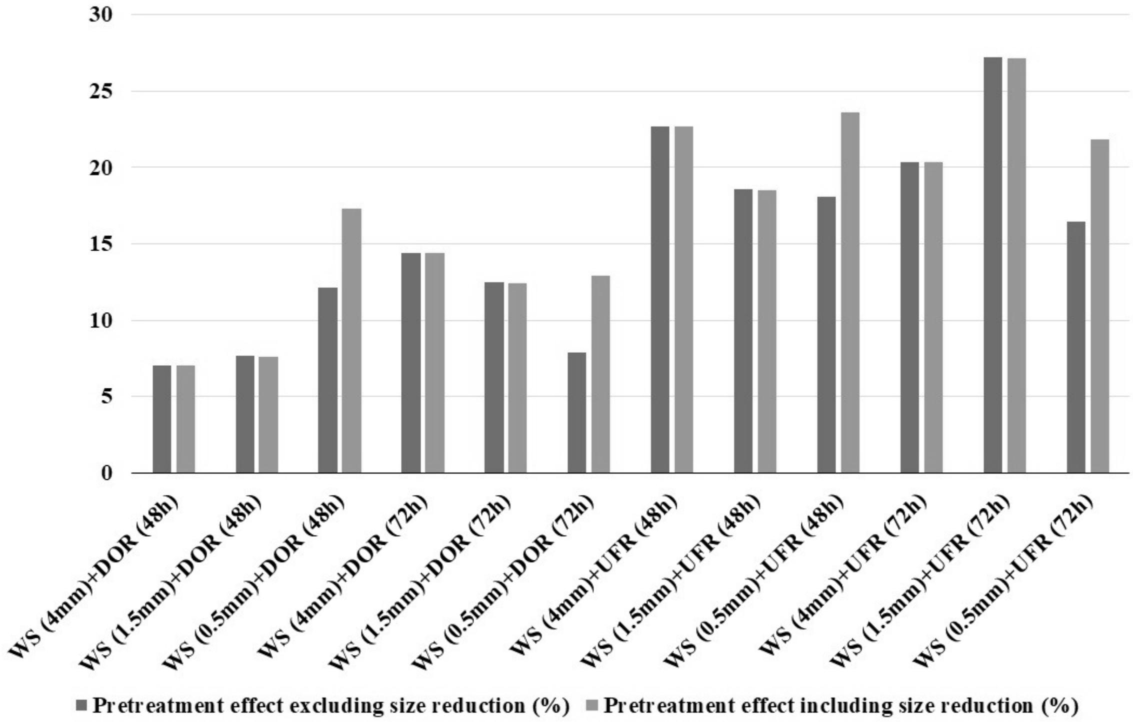

Figure 2 – The effect of mechanical and chemical pretreatment of WS on biomethane yield

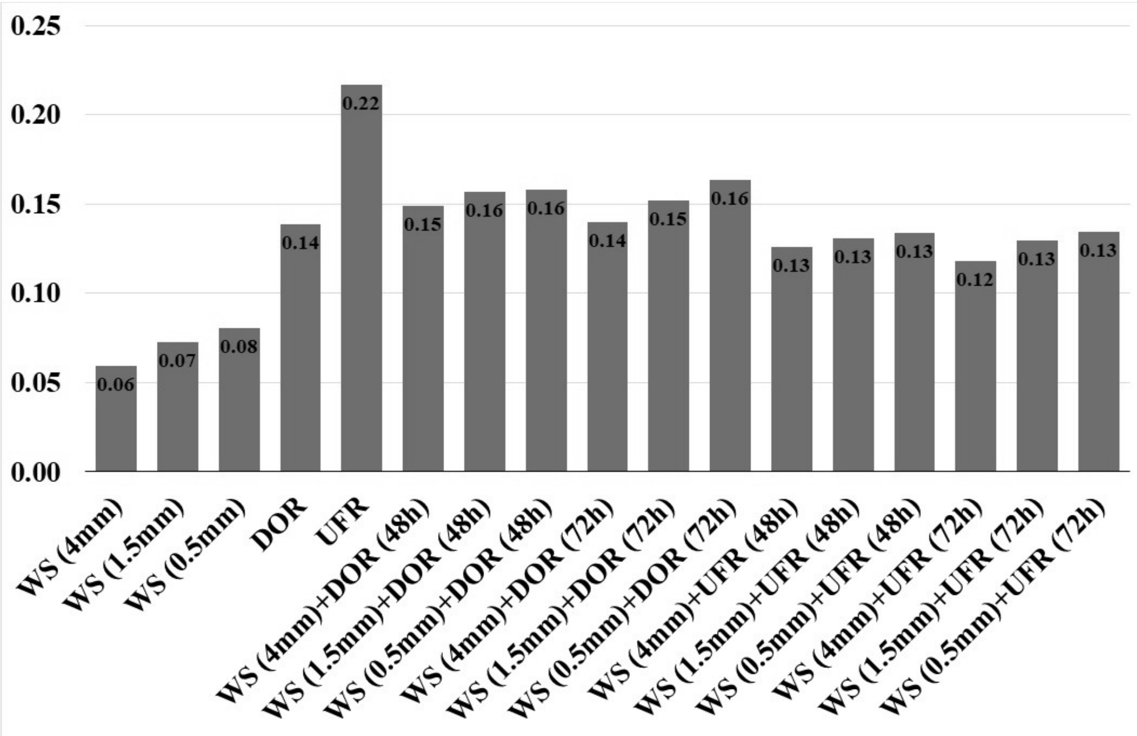

Figure 3 – The effect of mechanical and chemical pretreatment of WS on hydrolysis constant (1/day)

Table 1 – Characteristics of fresh and pretreated samples

Sample	DM (g/kg)	VS in DM (%)	VS (g/kg)	Acetic acid (g/kg)	Ethanol (g/kg)	Glycerol (g/kg)	Maltotriose (g/kg)	Maltose (g/kg)	Glucose (g/kg)	Fructose (g/kg)	BMP (CH4 NL/kg VS)
WS (4mm)	925 (±5)	94	868 (±10)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	6.61 (±0.15)	293 (±6)
WS (1.5mm)	929 (±3)	94	870 (±9)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	10.57 (±0.06)	293 (±12)
WS (0.5mm)	921 (±7)	94	865 (±15)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	4.83 (±0.20)	17.56 (±0.20)	307 (±1)
DOR	63 (±1)	95	59 (±1)	2.02 (±0.29)	2.61 (±0.09)	0.94 (±0.08)	0.00 (±0.00)	0.62 (±0.01)	0.00 (±0.00)	0.00 (±0.00)	483 (±6)
UFR	61 (±1)	90	55 (±2)	0.37 (±0.02)	2.61 (±0.08)	0.78 (±0.00)	0.00 (±0.00)	2.24 (±0.11)	0.19 (±0.05)	0.00 (±0.00)	424 (±15)
DOR+WS (4mm) 48h	152 (±3)	94	144 (±6)	3.45 (±0.37)	4.23 (±0.15)	0.73 (±0.06)	1.06 (±0.09)	2.03 (±0.03)	0.82 (±0.06)	0.00 (±0.00)	375 (±7)
DOR+WS (1.5mm) 48h	152 (±5)	94	143 (±3)	3.42 (±0.01)	3.73 (±0.19)	0.75 (±0.10)	2.43 (±0.15)	1.65 (±0.09)	0.92 (±0.11)	0.00 (±0.00)	376 (±5)
DOR+WS (0.5mm) 48h	152 (±4)	94	143 (±1)	3.70 (±0.08)	3.22 (±0.20)	0.91 (±0.02)	0.00 (±0.00)	1.43 (±0.13)	1.22 (±0.15)	0.00 (±0.00)	394 (±10)
DOR+WS (4mm) 72h	152 (±9)	94	144 (±8)	3.45 (±0.04)	4.22 (±0.05)	1.20 (±0.09)	0.95 (±0.10)	0.00 (±0.00)	1.74 (±0.12)	0.00 (±0.00)	389 (±2)
DOR+WS (1.5mm) 72h	153 (±6)	94	144 (±9)	3.86 (±0.05)	4.31 (±0.31)	1.00 (±0.12)	0.95 (±0.06)	2.63 (±0.16)	1.03 (±0.00)	0.00 (±0.00)	385 (±7)
DOR+WS (0.5mm) 72h	153 (±3)	94	144 (±7)	4.06 (±0.07)	3.86 (±0.25)	1.07 (±0.11)	2.62 (±0.00)	1.81 (±0.07)	0.82 (±0.00)	0.00 (±0.00)	386 (±9)
UFR+WS (4mm) 48h	149 (±0)	92	138 (±0)	1.12 (±0.10)	3.26 (±0.13)	0.97 (±0.00)	3.24 (±0.12)	1.76 (±0.06)	0.74 (±0.10)	0.00 (±0.00)	382 (±6)
UFR+WS (1.5mm) 48h	149 (±0)	92	138 (±6)	0.88 (±0.01)	3.72 (±0.14)	1.39 (±0.08)	0.00 (±0.00)	2.12 (±0.10)	1.11 (±0.05)	0.00 (±0.00)	374 (±9)
UFR+WS (0.5mm) 48h	149 (±5)	92	137 (±1)	0.94 (±0.03)	2.71 (±0.22)	1.08 (±0.06)	0.00 (±0.00)	0.00 (±0.00)	1.03 (±0.08)	0.00 (±0.00)	384 (±5)
UFR+WS (4mm) 72h	148 (±2)	92	137 (±0)	0.73 (±0.00)	2.77 (±0.03)	0.96 (±0.07)	0.00 (±0.00)	1.62 (±0.20)	0.86 (±0.06)	0.00 (±0.00)	378 (±10)
UFR+WS (1.5mm) 72h	149 (±8)	92	138 (±0)	0.92 (±0.02)	2.98 (±0.08)	1.06 (±0.05)	0.00 (±0.00)	1.69 (±0.01)	0.99 (±0.15)	0.00 (±0.00)	391 (±10)
UFR+WS (0.5mm) 72h	149 (±6)	92	137 (±5)	1.04 (±0.00)	2.73 (±0.09)	1.55 (±0.09)	0.00 (±0.00)	1.99 (±0.00)	1.20 (±0.20)	0.00 (±0.00)	381 (±4)